DYNAMICS OF POLYMERS SELF-ASSEMBLY

BY COMPUTER SIMULATION

by

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*We also certify that written approval has been obtained for any proprietary material contained therein.
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To my family
Table of Contents

Table of Contents ................................................................. i
List of Tables ................................................................. iv
List of Figures................................................................. vii
Acknowledgements............................................................... xv
Abstract.............................................................................. xvi

Chapter 1: Introduction.............................................................. 1

1.1 Polymer Self-assembly........................................................... 1
1.2 Background ........................................................................ 2
  1.2.1 Block Copolymer Micelles ................................................. 3
    1.2.1.1 Micelle Thermodynamics ............................................ 3
    1.2.1.2 Micelle Kinetics ......................................................... 6
  1.2.2 Supramolecular Polymers ................................................. 9
    1.2.2.1 Definition ................................................................ 9
    1.2.2.2 Thermodynamics ....................................................... 11
    1.2.2.3 Rheological Properties ............................................. 13
1.3 Motivation and Thesis Outline.............................................. 15
  1.3.1 Motivation .................................................................. 15
  1.3.2 Thesis Outline ............................................................. 17
1.4 Bibliography ..................................................................... 20

Chapter 2: Molecular Simulation Methods...................................... 24

2.1 Molecular Simulation .......................................................... 24
2.2 Molecular Dynamics Simulation ........................................... 25
2.3 DPD Simulation ............................................................... 27
2.4 Bibliography ................................................................... 30

Chapter 3: Equilibrium Properties of Block Copolymer Micelle Solution by DPD Simulation ....................................................... 35

3.1 Simulation Details ............................................................ 36
  3.1.1 DPD Model ............................................................... 36
  3.1.2 DPD Simulations ......................................................... 36
  3.1.3 Micelle Analysis .......................................................... 39
3.2 Results and Discussions ................................................................. 40
  3.2.1 Critical Micellar Concentration ............................................. 40
  3.2.2 Micelle Aggregation Number ................................................. 43
    3.2.2.1 Oligomer Concentration Effect ..................................... 44
    3.2.2.2 Interaction Energy Effect ........................................... 46
    3.2.2.3 Corona Block Length Effect ....................................... 49
  3.2.3 Micelle Structure ............................................................... 53
  3.3 Conclusions ............................................................................. 55
  3.4 Bibliography ........................................................................... 58

Chapter 4: Kinetics of Block Copolymer Micellization by DPD Simulation ........60
  4.1 Introduction ............................................................................. 60
  4.2 Simulation and Data Analysis .................................................. 65
  4.3 Results and Discussions ........................................................ 67
    4.3.1 Molecular Mechanism ....................................................... 67
    4.3.1.1 Micellization Kinetics ............................................... 67
    4.3.3.2 Three Stages ............................................................. 70
    4.3.2 Oligomer Concentration Effect ....................................... 80
    4.3.3 Interaction Energy Effect ............................................... 83
    4.3.4 Block Length Effect ....................................................... 85
  4.4 Conclusions ............................................................................. 90
  4.5 Bibliography ........................................................................... 94

Chapter 5: Kinetics of Equilibrium Chain Exchange by DPD Simulation.........96
  5.1 Introduction ............................................................................. 96
  5.2 Simulations and Data Analysis ................................................ 100
    5.2.1 DPD Simulations ............................................................. 100
    5.2.2 Micelle Hybridization Analysis ....................................... 103
  5.3 Results and Discussions ........................................................ 105
    5.3.1 Oligomer Concentration Effect ....................................... 105
    5.3.2 Interaction Energy Effect ............................................... 119
    5.3.3 Corona Block Length Effect .......................................... 123
  5.4 Conclusions ........................................................................... 128
Chapter 6: Rheology of Supramolecular Polymers by MD Simulation

6.1 Introduction
6.2 Model and Simulation Details
   6.2.1 Reversible Association Model
   6.2.2 MD Simulations
   6.2.3 Data Analysis
6.3 Results and Discussions
   6.3.1 Equilibrium Properties
      6.3.1.1 Ring-Chain Equilibrium
      6.3.1.2 Molecular Weight
   6.3.2 Rheological Properties
      6.3.2.1 Shear-thinning Behavior
      6.3.2.2 Equilibrium Viscosity
6.4 Conclusions
6.5 Bibliography

Chapter 7: Summary and Outlook

7.1 Summary
7.2 Outlook
7.3 Bibliography

Bibliography
List of Tables

Table 3.1 Equilibrium aggregation number determined from number- and weight-average aggregation number distributions \(M_{npeak}\) and \(M_{wpeak}\); number- and weight- average aggregation number \(M_n\) and \(M_w\); and unimer volume fraction \(\varphi_{unimer}\) for \(A_2B_3\) micellar solutions with different interaction parameters \(a_{AB}\) and for \(A_4B_4\), \(A_4B_6\), \(A_4B_8\) micellar solutions \((\varphi = 0.05)\)……………………………………………………………………………49

Table 4.1 Relative number of events (frequency) and fraction of chains exchanged in the event (contribution) involving unimers, small aggregates and micelles for stages II and III of the micellization process of \(A_2B_3\) micellar solution \((\varphi = 0.05, a_{AB} = 50)\)………………….77

Table 4.2 Relative number of events (frequency) and fraction of chains exchanged in the event (contribution) involving unimers, small aggregates and micelles for stages II and III of the micellization process of \(A_2B_3\) micellar solution \((\varphi = 0.02, a_{AB} = 50)\)…………………83

Table 4.3 Relative number of events (frequency) and fraction of chains exchanged (contribution) in the events involving unimers, small aggregates and micelles for stages II and III of the micellization process of \(A_4B_6\) micellar solution \((\varphi = 0.05, a_{AB} = 40)\), averaged over several simulation runs…………………………………………………………..86

Table 4.4 Relative number of events (frequency) and fraction of chains exchanged (contribution) in the events involving unimers, small aggregates and micelles for stages II and III of the micellization process of \(A_4B_8\) micellar solution \((\varphi = 0.05, a_{AB} = 40)\), averaged over several simulation runs……………………………………………………………90

Table 5.1 Equilibrium aggregation numbers determined from number-average aggregation number distributions \(M_{npeak}\) and unimer volume fractions \(\varphi_{unimer}\) for \(A_2B_3\), \(A_4B_4\), \(A_4B_6\), and \(A_4B_8\) micellar solutions for different interaction parameters \(a_{AB}\) (the corresponding \(\chi_{AB}\) values\(^{37}\) are listed as well) at \(\varphi = 0.05\)……………………………………………103
Table 5.2 Plateau level of the hybridization correlation function $I(t)$ calculated from Figure 2 (main text) in comparison with the value obtained by random labeling of chains in micelles for $A_2B_3$ micelle solutions with interaction energy $a_{AB}=50$ at different oligomer concentrations……………………………………………………………………………………107

Table 5.3 Unimer insertion time $\tau_{\text{insertion}}$ obtained by a single-exponential decay fitting of unimer insertion correlation function $U(t)$ for $A_2B_3$ micelle solutions with different interaction energies and oligomer concentrations…………………………………………………………………………………………112

Table 5.4 Characteristic times obtained by a single-exponential decay fitting of contrast function (eq.2), unimer formation (eq.3) and native chain expulsion (eq.4) for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ at different oligomer concentrations……………………………………………………………………………………………………114

Table 5.5 Relative frequency and contribution (fraction of chains exchanged) of different kinetic events, and corresponding relaxation times for native chain escaped by these mechanisms for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ at two different oligomer concentrations……………………………………………………………………………………………………115

Table 5.6 Characteristic times obtained by a single-exponential decay fitting of contrast correlation function $C(t)$ for $A_2B_3$ micelle solutions with different interaction energies at $\varphi=0.03$……………………………………………………………………………………………………120

Table 5.7 Relative frequency and contribution (fraction of chains exchanged) of different kinetic events for $A_4B_4$, $A_4B_6$ and $A_4B_8$ micelle solutions with interaction energy $a_{AB}=38$ at at $\varphi=0.05$……………………………………………………………………………………………………128

Table 6.1 Equilibrium properties of head-to-tail associating polymers at different temperatures ($T$) and association energies ($E_0$) for oligomer volume fraction $\varphi=0.2$: number-average ($M_n$) and weight-average ($M_w$) molecular weight (in units of oligomer
weight), polydispersity index ($PI = M_w/M_n$), degree of association ($p$), fraction of reversible bonds in rings ($f_{ring}$) and zero-shear viscosity ($\eta_0$)………………………………149

Table 6.2 Equilibrium viscosity of pure solvent at different temperatures determined from the data shown in Figure 6.13………………………………………………………… ..163

Table 6.3 Equilibrium viscosity of a solution of 8-bead associating oligomers at different oligomer volume fractions $\phi$ for $k_BT$ =1.0, $E_0$ = 25, determined from the data shown in Figure 6.8………………………………………………………………………………………………164
List of Figures

Figure 1.1 Examples of end-groups capable of forming quadruple hydrogen bond array (a) 2-ureido-4-[1H]pyrimidone dimer, and spacer with end-ligands capable of forming metal-ligand complexes (b) terpyridine-based oligomer

Figure 1.2 Theoretical relationship between the binding constant and average degree of polymerization (DP) at two different oligomer concentrations

Figure 2.1 NEMD simulation of steady shear flow by deforming the simulation box

Figure 3.1 (a) Schematic representation of a model A₄B₈ chain and (b) a snapshot of the simulation box containing A₄B₈ chains (a₂₄ = 40, φ = 0.05) (the hydrophobic block is shown by connected balls, the hydrophilic block is shown by connected bonds (i.e. balls omitted), solvent beads are not shown, rendered by VMD)

Figure 3.2 Weight-average aggregation number and unimer number density as a function of oligomer number density in A₂B₃ micellar solution (a₂₄ = 47.5) (Lines are the guides of eye only). The vertical line corresponds to the CMC at φ ≈ 3.7x10⁻³

Figure 3.3 Volume fraction of unimers, dimers and trimers in A₂B₃ micellar solutions (a₂₄ = 47.5) as a function of oligomer volume fraction (Lines are the guides of eye only).

Figure 3.4 Weight-average aggregation number distribution of A₂B₃ diblock copolymer solution (a₂₄ = 47.5) at different polymer volume fractions φ

Figure 3.5 Time-dependent weight-average aggregation number of block copolymer solution (a₂₄=50, φ = 0.05) in the DPD simulation
Figure 3.6 Weight-average aggregation number distribution of $A_2B_3$ micellar solutions ($a_{AB} = 47.5$) at different oligomer volume fractions: $\phi = 0.03, 0.04, 0.05$………………. 45

Figure 3.7 Weight-average (a) and number-average (b) aggregation number distribution for $A_2B_3$ micellar solutions with different interaction energies $a_{AB} = 47.5, 50, 52.5, 55$ for oligomer volume fraction $\phi = 0.05$………………………………………………………47

Figure 3.8 Weight-average (a) and number-average (b) aggregation number distribution for $A_4B_4, A_4B_6$ and $A_4B_8$ micellar solutions ($a_{AB} = 38$) for oligomer volume fraction $\phi = 0.05$……………………………………………………………………………………….51

Figure 3.9 Weight-average (a) and number-average (b) aggregation number distribution for $A_4B_4, A_4B_6$ and $A_4B_8$ micellar solutions ($a_{AB} = 40$) for oligomer volume fraction $\phi = 0.05$……………………………………………………………………………………….52

Figure 3.10 Monomer density profiles for core and corona of $A_2B_3$ micelles of aggregation number $P=35$ for different hydrophobic interaction energies ($a_{AB} = 47.5, 50, 52.5, 55$)……………………………………………………………………………………….53

Figure 3.11 Monomer density profiles for core and corona of $A_4B_4, A_4B_6, A_4B_8$ micelles of aggregation number $P = 40$ ($\phi = 0.05, a_{AB} = 40$)……………………………………………………………………………………….55

Figure 4.1 Snapshots of the simulation box containing $A_4B_8$ chains ($a_{AB} = 40, \phi = 0.05$) obtained in the course of micelle formation (the hydrophobic block is shown by connected balls, the hydrophilic block is shown by connected bonds (i.e. balls omitted), solvent beads are not shown, rendered by VMD)………………………………………………………68

Figure 4.2 (a) Number- and weight-average aggregation numbers and (b) weight-average fraction of aggregates in different size ranges as a function of time during the process of micelle formation in $A_2B_3$ solution ($a_{AB} = 50, \phi = 0.05$). Vertical dashed lines indicate the approximate boundaries between different stages of micellization process………………70
Figure 4.3 Ratio of aggregation numbers of small to large reactants in the micellization addition process of $A_2B_3$ ($a_{AB} = 50, \varphi = 0.05$) as a function of time. Vertical dashed lines indicate the approximate boundaries between different stages of micellization process. The inset shows the average aggregation number of the smaller reactant during the final stage of micellization as a function of $a_{AB}$.  

Figure 4.4 Weight fraction aggregation number distribution during the micellization process of $A_2B_3$ solution ($a_{AB} = 50, \varphi = 0.05$). Curves with symbols for different time steps are the running average. The equilibrium distribution is shown as a curve without symbols. Horizontal dashed lines indicate the approximate boundaries between different stages of micellization process.  

Figure 4.5 Time evolution of the aggregation number $P$ of selected individual micelles during the second stage of micellization process of $A_2B_3$ solution ($a_{AB} = 50, \varphi = 0.05$).  

Figure 4.6 Time-evolution of the weight-average aggregation number during the micellization process of $A_2B_3$ solution ($a_{AB} = 50$) for different oligomer volume fractions $\varphi = 0.02, 0.05$. The inset shows the average aggregation number of the smaller reactant in addition reactions during the final stage of micellization as a function of $\varphi$.  

Figure 4.7 Time-evolution of the weight-average aggregation number in the course of micellization of $A_2B_3$ solution ($\varphi = 0.05$) for different interaction energies $a_{AB} = 47.5, 55$.  

Figure 4.8 Time evolution of the aggregation number $P$ of selected individual micelles during the second stage of micellization process of $A_2B_6$ solution ($a_{AB} = 40, \varphi = 0.05$).  

Figure 4.9 Weight fraction aggregation number distribution during the micellization process of $A_2B_6$ micelle solution ($a_{AB} = 40, \varphi = 0.05$). Curves with symbols for different
time steps are the running average. The equilibrium distribution is shown as a curve without symbols.…………………………………………………………………………………………88

Figure 5.1 Schematic representation of the micelle hybridization process………………104

Figure 5.2 Hybridization autocorrelation function $I(t)$, eq.1, and contrast function $C(t)$, eq.2, (inset) for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ at different oligomer concentrations: $\varphi = 0.02, 0.03, 0.04, 0.05$ (from top to bottom curves in the main plot, color scheme is the same for the inset).…………………………………………………………108

Figure 5.3 Unimer formation $E(t)$, eq.5.3 and native chain expulsion $F(t)$, eq.5.4 (inset) correlation functions for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ for different oligomer concentration ($\varphi = 0.02, 0.03, 0.04, 0.05$, from bottom to top, color scheme is the same for the inset)……………………………………………………………………110

Figure 5.4 Unimer insertion correlation function $U(t)$, eq. 5.4, for $A_2B_3$ micelle solutions with interaction energy $a_{AB}=50$ at different oligomer concentrations ($\varphi = 0.02, 0.03, 0.04, 0.05$ from top to bottom)………………………………………………………………………………111

Figure 5.5 The unimer insertion time $\tau_{insertion}$ vs. the square of average distance $d^2$ between aggregates ($P>1$) for $A_2B_3$ micelle solutions with different interaction energies ($a_{AB}=50, 52.5, 55$), and oligomer concentrations ($\varphi = 0.02, 0.03, 0.04, 0.05$)………………113

Figure 5.6 Native chain expulsion correlation function $F(t)$ via unimer expulsion/insertion (black), small aggregate splitting/merging (red) and micelle fission/fusion (blue) for $A_2B_3$ micelle solution ($\varphi = 0.05, a_{AB}=50$)………………………………………………………………………………118

Figure 5.7 Contrast function $C(t)$, eq.2, obtained for $A_2B_3$ micelle solutions with different interaction energies ($a_{AB}=47.5, 50, 52.5, 55$) at the oligomer concentration $\varphi = 0.03$…………………………………………………………………………………………..119
Figure 5.8 Characteristic times for contrast $C(t)$ (squares), unimer formation $E(t)$ (circles) and native chain expulsion $F(t)$ (triangles) correlation functions for $A_2B_3$ micellar solutions at $\varphi = 0.03$ (filled symbols), and $A_4B_4$ (half-filled symbols), $A_4B_6$ (open symbols), $A_4B_8$ (crossed symbols) micelle solutions at $\varphi = 0.05$ as functions of reduced interaction energy $\chi_{AB}N_A=0.286N_A\Delta a_{AB}=0.286N_A(a_{AB} - a_{BB})$.

Figure 5.9 Contrast correlation function $C(t)$ for $A_4B_x$ micelle solutions with different corona block lengths ($N_B=4, 6, 8$) for (a) $a_{AB}=38$ and (b) $a_{AB}=40$, $\varphi=0.05$.

Figure 5.10 Characteristic times for contrast $C(t)$ (squares) and native chain expulsion $F(t)$ (triangles) correlation functions for $A_4B_4$ $A_4B_6$ and $A_4B_8$ micelle solutions with different interaction energies at $\varphi = 0.05$ as functions of corona block length $N_B$.

Figure 5.11 The average area per chain for the micelle corresponding to the maximum of the aggregation number distribution for $A_4B_x$ micelle solutions ($a_{AB}=38, 40$) at oligomer concentration $\varphi=0.05$.

Figure 5.12 Fraction of unimers in $A_4B_4$ and $A_4B_8$ micelle solutions with different interaction energies $\Delta a_{AB} = a_{AB} - a_{BB}$ ($a_{BB}=25$) at oligomer concentration $\varphi=0.05$.

Figure 6.1 The combined LJ and truncated pseudo-Coulombic potential (Eq.(3)) for donor/acceptor (D/A) and donor/donor (D/D) or acceptor/acceptor (A/A) interactions (solid curves, $E_0=30$) and shifted, long-range LJ potential (Eq.(4), dashed curve). Donor (D), acceptor (A), donor neighbor (DN) and acceptor neighbor (AN) are identified in the schematic representation of reversibly bonded donor-acceptor complex in 8-bead oligomer.

Figure 6.2 Average distribution of angles between a donor (D)-acceptor (A) reversible bond and acceptor-acceptor neighbor (AN) chemical bond (as shown in the schematic presentation) or donor-donor neighbor (DN) chemical bond in the absence (squares) and
in the presence (circles) of the long-range LJ repulsive interactions in an associating oligomer solution ($\phi = 0.2, k_B T=1, E_0=30$)…………………………………………………………..143

Figure 6.3 Fraction of reversible bonds in rings (open symbols) and chains (solid symbols) for solutions of 8-bead oligomers as a function of oligomer volume fraction for different association energies $E_0=20$ (squares), $E_0=25$ (circles) and $E_0=30$ (triangles) at $k_B T=1.0$………………………………………………………………………..148

Figure 6.4 Fraction of reversible bonds in rings (open symbols) and chains (solid symbols) for solutions of 8-bead oligomers as a function of oligomer volume fraction at different temperatures, $k_B T=1$ (squares) and $k_B T=1.5$ (triangles), for association energy $E_0=25$…………………………………………………………………………………150

Figure 6.5 The fractions of reversible associations in rings (open symbols) and chains (filled symbols) vs. oligomer number density in solutions of 8-bead (squares) and 20-bead associating oligomers (triangles) for $k_B T=1, E_0=30$. The horizontal dashed line indicates equal fraction of chains and rings and the vertical dashed lines mark the corresponding oligomer number density defined as the ring/chain transition point……………………………………………………………………………………151

Figure 6.6 Number density distribution of rings (squares) and chains (circles) in the associating solution of 8-bead oligomers ($\phi=0.2, E_0=30, k_B T=1.0$). The molecular weight is shown in units of oligomer weight………………………………………………………………………………...152

Figure 6.7 Weight-average molecular weight of associating solution of 8-bead oligomers for $E_0=20$ (circles), $E_0=25$ (triangles) and $E_0=30$ (squares) as a function of oligomer volume fraction. Weight-average molecular weight of associating solution of 20-bead oligomers for $E_0=30$ is shown in the inset. Solid symbols correspond to the chain-dominated regime and open symbols describe the ring-dominated regime……………..153
Figure 6.8 Solution viscosity of head-to-tail associating 8-bead oligomers for different a) association energies $E_0$ and b) temperatures as a function of shear-strain-rate for $\phi=0.2$. Shear-strain-rate dependent viscosity for non-associating oligomer solution (open symbols) and pure solvent are shown for comparison.  

Figure 6.9 Viscosity of solution of 8-bead associating oligomers as a function of shear strain rate for different oligomer volume fractions at $k_BT=1.0$, $E_0=25$.  

Figure 6.10 (a) Normalized reduced viscosity of 20-bead head-to-tail associated oligomer solution at different oligomer volume fractions ($\phi=0.07$ squares; $\phi=0.1$ circles; $\phi=0.2$ upper triangle; $\phi=0.3$ down triangle), (b) the average molecular weight of chains $<M_{\text{chain}}>$ (in units of oligomer weight) and the number of free oligomers $<N_{\text{free}}>$ for $\phi=0.2$, $E_0=30$ as functions of reduced shear rate for $k_BT=1$. The inset in (a) shows the normalized reduced viscosity of 8-bead associating oligomer solution for different association energies and temperatures (symbols are the same as in Figure 8) for $\phi=0.2$, $E_0=30$ as a function of reduced shear rate.  

Figure 6.11 Weighted chain length distribution in 8-bead head-to-tail associating oligomer solution ($\phi=0.2$, $E_0=30$) obtained at different shear strain rates and in the absence of shear. The inset shows the chain length probability distribution plotted in log-linear scale. The molecular weight is shown in units of oligomer weight.  

Figure 6.12 Number density distribution of rings in the associating solution of 8-bead oligomers under different shear strain rates for $\phi=0.2$, $k_BT=1.0$, $E_0=30$.  

Figure 6.13 Viscosity of pure solvent at different temperatures fitted as a function of $\gamma^{0.5}$.  

Figure 6.14 $\eta/\phi$ in the chain-dominated regime for 8-bead head-to-tail associating oligomer solutions with different association energies ($E_0=20$ circles, $E_0=25$ triangles
and $E_0=30$ (diamonds) and 20-bead associating oligomer solution for $E_0=30$ (squares) as a function of the weight average molecular weight (in units of oligomer weight)………165

Figure 6.15 Specific viscosity $\eta_{sp}$ of 8-bead (squares) and 20-bead (triangles) oligomer solutions as a function of oligomer volume fraction for $k_B T=1.0$, $E_0=0$. Error bars are of the symbol size……………………………………………………………………………166

Figure 6.16 Specific viscosity, $(\eta_{sp})$, for 8-bead head-to-tail associating oligomer solutions with different association energies ($E_0=20$ circles, $E_0=25$ triangles and $E_0=30$ diamonds) and 20-bead associating oligomer solution for $E_0=30$ (squares) in the chain-dominated regime as a function of oligomer volume fraction…………………………………………………167
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Dynamics of Polymer Self-assembly by Computer Simulation

Abstract

by

ZHENLONG LI

We studied the self-assembly dynamics of two polymeric systems, block copolymer micelles and supramolecular polymer solutions using computer simulation.

Dissipative Particle Dynamics simulations were applied to study the equilibrium properties, kinetics of micellization and equilibrium chain-exchange in $A_2B_3$ and $A_4B_x$ ($x=4,6,8$) diblock copolymer micelle solutions. The critical micelle concentration, micelle aggregation number distribution and micelle structure were found to agree well with previous experimental and theoretical studies. The time-evolution of micelles from unimers is found to follow three stages: unimer consumption, equilibration of the number of micelles progressing mainly by the fusion/fission mechanism and slow adjustment of the weight-average aggregation number by micelle fusion, unimer and small aggregate exchange. The effect of polymer concentration, hydrophobic interaction energy and block length on the kinetics of micellization were also considered. By performing micelle hybridization simulations, we found the equilibrium chain exchange follows a first-order kinetic process and the characteristic time, mainly determined by chain expulsion and does not depend on polymer concentration. The chain exchange characteristic time, $\tau$, increases exponentially with core block length, $N_A$ and interaction parameter between
blocks, $\chi_{AB}$ as $\tau \sim \exp(0.67\chi_{AB}N_A)$. We also found that in contrast to theoretical predictions, chain exchange between micelles occurs more rapidly for micelles with a longer corona-block length due to a higher compatibility of diblock copolymers and therefore a lower potential barrier for chain expulsion.

Using coarse-grained molecular dynamics simulations we studied the equilibrium and rheological properties of dilute and semi-dilute solutions of head-to-tail associating supramolecular polymers with our newly-developed model for spontaneous reversible association. We found that for a given spacer length all shear-rate-dependent reduced viscosity data collapse into one master curve with two power-law regions with increasing slopes due to change of the degree of self-assembling under shear. The equilibrium viscosity is found to obey a power-law scaling dependence with exponent 1.5 on oligomer volume fraction, in agreement with experimental observations for several dilute or semi-dilute solutions of supramolecular polymers, implying that dilute and semi-dilute supramolecular polymer solutions exhibit high polydispersity, but may not be sufficiently entangled to follow the reptation mechanism of relaxation, expected for wormlike micelles.
Chapter 1

Introduction

1.1 Polymer Self-assembly

Polymer self-assembly belongs to the general field of supramolecular chemistry.\textsuperscript{1-9} A supramolecular structure (or supermolecule) is a well-defined complex of molecules held together by noncovalent interactions. The noncovalent interactions responsible for the spatial organization of supramolecular assemblies include hydrogen bonding, metal coordination, hydrophobic force, van der Waals forces, pi-pi stacking interactions and electrostatic effects. For example, the biological world is full of supramolecular assemblies, such as cell membranes formed by self-assembly of lipids and other biological molecules, DNA double helix formed through hydrogen bonding of the individual strands and the quaternary structure formed by the assembly of protein molecules.

The process by which a supramolecular assembly forms is called molecular self-assembly. One basic topic of supramolecular science is to study the dynamics of molecular self-assembly. Scientists are interested in questions such as: how do molecules
self-assemble into a specific morphology under different conditions? What is the main driving force of molecular self-assembly? How do supramolecular assemblies maintain their morphological stability, determine microscopic biological function or macroscopic material properties? Answers to these questions are of fundamental importance to our understanding of biological world and material properties. Also knowledge of self-assembly dynamics provides insights into rational design of supramolecular assemblies with desired properties and functions.

In this thesis, we focus on the self-assembly dynamics of two polymeric systems in solutions: block copolymer micelles and supramolecular polymers. Block copolymer micelles are self-assembled aggregates of block copolymers in a selective solvent, similar to low-molecular-weight surfactant micelles. Supramolecular polymers are polymers whose monomer repeat units are held together by noncovalent interactions such as metal-ligand coordination, self-complementary hydrogen bonding and biorecognition interactions. The self-assembly dynamics of both systems have been actively studied during recent years, due to their fundamental importance to understanding polymer self-assembly and their potential for various industrial applications.

1.2 Background

In this section, we provide a concise review of experimental and theoretical results that contribute to our understanding of the thermodynamic and dynamic properties of block copolymer micelles and supramolecular polymer solutions. For block copolymer micelle solutions, we cover the thermodynamic properties, including the critical micelle
concentration, micelle aggregation number and structures, and the micelle dynamics, including micellization and equilibrium chain exchange kinetics. For supramolecular polymers, we review the self-assembling structure, thermodynamic and rheological properties of the solution phase. Extensive reviews can be found elsewhere for block copolymer micelles\textsuperscript{6,10-15} and supramolecular polymers\textsuperscript{5-7,9,16-18} respectively. Understanding of the thermodynamics and dynamics of both self-assembling systems will serve as the foundation for our further exploration of the self-assembly dynamics in this dissertation.

1.2.1 Block Copolymer Micelles

1.2.1.1 Micelle Thermodynamics

The driving force for self-assembly of the block copolymers is the system’s tendency to lower the associated surface free energy per chain. Upon dissolving in a selective solvent, the core blocks tend to aggregate to minimize contact with the solvent, while the corona blocks tend to expand and stay in contact with solvent. Governed by a delicate balance of the free energy contributions from each block together with the overall entropic properties, block copolymers spontaneously self-assemble into spherical micelles with a compact core containing the insoluble blocks and a swollen corona containing the soluble blocks in a dilute selective solvent.

Block copolymers self-assemble into spherical micelles only above certain threshold concentration, which is called the critical micelle concentration (CMC). As the concentration of block copolymer increases in the solution, more micelles are formed.
while the concentration of free chains, called unimers, remains constant. Theoretically the CMC depends on the free energy difference for a single chain in the micelle and in the bulk:

\[
CMC = \exp\left(\frac{F_{\text{micelle}}/P - F_{\text{unimer}}}{RT}\right)
\]  

(1.1)

where \(F_{\text{micelle}}\) is the free energy of a micelle, \(F_{\text{unimer}}\) is the free energy of a unimer in the bulk, \(P\) is the average micelle aggregation number at equilibrium, \(R\) is the universal gas constant, \(T\) is the absolute temperature and the CMC is expressed in mole fraction. Under the constant temperature condition, the parameters determining CMC include the interaction energy and block lengths. For example, an increase of interaction energy and core block length lead to decrease of the CMC, while increase of the corona block length leads to increase of the CMC.

Since micelle formation does not represent a phase transition, the definition of CMC is somewhat arbitrary and may depend on the criteria applied. For example, Ruckenstein et al. proposed that the CMC represents equilibrium between unimers, small aggregates and larger micelles and can be identified by the appearance of large micelles in the aggregation number distribution. Experiential determination of CMC usually depends on the methods used and the CMC is defined as the concentration at which a sufficient number of micelles are formed to be detected by a given method. For example, when estimated from plots of the surface tension as a function of the logarithm of the polymer concentration, the CMC is defined as the concentration at which the surface tension stops decreasing and reaches a plateau value.
In an equilibrated block copolymer micelle solution well above the CMC, the micelle aggregation number (size) follows a bimodal distribution, with the first peak corresponding to unimers and small aggregates and the second peak corresponds to the thermodynamically optimal aggregation number under certain conditions. Different theoretical approaches were developed to predict the thermodynamic properties of the spherical block copolymer micelles at equilibrium, such as aggregation number and micelle structure, as a function of the copolymer characteristics using scaling approach \(^{11,21-26}\) or mean-field theory \(^{19,27-29}\). In these theoretical models, the total free energy of the micelle \(F_{\text{micelle}}\) is expressed as the sum of several contributions:

\[
F_{\text{micelle}} = F_{\text{int}} + F_{\text{core}} + F_{\text{corona}}
\]

(1.2)

where \(F_{\text{int}}, F_{\text{core}}, \text{ and } F_{\text{corona}}\) are the corresponding contributions of the core-corona interface, micelle core and corona, respectively. The specific expressions for these free energy terms may be different in different models. Minimization of the total micelle free energy \(F_{\text{micelle}}\) with respect to the micelle aggregation number (or size) allows to obtain the equilibrium micelle characteristics as functions of the copolymer parameters.

Scaling theories \(^{21-25}\) have been widely used to predict the correlations between the molecular characteristics of the block copolymers, such as block length, interaction energy and the equilibrium properties of the micelles, such as the core radius \(R_c\), the corona thickness \(L\) and the aggregation number \(P\). Scaling approach assumes sharp interface between the core and corona blocks and often considers the limit of monodisperse diblock copolymers with very long block lengths. There are two limiting cases for AB diblock copolymers, with B being the corona block. For the case where
\( N_A \gg N_B \) theory predicts *crew-cut* micelles with \( R_c \gg L \), while for *hairy* micelles with \( N_A \ll N_B \) it is predicted that \( R_c \ll L \). For *crew-cut* micelles, the scaling relations were developed from the De Gennes/Alexander theories for a polymer brush\(^{21,22}\). By assuming uniformly stretched chains for the core radius \( R_c \), with an aggregation number \( P \), the following relationship holds:

\[
    R_c \sim \gamma^{\frac{1}{3}} N_A^{\frac{2}{3}} a, \quad P \sim \gamma N_A
\]

where \( \gamma \) is the interfacial tension and \( a \) is the segment length. For hairy micelles, the star polymer theory was adopted\(^{23}\). For star-like polymers in good solvents the segment density profile was defined as a function of the distance of the core center and the radius of the star polymer was predicted as:

\[
    R \sim N_B^{\frac{3}{5}} f^{\frac{1}{5}}
\]

where \( f \) is the number of the arms. In hairy micelles, the number of arms was considered as the aggregation number \( P \) and it follows that

\[
    P \sim N_A^{\frac{4}{5}}, \quad L \sim P^{\frac{1}{5}} N_B^{\frac{3}{5}}
\]

Similar scaling relations were also derived by Halperin\(^{25}\) and by Zhulina and Birshtein\(^{24}\) with more detailed considerations of the block copolymer structure.

### 1.2.1.2 Micelle Kinetics

Kinetics of block copolymer micelle solution usually refer to two dynamical processes. One is the micellization, which is the process of micelle formation from unimers. Another is chain exchange between micelles in equilibrated block copolymer micelle solution. Both processes are heterogeneous processes involving multiple relaxation times and the kinetics are very sensitive to the properties of the micelle solution, such as the
interaction energy between blocks (and/or solvent), temperature, block length and system composition.

Various theoretical models\textsuperscript{30-38} have been developed to describe the kinetics of the micellization and equilibrium chain exchange in a selective solvent. Most of the models are based on free energy and potential barrier considerations. These models are usually formulated based on one or two elementary mechanisms, such as unimer expulsion/insertion and/or micelle fission/fusion. Unimer expulsion/insertion (1.6) means the process a single chain $U$ is expelled out of a micelle $M_{P+1}$ with aggregation number $P+1$ and the process a single chain $U$ diffuses in the bulk and is inserted into a micelle $M_P$ with aggregation number $P$. Micelle fission/fusion (1.7) respectively involve the process in which a micelle $M_{i+j}$ with aggregation number $i+j$ breaks into two micelles $M_i$ and $M_j$ and two micelles $M_i M_j$ merge into one micelle $M_{i+j}$.

\begin{align*}
M_P + U & \xrightarrow{\text{Expulsion}} M_{P+1} \\ M_i + M_j & \xrightarrow{\text{Fission}} M_{i+j}
\end{align*}  \hspace{1cm} (1.6) \hspace{1cm} (1.7)

Halperin and Alexander\textsuperscript{36} developed a scaling theory to describe kinetics of block copolymer micelles based on the unimer expulsion/insertion mechanism extending the Aniansson-Wall model\textsuperscript{30-32} for low-molecular-weight surfactant micelle solution. In this model, the expulsion of a block copolymer from a micelle is a single exponential decay process and the unimer expulsion relaxation time $\tau_{\text{expulsion}}$ is dependent on the block copolymer structure parameters as:

$$
\tau_{\text{expulsion}} \sim f(N_A, N_B) \exp\left[\frac{N_A^{1/3} \gamma a^2}{k_BT}\right] 
$$

\hspace{1cm} (1.8)
where \( f(N_A, N_B) \) is a polynomial function of \( N_A \) and \( N_B \) determined by the micelle structure, \( k_B \) is the Boltzmann constant. According to this model, the chain exchange process is a first order and yields a single-exponential decay function with a relaxation time \( \tau_{un} \) determined by the potential barrier for unimer expulsion, which is concentration independent and occurs considerably slower than unimer insertion. Unimer expulsion considerably slows down with an increase in the interfacial tension \( \gamma \) between blocks (or between core-block and solvent) and core-block length \( N_A \). The dependence on corona-block length \( N_B \) comes only in a pre-exponential factor with \( \tau_{un} \) increasing with \( N_B \) as a power-law function \( \tau_{un} \sim N_B^{9/5} \), reflecting slower chain diffusion for longer corona blocks.\(^{36, 37}\)

Micelle fission/fusion mechanism was first proposed by Kahlweit et al.\(^{33-35}\) for low-molecular-weight surfactant micelle solution and later suggested to contribute to the micellization process of polymeric micelles by Dormidontova\(^{37}\). Similar to unimer expulsion, micelle fusion/fission slows down with an increase in incompatibility between blocks (or between the core-block and solvent), core-block length and to less extent the corona-block length. Micelle fusion/fission is expected to become more active with an increase of polymer concentration, as the probability of aggregate collision increases and the corresponding relaxation time \( \tau_{mic} \) decreases with concentration.
1.2.2 Supramolecular Polymers

1.2.2.1 Definition

Generally speaking, supramolecular polymers are polymers whose monomer repeat units are held together by noncovalent interactions. A comprehensive definition of supramolecular polymers was purposed by Meijer et al.\textsuperscript{16}: “Supramolecular polymers are defined as polymeric arrays of monomeric units that are brought together by reversible and highly directional secondary interactions, resulting in polymeric properties in dilute and concentrated solutions, as well as in the bulk. The monomeric units of the supramolecular polymers themselves do not possess a repetition of chemical fragments. The directionality and strength of the supramolecular bonding are important features of systems that can be regarded as polymers and that behave according to well-established theories of polymer physics.”

The non-covalent interactions that hold supramolecular polymers together include metal-ligand coordination, hydrogen bonding, π-π stacking, electrostatic forces, electronic donor-acceptor interactions, and hydrophobic interactions. To form supramolecular polymers, the non-covalent interactions should at the same time be reversible and strong enough to allow significant degree of polymerization. In addition, the non-covalent interactions are often highly directional.

The two main categories of supramolecular polymers are hydrogen-bonded and metal-ligand coordination polymers. Hydrogen-bonded polymers are supramolecular polymers formed by complimentary hydrogen-bonding arrays. The building blocks of hydrogen-
bonded supramolecular polymers are typically small organic molecules linked by a spacer with functional end-groups capable of forming hydrogen bond arrays with each other. Lehn et al. first introduced hydrogen-bonded supramolecular polymers hold by triple hydrogen bond array in 1990s. The Mejer group later developed a range of supramolecular polymers built by self-complementary quadruple hydrogen-bonding units, Ureidotriazine (UTr) and ureidopyrimidinone (UPy) (Figure 1.1a) groups based on pyrimidine and triazine. With an association constant in the order of $6 \times 10^7$ M$^{-1}$ in chloroform, the UPy-based linear supramolecular polymers and networks was found to reach high degrees of polymerization.

Metal-ligand supramolecular polymers are built by metal ions and small organic ligands connected to each other by a chemically different spacer. Common metal ions capable of forming metal-ligand coordination bonds include transition metal ions, as well as the metal ions immediately following (the III A and IV metals), and some lanthanide ions. Ligands have at least one lone electron pair that can be donated to an electron-deficient metal ion to form a metal-ligand complex structure. Lehn et al. also led the first step towards the synthesis of metallo-supramolecular polymers by reporting the self-assembly of oligo-2,2’-bipyridines around Cu$^+$ and Ni$^{2+}$ in 1990s. Rehahn et al. reported the first soluble supramolecular polymers based on metal-ligand interactions. In recent years, bipyridine and terpyridine (Figure 1.1b) are the most frequently used ligand groups.
Figure 1.1 Examples of end-groups capable of forming quadruple hydrogen bond array
(a) 2-ureido-4-[1H]pyrimidone dimer, and spacer with end-ligands capable of forming metal-ligand complexes (b) terpyridine-based oligomer.

1.2.2.2 Thermodynamics

Polymer scientists have devoted much attention to understanding of the general characteristics of supramolecular polymers using different experimental observations. The mechanism of supramolecular self-assembly has been actively studied both experimentally and theoretically and a reasonable level of understanding of the process has been achieved. The experimental observations concerning supramolecular self-assembly have been analyzed in the framework of classical condensation polymerization theory. The ring-opening polymerization model and the living polymer model by Ercolani and by Cates have also been adapted to explain the ring-chain equilibrium in supramolecular polymer solution.

The degree of polymerization of supramolecular polymers is mainly determined by the strength of the non-covalent interactions. In Figure 1.2, a theoretical relationship is shown to predict the typical correlation between the association constant and the degree
of polymerization using a simple isodesmic association function\textsuperscript{4, 65} in the absence of ring formation. As is seen, the degree of polymerization increases with the association constant, as well as the oligomer concentration. With this relationship, for a given supramolecular polymer system, the degree of polymerization also depends on factors that can influence the chemical equilibrium and the association constant, such as temperature, solvent, counterions, etc. The dependence of the association constant on these external conditions thus provides control of the degree of polymerization in a way not accessible to conventional polymers.

![Figure 1.2](image)

Figure 1.2 Theoretical relationship between the binding constant and average degree of polymerization (DP) at two different oligomer concentrations.\textsuperscript{17}

The presence of rings, in addition to linear chains, affects the properties of the supramolecular polymers. At thermodynamic equilibrium there is a dynamic equilibrium between rings and chains in supramolecular polymer solutions. Different factors, including oligomer concentration, temperature and the structure of the oligomers were
found to influence the ring-chain equilibrium. The effect of the oligomer concentration is usually explained based on the theoretical analysis of polycondensation reactions by Jacobsen and Stockmayer. According to this theory, rings are dominant in dilute solution; there is a critical concentration below which all oligomers exist in rings with the assumption that the binding constant between oligomers become close to infinity. With an increase of oligomer concentration the ring fraction decreases and becomes constant due to the increasing possibility to form intermolecular associations and finally linear chains become dominant. The effect of temperature on the ring-chain equilibrium is usually explained based on the ring-opening polymerization models. Generally speaking, an increase of temperature leads to a decrease of the binding constant, thus decreasing the fraction of rings since rings have higher probability to break down than linear chains. The chemical structure of oligomers, the orientational specificity of the binding, spacer length and rigidity, can also affect the ring-chain equilibrium. For example, increase of the orientational specificity suppresses formation of small rings and promotes formation of linear chains.

1.2.2.3 Rheological Properties

Supramolecular polymers demonstrate unique rheological properties determined by their self-assembling structures. In supramolecular polymers reversible associations break and reform constantly, leading to a dynamic equilibrium between associated and non-associated free ends. Such dynamics leads to different relaxation mechanism compared to conventional polymers. On the other hand, the rheological properties of supramolecular
polymers, especially the viscosity, reflect the self-assembling structure and have been widely used to characterize the structure of supramolecular polymers.

The dynamics of supramolecular polymers are usually considered within the framework of Cates’ model for living polymers. Cates’ model is based on the reptation model for conventional entangled polymers, to which the kinetics of constant bond breaking and recombining in worm-like micelles is added. With the assumption that reptation of living chain is the dominant stress relaxation mechanism, for semi-dilute living polymer solution in fast-breaking limit, (i.e, when the characteristic time for chain breaking is very short compared to the reptation time of the polymer chain), an exponential dependence of the equilibrium zero-shear viscosity (η) on the oligomer concentration (c) is predicted:

\[ \eta \sim c^{3.5} \]  

The Cates model was successfully applied to wormlike micelle solution and later has been frequently referred to for comparison with experimental results of supramolecular polymers.

Besides the oligomer concentration, the viscosity of supramolecular polymer solutions also depends on temperature, the structure of the oligomers and other factors that are able to alter the self-assembling structure. An increase of temperature leads to a decrease of the binding constant, hence the degree of polymerization, which in turn leads to a decrease of the viscosity. A change in the oligomer structure can also influence the viscosity by affecting the ring-chain equilibrium since rings and chains of the same length contribute differently to the overall viscosity. Generally speaking, rings have more
compact structure than linear chains, thus cyclization has been found to cause a significant decrease of the viscosity of supramolecular polymers.\textsuperscript{17, 74}

Similar to conventional polymers, supramolecular polymer melts or solutions are non-Newtonian fluids. Shear-thinning behavior, that is, the viscosity of the supramolecular polymer solution decreases as the shear strain rate increases, has been widely observed in experimental studies\textsuperscript{41, 42, 75}. Besides the structural origins for shear-thinning of conventional polymer solutions, such as the stretching and alignment of chains along the shear flow, reversible associations may also be broken by the external shear force, making the rheological behavior of supramolecular polymer in a shear flow complicated. Up to now, there are a few studies on the correlation between the structure evolution and the viscosity change of supramolecular solutions under shear due to the difficulty to characterize the structure of supramolecular polymers.

\section*{1.3 Motivation and Thesis Outline}

\subsection*{1.3.1 Motivation}

The motivation of this thesis is to investigate several fundamental problems of polymer self-assembly, including the dynamics of the formation of micelles composed of diblock copolymers, chain-exchange between micelles at equilibrium, and the dynamics and rheology of supramolecular polymers.

Dynamic processes in block copolymer micelle solution, including micellization and equilibrium chain exchange have been actively studied by both experimental and
theoretical approaches during the last decade. Experimentally, the challenge for the investigation of the micelle dynamics lies in the difficulty for real-time detection of the process, especially when unimers are involved, limited by the spatial and temporal resolution of current scattering techniques. Since experimental results usually depend heavily on the specific systems and detection methods, despite a large body of data collected, a complete understanding of the kinetics, especially the micellization and exchange mechanisms and influence of different factors, is still lacking. Theoretical studies strived to generalize the most important principles from experimental observations, while usually having to simplify the problem and sacrifice a detailed description of the systems.

In a supramolecular polymer solution, the reversible associations break and reform constantly, leading to a dynamic equilibrium between associated and non-associated free ends. These interesting characteristics lead to tunable rheological properties and at the same time create considerable challenges for experimental characterization. For example, it remains a challenge to determine the degree of polymerization of a supramolecular polymer since the chemical equilibrium has to be perturbed during the measurements by some conventional techniques that require systematic dilution (e.g. classical light scattering).

Aiming to provide perspectives at a generalized level that compliments current experimental and theoretical studies, we chose computer simulation methods for our purposes. Computer simulation has emerged as a third method complimentary to experimental and analytical theoretical methods in recent years thanks to the fast
development of computational methodologies and high-performance computing techniques. It can provide the necessary background for testing analytical model predictions and can address both the large-scale macroscopic properties studied experimentally and molecular details discussed in analytical approaches.

For a study of block copolymer micelle dynamics using computer simulation, one of the main challenges is the required time and length scale. In our studies, both processes are heterogeneous processes involving multiple time and length scales. To address the corresponding time and length scales we chose DPD simulations among all molecular simulation methods for our study of block copolymer micelle solution. For our study of supramolecular polymers one of the most important properties to characterize is the viscosity of the supramolecular solution. Molecular Dynamics simulations will be used to study the self-assembling structure and compute the solution viscosity. Both DPD and MD simulation methods will be introduced in the following chapter.

1.3.2 Thesis Outline

In chapter 1, we present the basic background as well as the prior art that motivate our research interests. This chapter also sets our research plan and goals.

In chapter 2, we introduce briefly the computer simulation methods and the advantages of those methods, including DPD simulation and Molecular Dynamics simulation methods, which were used for our studies of block copolymer micelles and supramolecular polymers respectively.
In chapter 3, we first present the thermodynamics of the block copolymer micelle solution obtained from our DPD simulations, such as the critical micelle concentration, aggregation number and micelle structure. These results serve as the thermodynamic foundation for study of micellization and chain exchange kinetics of block copolymer micelles, described in chapters 4 and 5.

In chapter 4, the micellization kinetics of block copolymers will be discussed based on our DPD simulations. We first review previous experimental and theoretical studies. We then describe the simulation and data analysis details, and discuss the results for micellization kinetics obtained from DPD simulations, including the molecular mechanisms and influence of various kinetics-controlling factors.

In chapter 5, the chain exchange kinetics of block copolymers will be discussed based on the DPD simulations. We first review previous experimental and theoretical studies on the chain exchange kinetics, then describe the simulation and data analysis details. In the results section we first discuss the polymer concentration effect and then investigate the influence of the interaction energy and block length on the kinetics of chain exchange.

In chapter 6, the rheological properties of supramolecular polymer solution studied by MD simulations will be discussed. We first review previous studies on the dynamic and rheological properties of supramolecular polymers. Then we describe the reversible association model and MD simulation details. We will also discuss the equilibrium
properties, shear-thinning behavior and equilibrium viscosity of the supramolecular polymer solution obtained from our simulations.

In chapter 7, we will summarize and draw conclusions based on all studies in this thesis. The outlook of future potential work will be presented as well.
1.4 Bibliography


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Chapter 2

Molecular simulation methods

In this chapter, we introduce briefly the molecular simulation methods used in this study, including Molecular Dynamics (MD) simulation and Dissipative Particle Dynamics (DPD) simulation.

2.1 Molecular simulation

Molecular simulation refers computer simulation of atomic or molecular systems.\textsuperscript{1,2} Over the past 60 years, molecular simulation has been developed as a mature “third” method complimenting traditional experimental and theoretical methods, and found widely application in chemistry, biology and material sciences. With rapid growth of computational power, molecular simulation has become a very useful bridge between the macroscopic world and the underlying phenomena occurring at microscopic level. Scientists design and conduct \textit{in silico} experiments, aiming to interpret experimental facts based on microscopic structures and interactions inaccessible by experimental techniques. Well-developed molecular simulation models, on the other side, enable prediction of
novel phenomena and material properties, and are useful to guide experimental study. Also molecular simulations are often used to test and compliment theoretical models based on statistical mechanical theories.

Molecular simulations include a family of computer simulation techniques. Common molecular simulation methods include *ab initio* quantum chemistry, Molecular Dynamics (MD) simulation, Monte Carlo (MC) simulation, Brownian Dynamics (BD) simulation, Dissipative Particle Dynamics (DPD) simulation, etc. In this thesis, based on the time and spatial scales involved in systems studied, we adapted MD simulation for study of supramolecular polymer solution and DPD simulation for study of block copolymer micelle solution.

### 2.2 Molecular Dynamics simulation

A detailed description of MD simulation technique can be found in several books.\(^2\) MD simulation consists of the numerical integration of Newton’s equation of motion with discrete time steps for a system with \(N\) particles:

\[
\frac{dr_i}{dt} = v_i, \quad \frac{dv_i}{dt} m_i = F_i
\]

Where \(r_i\) is the coordinate of the particle \(i\), \(m_i\) its mass, \(t\) the time, \(v_i\) the velocity and \(F_i\) the total force on the particles. The forces are composed of different components from different particles, defined by the potential functions. There are various potentials of different levels of physical accuracy. Classic empirical potentials most commonly used in chemistry and biology fields, so-called force fields, are based on molecular mechanics reduced from a fully quantum description of the systems. With the Born-Oppenheimer approximation, the nuclei are treated as point particles that follow classical Newtonian
dynamics and the effect of the electrons is approximated as a single potential energy surface, usually representing the ground state. Classic empirical potentials are usually able to reproduce structural and conformational changes without chemical reactions. In the cases higher accuracy is required, potentials based on quantum mechanics or hybrid classical/quantum potentials were developed. To the other end, coarse-grained models are usually applied to very large systems or long timescales that can’t easily be studied by all-atom force fields using current computer resources. For examples, to address the spatial and time scales in polymeric systems, a simple bead-spring model is usually used to represent a polymer chain in coarse-grained MD simulations.

Classical MD simulation samples systems at thermodynamic equilibrium. For study of the rheological properties of supramolecular polymers, we simulated supramolecular polymer solution under shear flow, which is away from equilibrium, using Non-Equilibrium MD (NEMD) simulation. NEMD simulation samples non-equilibrium ensemble by modifying the classical MD algorithms to incorporate a perturbation field into the systems. For example, in NEMD simulations, to simulate planar shear flows, the SSLOD algorithm is usually applied, in which Lees-Edwards shearing periodic boundary conditions, instead of fixed periodic boundary conditions, is used to generate a linear streaming velocity profile. It is also possible to generate shear flow by deforming the simulation box (Figure 2.1).
2.3 DPD simulation

Dissipative particle dynamics (DPD) simulation is a mesoscopic simulation method derived from MD simulation and BD simulation (or Langevin Dynamic simulation) techniques by Hoogerbrugge and Koelman.\(^6\)\(^,\)\(^7\) In DPD simulation, a complex fluid is modeled as a set of beads, with each bead represents a microscopic fluid region containing a group of atoms or molecules. Time evolution of the system is also governed by Newton’s equation of motion (equation 2.1), similar to Molecular Dynamics simulation. The pairwise interaction force between different beads contains three parts:

\[
F_i = \sum_{i \neq j} \left( F_{ij}^C + F_{ij}^D + F_{ij}^R \right)
\]  

(2.2)

where \(F^C\) is the conservative force, \(F^D\) is the dissipative force, and \(F^R\) is the random force. All forces have the same cutoff distance \(r_c\), which is the only length scale in the systems which defines the length units. The conservative force is a soft repulsion acting along the line of centers and is given by

Figure 2.1 NEMD simulation of steady shear flow by deforming the simulation box.
where \( a_{ij} \) is a maximum repulsion between two particles \( i, j \), and \( r_{ij} = r_i - r_j \). The dissipative force and random force are:

\[
F_{ij}^D = -\gamma w^D (r_{ij}) \hat{r}_{ij} \quad F_{ij}^R = \sigma w^R (r_{ij}) \theta_{ij}(t) \hat{r}_{ij}
\]

(2.4)

Where \( \gamma \) is the dissipative constant, and \( \sigma \) is the amplitude of statistical noise, \( w^D \) and \( w^R \) are \( r \)-dependent weight functions, \( v_{ij} = v_i - v_j \), and \( \theta_{ij}(t) \) is a randomly fluctuating variable with Gaussian statistics: \( <\theta_{ij}(t)> = 0 \) and \( <\theta_{ij}(t) \theta_{ij}(t')> = (\delta_{ij} \delta_{kl} + \delta_{il} \delta_{jk}) \delta(t-t') \). Both forces also act along the line of centers and conserve linear and angular momentum.

Espanol and Warren\(^8\) proved that the DPD simulation is simulated in the canonical NVT ensemble if the following relation holds for the amplitudes and weight functions:

\[
\gamma = \frac{\sigma^2}{2k_B T} \quad \text{and} \quad w^D (r_{ij}) = [w^R (r_{ij})]^2
\]

(2.5)

where \( k_B \) is the Boltzmann constant and \( T \) is the temperature. This relation is the so-called fluctuation-dissipation theorem. It makes the dissipative and random force to interact and build a thermostat and maintain the thermodynamic equilibrium, thus is essential for momentum conservation of the system. This relationship also indicates that the dissipative constant is correlated to the amplitude of statistical noise, and usually only the repulsive parameter in the conservative force is changeable (with established relation of the amplitudes).

In conventional DPD simulations, the conservative force is purely a linear soft repulsive interaction that drives particles to move away from each other. With this potential the simulation is normally performed under the periodic boundary conditions or in a confined
space. Using the standard repulsive potential many equilibrium and dynamic features of polymer solutions and blends were successfully reproduced. For instance, for a homopolymer in a good solvent the Flory exponent of 0.6 was obtained in DPD simulations for the radius of gyration and diffusion coefficient. To study the behavior of large particles such as colloidal particles, the standard DPD approach can be modified. Short range attractions can be simply implemented by adding a linear attractive force to the basic particle interactions. When two particles collide, they are pulled together to an equilibrium distance less than the interaction cutoff distance due to the combination of repulsive and attractive forces. This effect simulates bonds being formed spontaneously, which may break if the particles are pulled apart. The DPD method with a combination of short-range repulsive force and long-range attractive force has been used to simulate the behavior of liquid droplet surrounded by a gas phase. Groot and Stoyanov also developed a DPD model with attractive potential to account for the adhesive interaction and the liquid-gas co-existence in colloidal particles, powders, and granular solids systems.

The preparation step for a DPD simulation is to construct a DPD model to represent a real system by coarse-graining the system into different particles with specific interactions between different particles. Such a coarse-graining process usually includes the calculation of the atomistic interactions and substitution of the atomistic interactions with effective potentials between the centers of the particles. The first step is to set the length, time, and mass scales for the DPD simulation. The length and mass scales are determined by the diameter (the cutoff distance $r_c$) and mass of the particles. Instead of
defining a unit for time, the condition of \( k_B T = 1 \) is usually chosen, which effectively specifies a unit of time. To correctly describe the thermodynamic state of an arbitrary liquid, the fluctuations in the liquid should be described correctly. This requires that the compressibility of the system should be reproduced correctly in a DPD simulation. As the compressibility of a system is mainly determined by the particle density and the repulsive interaction between particles in a DPD simulation, Groot and Warren\(^{13} \) have proven that the repulsive interaction parameter of pure liquid \((a_{ij})\) is reciprocal to the density of liquids \((\rho)\): \( a_{ij} \rho = 75k_B T \). For example, at room temperature (300K), the dimensionless compressibility of water (15.9835) can be reproduced with particle number density \( \rho = 3 \) and repulsive parameter \( a_{ij} = 25 \). With this principle, a real system can be modeled at different coarse-grained levels, depending on the specific time and space scales to be addressed. It is conventional in the DPD framework to base the coarse grain mapping on that of water.\(^{14} \) Namely, the amount of matter contained in each DPD site is constant for all species and is taken as that of the mapping chosen for water. This means that, with the standard mapping of three water molecules per DPD site\(^{14} \), the coarse graining for polymers, such as PEO (polyethylene oxide) or PEE (polyethylethylene) gives the conventional mapping of approximately one monomer per site. To make a stronger link with experiments, the constraint of constant density of the beads for all species can be removed.\(^{15} \) The resulting coarse graining hence varies with species identity. This variation is chosen such that the bulk density of the pure species matches experimental data. For instance, with such mapping 1.392 repeat units of PEO and 0.774 units of PEE were used as for a bead size.\(^{15} \) Additionally bond lengths and bond angles can be adjusted to reproduce the experimental values for the radius of gyration of polymer chains.\(^{15} \)
The repulsive parameters $a_{AB}$ between different types of particles (A,B) in the DPD model is accessible from the Flory-Huggins parameter $\chi$. Groot and Warren\textsuperscript{13} determined a linear dependency between $a_{AB}$ and $\chi_{AB}$:

$$a_{AB} = a^0_{AB} + k_D(\rho)\chi_{AB}$$  \hspace{1cm} (2.6)

where $k_D(\rho)$ is a constant depending on the density $\rho$. The Flory-Huggins parameter can be obtained through the interpolation of experimental data, such as solubilization parameters, heat of vaporization, etc. Also it can be obtained by Quantitative-Structure-Activity-Relationship (QSAR) calculations, Molecular Dynamics (MD) simulations, or Monte Carlo (MC) simulations.

The advantages of DPD simulations are reflected when compared to Molecular dynamics and Brownian Dynamics simulations. While DPD simulation is also based on Newton’s laws of motion, similar to MD simulations, the time and length scales in DPD are greatly enhanced compared to MD simulation. Compared to Brownian Dynamics simulation, the system momentum is conserved during the simulation, thus the hydrodynamic behavior of fluids is correctly reproduced.\textsuperscript{16} With those advantages, DPD simulations have been widely used to simulate large-scale and complex self-assembly phenomena, such as surfactant and polymer micelles, vesicles, polymersomes, membranes and bilayers.\textsuperscript{15,17-23}

Applications of DPD simulations to polymer systems have been advanced by the relationship between the repulsive parameter $a_{ij}$ and the Flory-Huggins interaction parameter.\textsuperscript{13} Under the condition temperature $k_B T=1$, particle density $\rho=3$, and repulsive parameter between particles of the same type $a_{AA}=a_{BB}=25$, the repulsion between two
different types of particles A and B follows linear dependence on the Flory-Huggins parameter $\chi_{AB}$:

$$a_{AB} = 25 + 3.497\chi_{AB}$$  \hspace{1cm} (2.7)

Besides being widely used to study the static properties of polymeric systems, DPD simulation has also been frequently used to study polymer dynamics.\textsuperscript{9, 10, 24-26} It has been proven that DPD simulation can reproduce the scaling relationship for relaxation time and diffusion coefficients of polymers in both the melt and solutions with a chain length as short as 5.\textsuperscript{9, 10, 24}

With those advantages, it is promising to simulate the dynamical process of block copolymer micellization as well as the micelle solution at equilibrium using DPD simulations. In our DPD simulations, the block copolymers will be modeled as simple linear bead-spring chains. The length of the model chain is limited to around 10 due to available computing power, thus our simulations will provide insights for real block copolymer micelles formed by relatively short oligomers, as is the practice in many experimental studies.
2.4 Bibliography


Chapter 3

Equilibrium Properties of Block Copolymer Micelle Solution by DPD Simulation

In this chapter, DPD simulation study on the equilibrium properties of block copolymer micelle solution is presented. We first introduce the DPD simulation procedure and data analysis details, which is also useful for the simulations and data analysis for studies of block copolymer micellization and chain exchange discussed in later chapters. Then discussed are the equilibrium properties of the block copolymer micelle obtained in our DPD simulations, including the critical micelle concentration, micelle aggregation number, micelle structure. Those thermodynamic properties presented are the first, to our knowledge, systematic studies of block copolymer solution by DPD simulation. They are also necessary foundation for further studies of the dynamics of block copolymer micelles in later chapters.
3.1 Simulation Details

3.1.1 DPD Model

One of the continuing challenges for computer simulation studies on block copolymer solution is the time and length scales accessible to modern computing power. For examples, with an all-atomic model, we can only simulate one single surfactant micelles in aqueous solution for several nanoseconds with conventional MD simulation. This only allows us to study limited information of the micelles, such as the equilibrium structure. Aiming to study the equilibrium properties of block copolymer micelle solution, the micellization kinetics and the chain exchange dynamics, we chose DPD simulations among all molecular simulation methods, since DPD simulations is potentially able to simulate the overall process of micelle formation from randomly dispersed solution and to simulate several micelles in a solution for a long time period.

In our DPD simulations, a diblock copolymer (oligomer) chain was modeled as a linear bead-spring chain $A_mB_x$ with $m$ hydrophobic (A) beads and $x$ hydrophilic (B) beads linked by a harmonic potential $F_{\text{bond}} = k(r - b_0)^2$, where the force constant is $k = 100$ and an equilibrium bond length is $b_0 = 1$ (in reduced “DPD units”), as shown in Figure 3.1a. Solvent molecules were represented as single beads identical to the hydrophilic block bead (B) in a model chain. All the beads had the same diameter ($d = 1$) and mass ($m = 1$), which will be used as units of length and mass.
Figure 3.1 (a) Schematic representation of a model $A_4B_8$ chain and (b) a snapshot of the simulation box containing $A_4B_8$ chains ($a_{AB} = 40$, $\varphi = 0.05$) (the hydrophobic block is shown by connected balls, the hydrophilic block is shown by connected bonds (i.e. balls omitted), solvent beads are not shown, rendered by VMD).

In all simulations we used cubic simulation box ($30^3$) maintained by periodic boundary conditions (PBC). This rather large box size was selected to accommodate a larger number of oligomers (and hence micelles at equilibrium) and to minimize the possible influence of box-size effects on polymer chain diffusion coefficient. A snapshot of the simulation box is shown in Figure 3.1b. The density of all beads in a simulation box including polymer monomers and solvent was equal to 3 and the repulsive interaction parameters between same type of beads were $a_{AA} = a_{BB} = 25 \ k_BT/d_p^2$ to reproduce the compressibility of water at room temperature. In the following $k_BT/d_p^2$ will be omitted when referring to values of the interaction parameter $a_{ij}$. Based on the $a_{BB}$ interaction parameter, the B-block is in a good solvent with the Flory exponent 0.6 observed for the homopolymer radius of gyration and diffusion coefficient. The repulsive interaction
parameter between different types of beads $a_{AB}$ was larger than 25 to reflect the A-B hydrophobic interactions. Selection of absolute values of $a_{AB}$ was made based on simulation test runs for different chains, $A_2B_3$ and $A_xB_x$ ($x = 4, 6, 8$), to obtain spherical micelles, which are not kinetically frozen (i.e. chain exchange between micelles could be observed within the simulation time scale). For solutions of $A_2B_3$ chains, we varied the repulsive parameter ($a_{AB} = 47.5, 50, 52.5, 55$) and volume fraction of chains, $\varphi$, from $\phi = 9.3\times10^{-4}$ to 0.05 to study the effect of oligomer concentration and hydrophobic interaction energy on the properties of micelle solution. For solutions of $A_xB_x$ chains, we kept the hydrophobic block length ($N_A = 4$) and the volume fraction of chains ($\varphi = 0.05$) constant, and varied the hydrophilic block length ($N_B = 4, 6, 8$) and repulsive parameter ($a_{AB} = 38, 40$) to study the chain length and hydrophobic interaction energy effects.

3.1.2 DPD Simulations

In our simulations, the cutoff distance for all DPD forces $r_c$ was chosen as the unit of length, beyond which the pair-wise interaction between two beads becomes zero. The friction coefficient $\gamma$ for the dissipative force was chosen to be 3.0, and the noise amplitude is $\sigma = (2\gamma k_BT)^{1/2}$ in all simulations$^3$. Thus in all the simulations NVT ensemble was adopted ($k_B T = 1$). The equation of motion was integrated with a modified version of the velocity-Verlet algorithm$^5$ with time step $\Delta t = 0.04$.

We used a free-source code LAMMPS$^6$ for the DPD simulations on the HPC computer cluster at Case Western Reserve University. All DPD simulations started from a random dispersion of model chains in the solution. Initially we applied repulsive parameter $a = 25$
for all pair interactions between the beads and after $t = 4 \times 10^4$ simulation time steps all the chains were homogeneously dispersed in the solution (Figure 3.1a). Then the hydrophobic interaction was imposed by increasing $a_{AB}$ to the desired value and the process of micelle formation was monitored. The movement trajectories were collected every 100 time steps for data analysis.

By monitoring the time-dependent weight-average aggregation number, the equilibrium state of micelle solution was determined (when the average aggregation number reaches a plateau level with deviations less than 15% of the average value). The simulations were conducted for an additional period of time to characterize the equilibrium properties of the micellar solution. For solutions with $A_2B_3$ chains, the simulation time for each system at equilibrium was about $t = 3.2 \times 10^5$, and for systems with $A_4B_x$ chains, it was about $t = 1.2 \times 10^6$. In the polymer volume fraction range studied ($\varphi \leq 0.05$), all final micelles had spherical form.

### 3.1.3 Micelle Analysis

We used VMD\textsuperscript{7} for displaying movement trajectories and data analysis. In all simulation runs we observed that the originally randomly dispersed free chains self-assemble into small aggregates very quickly and then large spherical micelles gradually form during the course of simulations. To distinguish different aggregates, we used a general distance criterion.\textsuperscript{8} With this criterion, any pair of chains within a certain cut-off distance between the centers of mass of hydrophobic blocks belongs to the same aggregate. After testing the criterion on different systems, we determined that the result does not depend on the
precise choice of the cutoff distance, and a general cut-off distance of 1.2 was used to
distinguish different aggregates for all systems with A₂B₃ chains, and cut-off distance of
1.5 was used for aggregates composed of A₄Bₓ chains. In this way the instantaneous
affiliation of each chain, as well as the aggregation number and composition of each
aggregate, are clearly determined. With all the aggregates identified, the number- (\(M_n\))
and weight-average (\(M_w\)) aggregation number of micelles was calculated as
\[
M_n = \frac{\sum_i n_i P_i}{\sum_i n_i}, \quad M_w = \frac{\sum_i n_i P_i^2}{\sum_i n_i P_i}
\]  
(3.1)
where \(n_i\) is the number of aggregates (including unimers) containing \(P_i\) oligomers.

3.2 Results and Discussions

3.2.1 Critical Micellar Concentration

As there is seldom any report about determination of critical micelle concentration in
DPD simulations of block copolymer solution, we first studied the CMC in one of our
DPD simulation. Because micelle formation does not represent a phase transition, the
definition of CMC is somewhat arbitrary and may depend on the criteria applied. ⁹⁻¹⁶ To
determine the CMC for A₂B₃ micellar solution with repulsive parameter \(\sigma_{AB} = 47.5\), we
calculated the weight average aggregation number and the volume fraction of unimers
and small aggregates in a range of system compositions \(\phi \approx 9 \times 10^{-5} - 0.05\), as is seen in
Figure 3.2. The fraction of unimers (and other small aggregates) increases with oligomer
volume fraction and reaches a plateau level at about \(\phi \approx 3.7 \times 10^{-3}\). At that point the weight
average aggregation number starts to rapidly increase. Thus based on the behavior of both
the unimer volume fraction ¹⁰, ¹⁴, ¹⁶ and weight-average aggregation number, we
determined that CMC for this case is \(\phi \approx 3.7 \times 10^{-3}\).
Figure 3.2 Weight-average aggregation number and unimer number density as a function
of oligomer number density in $A_2B_3$ micellar solution ($a_{ab} = 47.5$) (Lines are the guides
of eye only). The vertical line corresponds to the CMC at $\phi \approx 3.7 \times 10^{-3}$.

We note that the plateau level for unimer volume fraction (about $1.9 \times 10^{-3}$) is lower than
the CMC value. It is possibly because of the contribution of small aggregates such as
dimers, trimers, etc.\textsuperscript{16} Such small aggregates exist (in addition to unimers) over the whole
concentration range considered and their volume fraction reaches plateau levels at
different oligomer concentrations, as seen in Figure 3.3. The volume fraction of dimers
and trimers is lower than that for unimers and reach the corresponding plateau levels at
higher oligomer volume fractions. Thus, the CMC represents equilibrium between
unimers, small aggregates and larger micelles and can be identified by the appearance of
large micelles in the aggregation number distribution, as proposed by Ruckenstein and
Nagarajan.\textsuperscript{12}
Figure 3.3 Volume fraction of unimers, dimers and trimers in $A_2B_3$ micellar solutions ($a_{AB} = 47.5$) as a function of oligomer volume fraction (Lines are the guides of eye only).

As the total volume fraction of oligomer increases from zero, the appearance of the shoulder and/or a peak of the aggregation number distribution can also be considered as a signature of CMC. As is seen in Figure 3.4, the aggregation number distribution of block copolymer solution below the CMC is an exponential decay function. With an increase in oligomer volume fraction above the CMC ($\approx 3.7 \times 10^{-3}$) the distribution starts to develop a shoulder. At even higher oligomer number density the distribution exhibit a maximum, corresponding to the thermodynamically preferable micelle aggregation number.
Figure 3.4 Weight-average aggregation number distribution of A₂B₃ diblock copolymer solution ($a_{AB} = 47.5$) at different polymer volume fractions $\phi$.

It is worthwhile to note that CMC depends on other conditions such as the hydrophobic interaction energy and chain length: as the hydrophobic interaction energy increases or corona block length decreases (which leads to an increase of the average aggregation number), the CMC decreases.$^{10,15-17}$ For comparison, we listed the unimer concentration at equilibrium for different micellar systems (at $\phi = 0.05$) in Table 3.1 in section 3.2.2 where the equilibrium properties of all micelle solution were summarized.

### 3.2.2 Micelle Aggregation Number

In Fig. 5, the time-dependent weight-average aggregation number of block copolymer solution ($a_{AB}$=50, $\phi = 0.05$) was shown. As is seen, the aggregation number increases quickly as the simulation starts, and reach a plateau level finally (when the average aggregation number reaches a plateau level with deviations less than 15% of the average
value). The first stage, i.e., micellization stage was used for analysis of micellization kinetics. And the second stage, equilibrium simulation, which represents the majority of the entire simulation, was used to analyze the equilibrium properties of the micelle solution. The number- and weight-average aggregation number distributions were calculated based on the occurrence probability of aggregates collected over the entire time range of equilibrium micelle state simulations.

![Figure 3.5](image)

**Figure 3.5** Time-dependent weight-average aggregation number of block copolymer solution \((a_{AB}=50, \phi = 0.05)\) in the DPD simulation.

### 3.2.2.1 Oligomer Concentration Effect

Figure 3.6 shows the weight-average aggregation number distribution for A₂B₃ micellar solutions with the same interaction energy \((a_{AB} = 47.5)\) for different oligomer volume fractions. As is seen, all distributions are relatively smooth and exhibit one minimum and one maximum, indicating equilibrium between unimers (and small aggregates) and larger micelles. The maximum of the distribution corresponds to the thermodynamically
preferable micelle aggregation number under the specific conditions. The preferable aggregation numbers are all similar to each other for different concentration, as the corresponding distribution peaks are nearly the same. This is to be expected for micellar solutions well above the CMC, as the polymer concentration does not affect the micelle aggregation number. The position of the minimum of the distribution is also rather similar indicating that such aggregates are the least stable in all cases, while the absolute values at the minimum are somewhat different: for lower oligomer volume fractions the probability of finding small aggregates is slightly higher (and the corresponding average aggregation number is slightly lower).

![Graph](attachment:image-url)

Figure 3.6 Weight-average aggregation number distribution of A$_2$B$_3$ micellar solutions ($a_{AB}= 47.5$) at different oligomer volume fractions: $\varphi = 0.03, 0.04, 0.05$. 

45
3.2.2.2 Interaction energy effect

Figure 3.7 shows the weight-average (a) and number-average (b) aggregation number distribution for A$_2$B$_3$ micellar solutions for different interaction energies at oligomer volume fraction $\varphi = 0.05$. For A$_2$B$_3$ micellar solutions at different oligomer volume fractions, the preferable aggregation numbers and the corresponding distribution peaks are nearly the same. For lower oligomer volume fractions the probability of finding small aggregates is slightly higher and the corresponding average aggregation number is slightly lower as expected for micellar solutions well above the CMC. With an increase in the interaction energy $a_{AB}$ the equilibrium aggregation number for A$_2$B$_3$ micelles increases and the peak position of the distribution shifts to higher values. An increase in $a_{AB}$ (which is related to the interfacial tension) implies the larger incompatibility with a solvent (and corona block) that drives the chain self-assembly to form larger micelles in order to minimize the interfacial tension.
Figure 3.7 Weight-average (a) and number-average (b) aggregation number distribution for A₂B₃ micellar solutions with different interaction energies $a_{AB} = 47.5, 50, 52.5, 55$ for oligomer volume fraction $\varphi = 0.05$. 
The aggregation numbers at peak positions $M_{\text{wpeak}}$ and $M_{\text{npeak}}$ of the weight- and number-average aggregation number distributions were calculated by fitting the peak area with normal distribution. Table 3.1 shows the results for $A_2B_3$ micellar solutions at the same oligomer volume fraction ($\varphi = 0.05$) for different interaction energies ($a_{AB} = 47.5, 50, 52.5, 55$). As is seen, the values of $M_{\text{npeak}}$ and $M_{\text{wpeak}}$ are rather similar for a given $a_{AB}$ value. For comparison, the corresponding number-average $M_n$ and weight-average aggregation numbers $M_w$ are also listed in the Table 3.1. Since $M_n$ includes all the aggregates and unimers, it is lower than $M_{\text{npeak}}$ calculated by fitting the high-end of the aggregation number distribution. With an increase in $a_{AB}$ the minimum of the distribution becomes broader and the probability of finding unimers or small aggregates decreases. The corresponding volume fractions of unimers for the micellar solutions are listed in Table 3.1. As is seen, increasing the hydrophobic interaction energy causes the average aggregation number to increase and average unimer concentration to decrease. Similar results have been observed in DPD and Monte Carlo simulations of diblock copolymer micelle solutions.\textsuperscript{14-16, 18}
Table 3.1 Equilibrium aggregation number determined from number- and weight-average aggregation number distributions $M_{\text{npeak}}$ and $M_{\text{wpeak}}$; number- and weight- average aggregation number $M_n$ and $M_w$; and unimer volume fraction $\varphi_{\text{unimer}}$ for $A_2B_3$ micellar solutions with different interaction parameters $a_{AB}$ and for $A_4B_4$, $A_4B_6$, $A_4B_8$ micellar solutions (\(\varphi = 0.05\)).

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$a_{AB}$</th>
<th>$M_{\text{npeak}}$</th>
<th>$M_{\text{wpeak}}$</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$\varphi_{\text{unimer}} \times 10^{-4}$*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2B_3$</td>
<td>47.5</td>
<td>24±7</td>
<td>26±6</td>
<td>10±1</td>
<td>25±2</td>
<td>19.0±0.6</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>50</td>
<td>31±6</td>
<td>33±6</td>
<td>16±1</td>
<td>32±1</td>
<td>9.9±0.5</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>52.5</td>
<td>36±6</td>
<td>37±5</td>
<td>24±3</td>
<td>38±2</td>
<td>4.9±0.1</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>55</td>
<td>43±8</td>
<td>43±5</td>
<td>32±3</td>
<td>41±2</td>
<td>2.8±0.4</td>
</tr>
<tr>
<td>$A_4B_4$</td>
<td>38</td>
<td>39±10</td>
<td>43±12</td>
<td>14±2</td>
<td>39±3</td>
<td>15.8±3.2</td>
</tr>
<tr>
<td>$A_4B_6$</td>
<td>38</td>
<td>26±7</td>
<td>30±9</td>
<td>9±2</td>
<td>26±2</td>
<td>24.7±3.5</td>
</tr>
<tr>
<td>$A_4B_8$</td>
<td>38</td>
<td>17±4</td>
<td>22±7</td>
<td>7±1</td>
<td>19±2</td>
<td>32.6±4.1</td>
</tr>
<tr>
<td>$A_4B_4$</td>
<td>40</td>
<td>51±6</td>
<td>55±7</td>
<td>32±5</td>
<td>54±4</td>
<td>4.9±2.9</td>
</tr>
<tr>
<td>$A_4B_6$</td>
<td>40</td>
<td>38±4</td>
<td>40±4</td>
<td>21±3</td>
<td>38±3</td>
<td>8.9±3.3</td>
</tr>
<tr>
<td>$A_4B_8$</td>
<td>40</td>
<td>31±4</td>
<td>34±3</td>
<td>15±2</td>
<td>31±2</td>
<td>12.9±4.3</td>
</tr>
</tbody>
</table>

* For all $A_2B_3$ micelle solutions $\varphi_{\text{unimer}}$ was calculated for a given $a_{AB}$ by averaging over different volume fractions, while for $A_4B_x$ micelle solutions it was calculated by averaging over time.

### 3.2.2.3 Corona block length effect

To investigate the effect of hydrophilic block length we have varied the B-block lengths: $N_B = 4, 6, 8$ while keeping core block the same $N_A = 4$. The weight-average and number-
average aggregation number distributions for $A_4B_4$, $A_4B_6$ and $A_4B_8$ micellar solutions ($\varphi = 0.05$) are shown in Figure 3.8 for $\alpha_{AB} = 38$. The weight-average and number-average aggregation number distributions for $A_4B_4$, $A_4B_6$ and $A_4B_8$ micellar solutions ($\varphi = 0.05$) are also shown in Figure 3.9 for $\alpha_{AB} = 40$. As is seen, the longer the hydrophilic block length, the smaller the equilibrium aggregation number and more narrow the distribution. The observed decrease in the aggregation number is due to the larger loss in conformational and translational entropy for a longer chain to become part of a large micelle. Qualitatively similar results were observed experimentally$^{19,20}$ and in computer simulations of block copolymer micelles.$^{16,18}$ Decrease in the average aggregation number with an increase in B-block length is accompanied by the increase in the fraction of unimers and small aggregates. Table 3.1 lists the equilibrium aggregation numbers, weight- and number average aggregation numbers and unimer volume fraction.
Figure 3.8 Weight-average (a) and number-average (b) aggregation number distribution for A₄B₄, A₄B₆ and A₄B₈ micellar solutions ($a_{AB} = 38$) for oligomer volume fraction $\phi = 0.05$. 

51
Figure 3.9 Weight-average (a) and number-average (b) aggregation number distribution for A₄B₄, A₄B₆ and A₄B₈ micellar solutions ($a_{AB} = 40$) for oligomer volume fraction $\varphi = 0.05$. 

52
3.2.3 Micelle Structure

To characterize the structure of the micelles obtained in our simulations the density profiles of the micelle core (hydrophobic blocks) and corona (hydrophilic blocks) were calculated as a function of the distance from the micelle center of mass.

Monomer density profiles for core and corona of $A_2B_3$ micelles of the same aggregation number ($P = 35$) with different hydrophobic interaction energies $a_{AB}$ are shown in Figure 3.10. As is seen, the density profile is almost the same in all cases. In the core part, the density of hydrophobic beads is around 3 (equal the overall density of all beads in the simulation box), indicating that the core is a dense melt of the hydrophobic blocks.

![Graph](image)

Figure 3.10 Monomer density profiles for core and corona of $A_2B_3$ micelles of aggregation number $P = 35$ for different hydrophobic interaction energies ($a_{AB} = 47.5, 50, 52.5, 55$).
Figure 3.11 shows the density profiles for $A_4B_4$, $A_4B_6$ and $A_4B_8$ micelles with the same aggregation number $P = 40$, ($\alpha_{AB} = 40, \varphi = 0.05$). The density profiles for the core monomers are practically the same for all three cases. The plateau value of the hydrophobic beads density inside the core is close to 3, implying that there are no hydrophilic beads or solvent inside the core (one can recall that the density in our simulations was equal to 3). The core/corona interfaces are very similar in all cases with interfacial width being about 1 (i.e. comparable to the bond length). The main difference seen in the density profiles concerns the monomer density in the corona: as the hydrophilic block length increases, the monomer density in the corona extends to a larger distance. The density profiles of $A_2B_3$ micelles of the same aggregation number with different interaction energies $\alpha_{AB}$ do not show obvious difference (see supporting information). Similar monomer density profiles were obtained in Monte Carlo simulations of diblock copolymer micelles. $^{10, 14-16}$ All micelles observed in our simulations were of a spherical shape except for the transient (non-stable) aggregates formed just after micelle fusion or just before micelle fission.
In this chapter, using DPD simulation technique we studied the equilibrium properties of the equilibrated dilute block copolymer micelle solution, such as the CMC, aggregation number and micelle structure.

We first described the model and DPD simulations details. In our simulations, the diblock copolymer micelle solutions were composed of linear bead-spring chains immersed in an explicit solvent environment. The hydrophobic interaction between the hydrophobic blocks and the hydrophilic blocks (as well as the solvent) was introduced by a repulsive parameter which is larger than the repulsion between identical blocks. Upon imposing of the hydrophobic interaction, randomly dispersed block copolymers self-assembly into big
spherical micelles quickly. Further DPD simulations of equilibrated micelle solution provided useful information on the equilibrium properties of obtained micelle solution. In agreement with previous reports, DPD simulation is found to be a very efficient simulation technique to study the equilibrium properties of diblock copolymer micelle solutions.

The CMC of the block copolymer solution was determined in our simulations by the shared transition point where the unimer concentration stabilizes and the average aggregation number increases sharply (with an increase in $\varphi$) due to the formation of large micelles. We found that the CMC exceeds the unimer concentration at equilibrium due to the contribution of small aggregates (dimers, trimers, etc.).

We obtained the aggregation number distributions for micellar solutions of $A_2B_3$ and $A_4B_x$ ($x=4,6,8$) diblock copolymers. In all cases the aggregation number distribution was rather smooth and exhibited one minimum and one maximum, indicating equilibrium between unimers (and small aggregates) and larger micelles. We found, as is expected, that increasing the polymer concentration does not change the average aggregation number, while increasing the hydrophobic interaction energy causes the unimer concentration to decrease and the average aggregation number to increase. Increasing the hydrophilic chain length causes the unimer volume fraction at equilibrium to increase and average aggregation number to decrease.
Micelle structure was characterized by the density profile of the micelle core and corona as a function of the distance from the micelle center of mass. For micelles with same core block length and aggregation number, while different corona block length, the density profiles for the core monomers are practically the same. The main difference seen in the density profiles is that as the hydrophilic block length increases, the monomer density in the corona extends to a larger distance. The density profiles of A_2B_3 micelles of the same aggregation number with different interaction energies $a_{AB}$ do not show obvious difference.

Those equilibrium properties of block copolymer micelle solution reported in this chapter were the first systematic studies on the thermodynamics of dilute block copolymer micelle solution. Our simulation results indicated that DPD simulation is a very efficient to study the properties of diblock copolymer micelle solutions. Results in this chapter will serve as the thermodynamic foundation for further study on the micelle dynamics in the following two chapters.
3.4 Bibliography


Chapter 4

Kinetics of Block Copolymer Micellization by DPD Simulation

In this chapter, the kinetics of block copolymer micellization studied by DPD simulation is presented. We first review previous experimental and theoretical studies, then describe simulation and data analysis details. In the results section, we first discuss using the example of A_2B_3 solution the general features and possible mechanisms of the micelle formation process from unimers and then investigate the influence of different factors such as oligomer concentration, interaction energy and block length, on the kinetics of the micellization process. Finally, we summarize the main finding in this chapter.

4.1 Introduction

Various experimental techniques, such as nonradiative energy transfer and fluorescence-quenching techniques, time-resolved light, small angle neutron and synchrotron X-ray scattering or stopped-flow have been applied to study the process of micelle formation or re-equilibration induced by sudden change in temperature (T-jump), pH or solvent.\textsuperscript{2-15}
There are several experimental challenges for the investigation of the micellization kinetics. Firstly, real-time detection of the micellization process, especially the very early stage, is limited by the spatial and temporal resolution of current scattering techniques. Often the signal strength is insufficient to detect either individual unimers, or small aggregates, such that only reasonably large micelles can be monitored. Honda and coworkers\textsuperscript{5, 6} have studied the relaxation kinetics of micellization of a block copolymer solution induced by a T-jump by monitoring the time evolution of the apparent molecular weight and radius of gyration. The corresponding time constant associated with the average molecular weight growth has been found to decrease with an increase of polymer concentration. Micellization depends strongly on the experimental conditions, such that it is often difficult to compare the results obtained using different measurement techniques or methodologies for the induction of micellization. In a series of rapid micromixing homogenous precipitation experiments Johnson and coworkers\textsuperscript{8} found that the mechanism of block copolymer self-assembly depends on the rate and magnitude of the solvent quality change. They showed that using high supersaturation for a low critical micelle concentration produced frozen micelles, with the characteristic micellization time decreasing with an increase of concentration, which is consistent with the micelle fusion mechanism of micellization. On the other hand, under the conditions of a slow solvent quality change, both unimer exchange and micelle fusion take place during the micellization process. Liu and coworkers\textsuperscript{9,10,14-16} studied diblock copolymer micellization kinetics induced by a pH-jump or solvent-jump. Time-dependent light scattering has been used to probe the pH-induced micellization kinetics of diblock and triblock copolymers. In all cases the obtained dynamic traces were well-fitted with a double-exponential
function, with the fast time ascribed to the formation of quasi-equilibrium micelles, and the slow time associated with relaxation into the final equilibrium micelles. For the triblock copolymer system it was found that the slow process proceeds mainly via unimer exchange mechanism as the corresponding relaxation time was concentration independent. On the other hand, at elevated salt concentration the slow process of triblock copolymer micelle relaxation proceeds via micelle fusion/fission. In most cases for diblock copolymer micelles the slow relaxation time is found to be strongly concentration dependent. The process proceeds via micelle fusion/fission with an estimated activation energy decreasing with an increase of hydrophobic chain length. For a shorter hydrophobic block unimer exchange becomes active and dominates the slow relaxation process, with the relaxation time independent of polymer concentration. In another series, a non-solvent-induced micellization of pyrene end-labeled diblock copolymers was studied via a combination of stopped-flow light scattering and fluorescence techniques. The dynamic traces of scattered intensity were successfully fitted by double exponential functions with both fast and slow relaxation times decreasing with concentration. This indicates that both the formation of quasi-equilibrium micelles and the slow relaxation into final equilibrium micelles proceed primarily via the micelle fusion/fission mechanism. The excimer to monomer fluorescence emission intensity traces fitting required a triple exponential function with the two longer relaxation times being the same (and presumably reflecting the same processes) as obtained in the light scattering fit. The fast relaxation process, which could only be detected by the fluorescent technique contributed about 75% of initial emission intensity increase and was attributed to the fusion of small aggregates at the early stage of micellization. Fluorescence is very
sensitive to small aggregates, while the corresponding scattering intensity change was very small due to small size of the aggregates at early times. Lund and co-workers\textsuperscript{13} applied the high resolution of the synchrotron X-ray scattering technique to study the time-dependent aggregation number evolution following solvent jump. They also found that micellization proceeds quicker at higher polymer concentration and argue that there are multiple time scales associated with the micellization process.

Theoretical and computational studies have also played a very important role for our understanding of micellization kinetics. An overview of various theoretical models\textsuperscript{17-26} can be found in the first chapter. Among those theoretical models, the model by Dormidontova\textsuperscript{24} provides a detailed description of the micellization process in three stages. According to this model, during the first nucleation stage free unimers couple with each other very quickly; in the next stage fusion of micelles of comparable size becomes dominant while during the last stage micelles grow very slowly by both unimer exchange and fusion/fission of strongly non-equal size micelles.

There are relatively few computational studies on the kinetics of micellization.\textsuperscript{1,27-31} Mattice and coworkers\textsuperscript{27} have used Monte Carlo simulations to study the evolution of dispersed unimers to form micelles. They investigated the evolution of number-average aggregation number and found that an increase of interaction energy or soluble block length results in freezing the self-assembly process at some metastable state. By monitoring the change of unimer volume fraction, weight-average aggregation number and aggregation number of the large micelles, Wang and co-authors\textsuperscript{28} found that the
unimer volume fraction decreases very quickly to a stable level, while the weight-average aggregation number keeps slowly increasing before reaching a plateau level and may become frozen if there is a high degree of incompatibility between blocks. Pepin and coworkers\textsuperscript{29} have analyzed autocorrelation times for chain extraction and exchange as a function of interaction energy for diblock copolymer micelles in the presence of a homopolymer solubilisate. Marrink and coworkers\textsuperscript{30} applied atomistic Molecular Dynamics (MD) simulations to study formation of a single micelle from 54 dodecylphosphocholine (DPC) surfactant molecules in water. Based on three simulation runs the dynamic processes of formation of a spherical micelle at low concentration of DPC molecules was investigated by monitoring the time evolution of the total number of aggregates, emergence and disappearance of aggregates of different size ranges during the spontaneous aggregation process. It was found that during the micellization process single surfactants frequently escape aggregates with a rate that is independent of cluster size. Chen et. al.\textsuperscript{31} recently applied a coarse-grained Brownian Dynamics (BD) simulations with an implicit solvent model to study the self-assembly process of polystyrene-b-poly(ethylene oxide) copolymers into a single micelle in aqueous solution, aiming to compare the simulation results with flash nano-precipitation experiments.\textsuperscript{8} The evolution of the number of aggregates and the size of the largest aggregate in the course of unimer-to-micelle conversion has been monitored as a function of the friction coefficient. The overall micellization time was found to be considerably smaller than observed in experiments. The cluster size distribution and the average cluster size were investigated as a function of polymer concentration and cooling rate (which imitated the experimental rate of change of solvent quality).
4.2 Simulation and Data Analysis

Our procedure to perform the DPD simulations in this study is very similar to the simulation described in the first section of chapter 3. In our simulations, a diblock copolymer (oligomer) was modeled as a coarse-grained linear bead-spring chain $A_mB_x$ with $m$ hydrophobic (A) beads and $x$ hydrophilic (B) beads linked by a harmonic bond force with a force constant $k = 100 \frac{k_b T}{d_p^2}$ ($k_b$ is the Boltzman constant, $T$ is temperature) and equilibrium bond length $b_0 = d_p$, where $d_p$ is the bead diameter. Solvent molecules were modeled as single beads identical to the hydrophilic block bead (B) in a model chain. All beads in our simulations had the same mass $m_0$ and diameter $d_p$ which will be used as units of mass and length. All simulations were performed under periodic boundary conditions in a cubic box ($30d_p \times 30d_p \times 30d_p$) containing 81000 beads. The density of all beads including polymer monomers and solvent was equal to $3d_p^3$ and the repulsive interaction parameters between same type of beads were $a_{AA} = a_{BB} = 25 (k_b T/d_p^2)$, to reproduce the compressibility of water at room temperature (In the following $k_b T/d_p^2$ will be omitted when referring to values of the interaction parameter $a$). Based on the $a_{BB}$ interaction parameter, the B-block is in a good solvent with the Flory exponent 0.6 observed for the homopolymer radius of gyration and diffusion coefficient. The cutoff distance for all DPD forces, including conservative force, dissipative force and random force is the same $r_c = d_p$. The fraction coefficient for dissipative force is $3.0 (k_b T/d_p^2)$ and the noise amplitude for random force is $\sigma = (2\gamma k_b T)^{1/2}$ in all simulations. For solutions of $A_2B_3$ chains, we varied the repulsive parameter ($a_{AB} = 47.5, 50, 52.5, 55$) and volume fraction of chains, $\phi$, from 0.02 to 0.05 to study the interaction energy and oligomer concentration effects on the chain exchange kinetics. For solutions of $A_4B_x$
chains, we kept the hydrophobic block length \((N_A = 4)\) and the volume fraction of chains \((\varphi = 0.05)\) constant, and varied the hydrophilic block length \((N_B = 4, 6, 8)\) and repulsive parameter \((a_{AB} = 38, 40)\) to study the chain length and hydrophobic interaction energy effects. In all simulations the NVT ensemble was adopted \((k_B T =1)\) and the equations of motion were integrated with a modified version of the velocity-Verlet algorithm\(^{3535}\) with time step \(\Delta t = 0.04(m_0d_p^2/k_B T)^{1/2}\). We used a free-source code LAMMPS\(^{36}\) for the DPD simulations on the HPC computer cluster at Case Western Reserve University.

For the simulation of micelle formation, we initially applied the repulsive parameter \(a = 25\) for all pair interactions between the beads and ran DPD simulation for \(t = 4\times10^4\) to make sure all the chains homogeneously dispersed in the solution. Then the process of micelle formation were simulated with desired \(a_{AB}\) value and the time-dependent weight-average aggregation number was monitored to determine the equilibrium state (when the average aggregation number reaches a plateau level with deviations less than 15\% of the average value). Aggregates were distinguished by a general distance criterion\(^{1, 30}\), in which, any pair of chains within a certain cut-off distance between the centers of mass of hydrophobic blocks belongs to the same aggregate. A cut-off distance of \(1.2d_p\) was used to distinguish different aggregates for all systems with \(A_2B_3\) chains, and cut-off distance of \(1.5d_p\) was used for aggregates composed of \(A_4B_x\) chains. After equilibration, the simulations for equilibrated micelle solutions were conducted for \(t = 3.2\times10^5\Delta t\) for solutions with \(A_2B_1\) chains and for \(t = 1.2\times10^6\Delta t\) for systems with \(A_4B_x\) chains. The movement trajectories were collected every 100 time steps for data analysis. We used VMD\(^{37}\) for displaying movement trajectories and data analysis.
4.3 Results and Discussions

4.3.1 Molecular Mechanism

4.3.1.1 Micellization Kinetics

As discussed in the simulation details section, we studied the process of oligomer self-assembly into spherical micelles starting from a homogeneously dispersed unimer solution. This was accomplished by increasing the interaction energy $a_{AB}$ from 25 (neutral solvent/B-block interactions) to larger values (bad solvent for A, repulsive interactions with B-block) at $t = 0$. Once the hydrophobic interaction was imposed, unimers were observed to self-assemble into small aggregates quickly and finally we saw large spherical micelles in all cases. Figure 4.1 shows several snapshots of the simulation box containing $A_4B_8$ chains ($a_{AB} = 40$, $\varphi = 0.05$) obtained in the course of micelle formation.
Figure 4.1 Snapshots of the simulation box containing $A_4B_8$ chains ($a_{AB} = 40, \varphi = 0.05$) obtained in the course of micelle formation (the hydrophobic block is shown by connected balls, the hydrophilic block is shown by connected bonds (i.e. balls omitted), solvent beads are not shown, rendered by VMD).

The progress of unimer self-assembly into micelles can be characterized by monitoring the average micelle aggregation number as a function of time starting from the very early stages of micellization. Figure 4.2a shows both the number- and weight-average aggregation numbers as functions of time during the micellization process for $A_2B_3$ solution with $a_{AB} = 50$ at an oligomer volume fraction $\varphi = 0.05$. As is seen $M_n$ and $M_w$ quickly increase until reaching their respective equilibrium plateau level. As will be
discussed below equilibration of number-average aggregation number occurs quicker than the $M_w$. Besides the macroscopic characteristics of the process we can also obtain from our simulations the time-dependent population of different aggregates. Figure 4.2b shows the time evolution of the weight fraction of different aggregates, which for clarity were grouped into size ranges. As is seen, early in the micellization process the fraction of unimers decreases very quickly as they merge into small aggregates and the average aggregation number starts to increase. As time goes by, larger aggregates start to appear while the fraction of small aggregates declines. At this stage redistribution of chains occurs very actively and the average aggregation number continue to increase. At the later stages of micellization most of the chains exist in large micelles and the number- and weight-average aggregation numbers stabilize, dominated mainly by the contribution of large micelles.
Figure 4.2 (a) Number- and weight-average aggregation numbers and (b) weight-average fraction of aggregates in different size ranges as a function of time during the process of micelle formation in $A_2B_3$ solution ($a_{AB} = 50$, $\varphi = 0.05$). Vertical dashed lines indicate the approximate boundaries between different stages of micellization process.

4.3.1.2 Three Stages

In order to distinguish the contributions of different mechanisms of micellization over the course of time, we subdivide the micellization into three stages similar to our earlier analytical model. During the first stage the unimer concentration decreases very sharply and stabilizes at about $t \approx 100 – 200$ (Figure 4.2b). During this stage unimers couple with
each other forming dimers, which can also merge with each other or unimers. Figure 4.3 shows the time-dependent aggregation number ratio between the smaller reactant (with aggregation number $P_a$) and the large reactant (with aggregation number $P_b$) in all aggregate addition reactions. An aggregate addition reaction is defined as the process of merging of two reactants (including unimers) $a$ and $b$ with aggregation numbers $P_a$ and $P_b$ with the formation of a new aggregate, which lasts for at least two statistical time steps ($\Delta t = 8$).

Figure 4.3 Ratio of aggregation numbers of small to large reactants in the micellization addition process of $A_2B_3$ ($a_{AB} = 50$, $\phi = 0.05$) as a function of time. Vertical dashed lines indicate the approximate boundaries between different stages of micellization process. The inset shows the average aggregation number of the smaller reactant during the final stage of micellization as a function of $a_{AB}$. 

71
As is seen, during the first stage of micellization the reactant ratio decreases from about 0.9, indicating mainly the merger of equal aggregates, to about 0.6, where fusion of aggregates of non-equal sizes starts to play a role. These findings agree well with the scenario of micellization predicted in an earlier analytical model by Dormidontova and with the results of a recent experimental study on solvent-jump micellization of a pyrene end-labeled diblock copolymers. In the latter study it was found that the fastest relaxation process, which contributed about 75% of the initial emission intensity increase, is attributed to the fusion of small aggregates at the early stage of micellization. As is seen from Figure 4.2, during the first stage of micellization only rather small aggregates are formed with the weight-average aggregation number being about 10 by the end of this stage after most unimers are consumed.

At the beginning of the second stage of micellization the average aggregation number is far from the equilibrium value and the weight-average aggregation number distribution exhibits just a single maximum around the average aggregation number (of about 10), as is seen in Figure 4.4. As time goes by, fraction of small aggregates decreases and large micelles start to form and become dominant. The ratio of aggregation numbers between the reactants in the aggregate addition reaction continues to decrease (Figure 4.3). Micelle fusion between aggregates of non-equal sizes and the increasing contribution of unimer exchange are the main contributing factors. By the end of the second stage of micellization, the number-average aggregation number reaches its equilibrium level (Figure 4.2), indicating that the total number of aggregates has achieved the equilibrium value, while the weight-average aggregation number continues to increase. The ratio of
aggregation numbers between reactants in the aggregate addition reaction also reaches a plateau value (about 0.4) by the end of the second stage (Figure 4.3) indicating that the process of active growth is finalized and only chain redistribution between aggregates will be occurring during the final stage of micellization. It is interesting to note that by the end of the second stage the weight fraction aggregation number distribution exhibits two maxima, one below ($P \approx 27$) and one above ($P \approx 50$) the equilibrium aggregation number, $P_{eq} \approx 33$, (Figure 4.4).

Figure 4.4 Weight fraction aggregation number distribution during the micellization process of $A_2B_3$ solution ($a_{AB} = 50$, $\varphi = 0.05$). Curves with symbols for different time steps are the running average. The equilibrium distribution is shown as a curve without symbols. Horizontal dashed lines indicate the approximate boundaries between different stages of micellization process.
To investigate the growth pathways during the second stage of micellization we trace all the micelles with the characteristic aggregation number \(25 < P < 35\) at \(t = 1,000\) back to the earlier times. The predecessor of a micelle was defined as the micelle which contains more than half the chains on the previous time step. The statistic interval was chosen to be \(\Delta t = 4\) to ensure correct counting of the instantaneous change of the micelles. In Figure 4.5, the time evolution of the aggregation number of some representative micelles is shown during the second stage of micellization. As is seen for all micelles, the aggregation number increases mainly by a few fusion events, normally 3-4, between micelles of comparable sizes, so that the instantaneous aggregation number exhibit large jumps. Further refinement of the aggregation number occurs via fission events involving expulsion of a small aggregate or by unimer expulsion. The bimodal weight-average aggregation number distribution shown in Figure 4.4 is the result of such an active micelle fusion process. If the micelle formation process involved unimer insertion only then one would expect a smooth evolution of the distribution to the final one without a significant change of its shape or especially formation of micelles of larger than equilibrium size.
A qualitatively similar micelle size evolution as shown in Figures 4.4 and 4.5 was also observed for longer chains (A\textsubscript{4}B\textsubscript{x}), as will be discussed below. These results demonstrate the importance of the contribution of micelle fusion to the process of micelle formation and are in accord with recent experimental observations\textsuperscript{8,15,16}. In rapid micromixing homogenous precipitation experiments, Johnson and coworkers\textsuperscript{8} found that under the conditions of a slow solvent quality change both unimer exchange and micelle fusion take place during the micellization process. The analysis of dynamic traces of light scattering intensity obtained by Liu and coworkers\textsuperscript{15,16} in their study of diblock copolymer micellization kinetics induced by pH-jump and solvent-jump revealed that in many cases both the fast and slow relaxation times decrease with concentration,
indicating that both the formation of quasi-equilibrium micelles and the slow relaxation into final equilibrium micelles proceed primarily via micelle fusion/fission mechanism.

We have also analyzed our data to characterize the frequency of occurrence of different processes, such as unimer exchange or micelle fusion/fission, during the second stage of micellization. Strictly speaking unimer exchange involves single chain insertion/expulsion or exchange between micelles and for the second stage of A₂B₃ micellization in solution ($\phi=0.05$, $d_{AB}=50$) its probability of occurrence was about 56%, as is seen from Table 4.1 while the rest (44%) can be attributed to collective micelle fusion/fission events. Thus both processes contributed the micellization to a comparable extent. At the same time if one considers the number of chains exchanged by either of the processes, then unimer exchange was responsible for only 18% with the majority (82%) of chains being exchanged by collective micelle fusion/fission. Hence we can conclude that contribution of micelle fusion/fission was dominant in this stage of micellization, in agreement with recent experimental findings.¹⁵,¹⁶
Table 4.1 Relative number of events (frequency) and fraction of chains exchanged in the event (contribution) involving unimers, small aggregates and micelles for stages II and III of the micellization process of A$_2$B$_3$ micellar solution ($\varphi = 0.05$, $a_{AB} = 50$).

<table>
<thead>
<tr>
<th>Process involving</th>
<th>Stage II</th>
<th>Stage III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>frequency</td>
<td>contribution</td>
</tr>
<tr>
<td>Unimers</td>
<td>56%</td>
<td>18%</td>
</tr>
<tr>
<td>Small aggregates</td>
<td>13%</td>
<td>17%</td>
</tr>
<tr>
<td>$(2 \leq P \leq 4)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micelles $(P \geq 5)$</td>
<td>31%</td>
<td>65%</td>
</tr>
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</table>

As discussed above, the CMC reflects not only unimers but also small aggregates. We have separated the contribution of small aggregates $(2 \leq P \leq 4)$ into the micellization process in Table 4.1. We note that the choice of the upper size boundary for small aggregates was dictated by the position of the minimum in micelle size distribution. As is seen from Table 4.1 expulsion/insertion and exchange of small aggregates between micelles contributed about 13% of events and 17% of exchanged chains. It is worthwhile to note that if one considers “unimer exchange” more broadly and includes processes involving small aggregates, then it becomes the dominant process regarding the probability of occurrence, but is still in a minority regarding its contribution to chain exchange (35%). Processes involving small aggregates play an important role in the micellization kinetics as will be discussed below. The small aggregate contribution to micelle formation process has recently been detected for pyrene end-labeled diblock
copolymers studied via a combination of stopped-flow light scattering and fluorescence
techniques.\textsuperscript{15} Due to the high sensitivity of the fluorescent technique to small aggregates a third relaxation time attributed to the fusion of small aggregates has been determined (in addition to the two slower relaxation times obtained from light scattering) and is found to be concentration dependent.

At the beginning of the third stage ($t \approx 1000$), the aggregation number distribution reflects a bimodal population of micelles (Figure 4.4) with aggregation numbers somewhat larger ($P \approx 50$) or smaller ($P \approx 27$) than the final equilibrium number ($P \approx 33$). At this time the number average aggregation number is practically equilibrated, implying that the number of aggregates has reached the thermodynamically preferred value, while the weight average aggregation number is somewhat smaller than the equilibrium value. Thus the main development of the last stage of micellization process is redistribution of chains among micelles to achieve the equilibrium weight average aggregation number distribution. As is seen from Figure 4.3 the ratio of aggregation numbers of reactants in aggregate addition reactions does not appreciably change (compared to the previous stages of micellization), but fluctuates strongly indicating participation of different size reactants in the process. Statistical analysis of different events occurring during the last stage of micellization shows that unimer exchange becomes more dominant, with its probability of occurrence increasing to about 70\%. Exchange of small aggregates ($2 \leq P \leq 4$) between micelles becomes more frequent as well (about 24\%) and the probability of micelle fusion declines (8\%). The latter is not surprising as the number of micelles is considerably smaller and their size is bigger. Still, the contribution of micelle fusion into
overall chain redistribution remain at considerable level – 44% of chains are exchanged via micelle fusion, which is larger than either the contribution of unimer exchange (30%) or processes involving small aggregates (26%). This is in agreement with experimental findings by Johnson and coworkers\textsuperscript{8} and Liu and coworkers\textsuperscript{9,14-16} who studied the diblock (and triblock) copolymer micellization kinetics induced by pH-jump and solvent-jump: in most of the cases the slow relaxation time was found to be strongly concentration dependent, indicating that micelle fusion/fission plays an important role in the slow relaxation into the final equilibrium micelles. The weight-average aggregation number distribution, which still exhibits a bimodal shape at the earlier times of the final stage of micellization, gradually becomes unimodal with the peak position corresponding to the final equilibrium aggregation number. The analysis of time evolution for individual micelles shows that large micelle fusion becomes rather rare and normally involves a fission event immediately afterwards. In general the dynamic features of the last stage of micellization are rather similar to the equilibrium chain-exchange dynamics of micellar solution.

It is important to note that micellization is a continuous process, and our purpose in designating stages is merely to distinguish the most representative pathways of micelle growth. During the first two stages, which proceed noticeably quicker compared to the last stage, the major part (about 80-85%) of micelle growth is accomplished by fusion of small unstable aggregates. The probability of aggregate encounter is high and the energy barrier for fusion is low, such that the contribution of micelle fusion is considerable at this stage. As the micellization progresses to the last stage, the average size of micelles
increases and their number decreases to nearly the equilibrium value, making it less likely for large micelle fusion to occur. Still, micelle fusion/fission together with unimer and small aggregate exchange all contribute to the slow process of weight average aggregation number growth/adjustment. The boundaries between different stages and the relative contribution of different kinetic processes to micellization depend on the system properties, such as block ratio, interaction between blocks and solvent, polymer concentration, block length, etc. The influence of some of these parameters on micellization kinetics will be discussed below.

4.3.2 Oligomer Concentration Effect

The time-evolution of the weight-average aggregation number during the micellization processes of $A_2B_3$ solutions (with interaction energy $a_{AB} = 50$) is shown in Figure 4.6 for different oligomer volume fractions: $\varphi = 0.02, 0.05$. As is seen, the growth of the weight-average aggregation number occurs in a qualitatively similar way: a rapid increase in the beginning and gradual saturation to a plateau level later on. Comparing the time-scales of different stages of the process at different oligomer volume fractions one can find that an increase in oligomer content speeds up the micellization process: e.g. it takes almost twice the time to reach stage 2 or stage 3 of the micellization at $\varphi = 0.02$ compared to $\varphi = 0.05$. Correspondingly equilibrium is reached noticeably quicker at higher oligomer content. This observation is consistent with the results of recent X-ray experiment\textsuperscript{13} and analytical predictions.\textsuperscript{25} One of the reasons for this effect is that the denser is the solution, the shorter the distance for chains and aggregates to travel before they can merge with each other. Also larger number of aggregates increases the probability of micelle fusion,
which is one of the important components of the micellization process. The frequency of micelle fusion/fission during the second stage of micellization increases by 20% and the fraction of chains exchanged via micelle fusion/fission mechanism during the third stage of micellization doubles upon an increase in oligomer volume fraction from $\varphi = 0.02$ to $\varphi = 0.05$. Strong concentration dependence of the slowest relaxation time associated with micelle fusion/fission has been observed in a series of pH-jump and solvent-jump experiments$^{9,14-16}$ as well as computer simulations.$^{38}$ Our simulations show that for a low oligomer concentration the weight-average aggregation number distribution exhibits primarily a single maximum (not shown) evolving towards the equilibrium value, which is consistent with a strong contribution of unimer (and small aggregate) exchange in this case. The size of the smaller reactant in addition reactions consistently increases with an increase in oligomer volume fraction, as is seen in Figure 4.6 (inset). Thus, an increase in oligomer content enhances probability of micelle fusion/fission events and speeds up the micellization process.
We have analyzed our data to characterize the frequency of occurrence of different processes, such as unimer exchange or micelle fusion/fission, during the second and third stages of micellization for $A_2B_3$ micellar solution at low oligomer volume fraction ($\phi = 0.02$). The results are shown in Table 4.2. As is seen, at $\phi = 0.02$ micelle fission/fusion events are more rare compared to $\phi = 0.05$ (Table 4.2). Correspondingly, the contribution of micelle fission/fusion to the growth of micelles at the third stage is lower.
Table 4.2 Relative number of events (frequency) and fraction of chains exchanged in the event (contribution) involving unimers, small aggregates and micelles for stages II and III of the micellization process of $A_2B_3$ micellar solution ($\varphi = 0.02$, $a_{AB} = 50$).

<table>
<thead>
<tr>
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<th>Stage II</th>
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<th>Stage III</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>frequency</td>
<td>contribution</td>
<td>frequency</td>
<td>contribution</td>
</tr>
<tr>
<td>Unimers</td>
<td>61%</td>
<td>23%</td>
<td>68%</td>
<td>30%</td>
</tr>
<tr>
<td>Small aggregates ($2 \leq P \leq 4$)</td>
<td>13%</td>
<td>12%</td>
<td>26%</td>
<td>49%</td>
</tr>
<tr>
<td>Micelles ($P \geq 5$)</td>
<td>26%</td>
<td>65%</td>
<td>6%</td>
<td>21%</td>
</tr>
</tbody>
</table>

4.3.3 Interaction Energy Effect

The time-evolution of the weight-average aggregation number during the course of micellization of $A_2B_3$ solutions ($\varphi = 0.05$) with different interaction energies ($a_{AB} = 47.5, 55$) is compared in Figure 4.7. At the very early times the micelle growth occurs following nearly the same pathway independent of the interaction energy. The difference in the micellization process lies in the later times, when micellization of oligomers with higher interaction energies is noticeably slower.
Figure 4.7 Time-evolution of the weight-average aggregation number in the course of micellization of A$_2$B$_3$ solution ($\phi = 0.05$) for different interaction energies $a_{AB} = 47.5$, 55.

We have also analyzed and compared the micellization process for A$_4$B$_x$ systems with different interaction energies ($a_{AB} = 38$ and 40). In all cases the corresponding time windows for the first, second and third stages of micellization noticeably expand with an increase in $a_{AB}$. One reason for this effect is that the higher interaction energy implies higher equilibrium aggregation number, which requires a larger number of events (unimer exchange, micelle fusion/fission). Also the potential barrier for unimer expulsion or micelle fission is higher for larger $a_{AB}$, which would slow down the micellization process as well. Similar observations have been made in stop-flow experiments of non-solvent-induced micellization$^{15}$ and in computer simulations$^{27}$ as well as been predicted analytically.$^{26}$ The analysis of the statistics of micelle evolution (performed for both A$_2$B$_3$ and A$_4$B$_x$ systems) shows that the frequency of occurrence and contribution of unimer exchange to the micellization process generally increase with an increase in $a_{AB}$,
especially during the final stage of micellization. Correspondingly the frequency and contribution of processes involving small aggregates decrease. Micelle fusion/fission becomes somewhat less frequent during the second stage of micellization, while the fraction of chains exchanged via micelle fusion increases with an increase in interaction energy. This is likely due to the larger average micelle size achieved by the end of the second stage of micellization at larger $a_{AB}$, which makes fusion less likely to occur, but more efficient i.e. more chains are exchanged per event, as is seen from Figure 4.3 (inset). The contribution of micelle fusion to the last stage of micellization does not appreciably change with an increase in $a_{AB}$ for $A_4B_x$ systems and it slightly increases for $A_2B_3$ solutions, where micelle fusion events are more likely in general, as will be discussed below.

### 4.3.4 Block Length Effect

Comparing the process of micelle self-assembly from unimers for $A_4B_x$ and $A_2B_3$ solutions, one can conclude that the overall process proceeds via the same stages, as discussed above. In general the time window for the different stages expands with an increase of oligomer length, while the frequency and contribution of unimer exchanges increases and probability of micelle fusion/fission decreases, as shown in Table 4.3. The time evolution of the aggregation number of selected micelles shows fewer fusion/fission events, but otherwise is qualitatively similar to $A_2B_3$ solutions (Figure 4.5), as shown in Figure 4.8.
Table 4.3 Relative number of events (frequency) and fraction of chains exchanged (contribution) in the events involving unimers, small aggregates and micelles for stages II and III of the micellization process of $A_4B_6$ micellar solution ($\phi = 0.05$, $a_{AB} = 40$), averaged over several simulation runs.

<table>
<thead>
<tr>
<th>Process involving</th>
<th>Stage II</th>
<th></th>
<th>Stage III</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency (%)</td>
<td>Contribution (%)</td>
<td>Frequency (%)</td>
<td>Contribution (%)</td>
</tr>
<tr>
<td><strong>Unimers</strong></td>
<td>81±2</td>
<td>52±5</td>
<td>88±2</td>
<td>68±1</td>
</tr>
<tr>
<td><strong>Small aggregates</strong> ($2 \leq P \leq 4$)</td>
<td>14±2</td>
<td>21±2</td>
<td>10±2</td>
<td>18±4</td>
</tr>
<tr>
<td><strong>Micelles ($P \geq 5$)</strong></td>
<td>5±1</td>
<td>27±4</td>
<td>2±1</td>
<td>14±5</td>
</tr>
</tbody>
</table>

Figure 4.8 Time evolution of the aggregation number $P$ of selected individual micelles during the second stage of micellization process of $A_4B_6$ solution ($a_{AB} = 40$, $\phi = 0.05$).
We note that the oligomer volume fraction was $\varphi = 0.05$ for all $A_4B_x$ systems, implying a smaller number of chains and micelles at equilibrium (for similar average aggregation numbers) compared to $A_2B_3$ micelle solution. The decrease in the number of aggregates is a contributing factor to the overall micelle fusion/fission decrease. At the same time, the fraction of chains exchanged by micelle fusion/fission remains substantial (15-50%), so that this mechanism of micelle growth and chain exchange remains active. As shown in Figure 4.9, comparing the aggregation number distribution at different time steps for $A_4B_6$ system we also observe a bimodal distribution at intermediate time steps similar to $A_2B_3$ micelle solution (Figure 4.4). This serves as an additional confirmation of importance of micelle fusion in the micelle growth process and the similarity of micelle formation for $A_4B_x$ and $A_2B_3$ solutions. Another common feature of the micellization kinetics in all cases is a noticeable contribution of the processes involving small aggregates ($2 \leq P \leq 4$), which account for 15-35% of chains exchanged.
Figure 4.9 Weight fraction aggregation number distribution during the micellization process of A$_4$B$_6$ micelle solution ($\alpha_{AB} = 40$, $\phi = 0.05$). Curves with symbols for different time steps are the running average. The equilibrium distribution is shown as a curve without symbols.

Comparing the micellization process for oligomers with the same hydrophobic block and different hydrophilic block lengths, one can expect that different kinetic processes may be affected to a different extent. For instance, one can imagine that micelle fusion may become less likely as a larger corona may prevent the core contact necessary for micelle merging. Statistical analysis of micelle evolution (for both $\alpha_{AB} = 38$ and $\alpha_{AB} = 40$) reveals that for systems with a longer hydrophilic block the overall number of kinetic events decreases, while the relative frequency of different events remains at comparable levels. This is likely the outcome of several counteracting factors: e.g. oligomers with a longer hydrophilic block (which could negatively affect the likelihood of micelle fusion) will
form smaller micelles in equilibrium, as discussed above (which would make micelle fusion easier). There is a slight indication that with an increase in corona-block length the contribution of unimer exchange to the micellization process may even decrease while the fraction of chains exchanged via micelle fusion/fission may slightly increase. In general, the size of the smaller aggregates participating in aggregate addition reactions decreases with an increase of hydrophilic block length (see supporting information), while the ratio of reactants in aggregate addition reactions $P_a/P_b$ increases. The first two stages of micellization process, i.e. consumption of unimers and equilibration of $M_n$ often proceed slower for the system with longer hydrophilic block as a result of the lower diffusion coefficient (see supporting information) and larger distance to travel between unimers. At the same time the overall micellization process can often take a comparable time as oligomers with shorter hydrophilic block (such as $A_4B_4$) are prone to considerable fluctuations in aggregation number, which is larger at equilibrium (compared to $A_4B_6$ or $A_4B_8$ cases). It is important to emphasize that fractions of chains exchanged via micelle fusion (15-35%) or processes involving small aggregates (~20%) in all cases add up to 32-60% (see Table 4.3 and Table 4.4) indicating the importance of these processes in the kinetics of micelle formation.
Table 4.4 Relative number of events (frequency) and fraction of chains exchanged (contribution) in the events involving unimers, small aggregates and micelles for stages II and III of the micellization process of $A_4B_8$ micellar solution ($\varphi=0.05$, $a_{AB} = 40$), averaged over several simulation runs

<table>
<thead>
<tr>
<th>Process involving</th>
<th>Stage II</th>
<th>Stage III</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency (%)</td>
<td>Contribution (%)</td>
</tr>
<tr>
<td>Unimers</td>
<td>69±16</td>
<td>39±18</td>
</tr>
<tr>
<td>Small aggregates</td>
<td>20±8</td>
<td>26±3</td>
</tr>
<tr>
<td>Micelles (P≥5)</td>
<td>11±8</td>
<td>35±15</td>
</tr>
</tbody>
</table>

4.4 Conclusions

In this chapter, we studied the kinetics of block copolymer micelle formation from randomly dispersed state using DPD simulations. The kinetics of the micellization process was analyzed by monitoring the time-evolution of the average aggregation number and fraction of aggregates of different sizes.

We find that micellization can be characterized as a three-stage process. At the earliest stage the unimer concentration decreases sharply to a constant value due to the rapid coupling of unimers into small aggregates. A close examination of the aggregation number evolution of individual micelles during the second stage clearly indicates that micelles grow mainly by fusion of sub-micelles with intermediate aggregation numbers, in agreement with an earlier analytical model by Dormidontova. As a result of the
active micelle fusion process the aggregation number distribution starts to exhibit a bimodal character with two maxima, above and below the equilibrium aggregation number. As micellization progresses the ratio of aggregation numbers between aggregates in addition reactions (including unimers) decreases indicating that fusion of unequal size micelles or unimer exchange become more active. Analysis of the frequency of different events indicates that the processes involving small aggregates (dimers, trimers, etc.) play an important role in the micelle growth process as the fraction of chains exchanged by this mechanism is comparable to the fraction of unimers exchanged between micelles. This finding agrees well with recent experimental data for pyrene end-labeled diblock copolymers studied via a combination of stopped-flow light scattering and fluorescence techniques.\(^{15}\) Micelle fission/fusion is the dominant mechanism of micelle growth during the second stage as the number of chains exchanged by this mechanism is the largest. By the end of the second stage the number average aggregation number equilibrates, which indicates that the number of aggregates becomes stable. During the third stage the weight average aggregation number continues to increase very slowly due to the adjustment of the aggregation number distribution. The weight-average aggregation number distribution, which still exhibits a bimodal shape in the earlier times of the final stage of micellization, gradually becomes unimodal with the peak position corresponding to the final equilibrium aggregation number. Statistical analysis of different events occurring during stage three shows that exchange of unimers and small aggregates with micelles becomes more dominant and the probability of micelle fission/fusion declines, although the contribution of micelle fusion to the overall chain redistribution remains significant as these multi-oligomer events are rather effective.
The boundaries between different stages and the relative contribution of different kinetic processes to micellization depend on the system properties, such as the interaction energy between blocks and solvent, polymer concentration, block length, etc. We found that increasing the polymer concentration speeds up not only the initial stage of unimer coupling, but also the whole micellization process due to an increase of the probability of micelle fusion/fission events.

An increase in the hydrophobic interaction energy $a_{AB}$ dramatically slows down the micellization process: while micelle growth at early times follows nearly the same pathway independent of the interaction energy, more events are required to achieve the larger final equilibrium aggregation number. With an increase in the interaction energy, micelle fusion/fission becomes somewhat less frequent during the second stage of micellization, although the fraction of chains exchanged via micelle fusion increases. The analysis of the statistics of micelle evolution (performed for both $A_2B_3$ and $A_4B_x$ systems) show that the frequency of occurrence and contribution of unimer exchange to the micellization process generally increases with an increase in $a_{AB}$, especially during the final stage of micellization. Comparing the process of micelle self-assembly from unimers for $A_4B_x$ and $A_2B_3$ solutions, we found that the overall process proceeds via the same stages, but the time windows for the different stages noticeably expand with an increase of oligomer length.
We have also investigated the effect of hydrophilic block length and found that the overall micellization process is slower for the shorter oligomers, which have a larger equilibrium aggregation number, requiring a longer pathway (of chain exchange and aggregate fusion) to reach equilibrium. Statistical analysis of the micelle evolution reveals that the frequency and contribution of unimer exchange increases and probability of micelle fusion/fission decreases with increased chain length. At the same time, the fraction of chains exchanged by micelle fusion/fission and by processes involving small aggregates remains substantial.
4.5 Bibliography


(22) Kahlweit, M. J. Colloid Interface Sci. 1982, 90, 92-99.


Chapter 5

Kinetics of Equilibrium Chain Exchange by DPD Simulation

In this chapter, the kinetics of equilibrium chain exchange between micelles is studied by DPD simulation. We first review previous experimental and theoretical studies on the chain exchange kinetics, then describe simulation and data analysis details. In the results section, we first discuss the polymer concentration effect, then investigate the influence interaction energy and block length, on the kinetics of chain exchange kinetics. Finally, we summarize the main finding in this chapter.

5.1 Introduction

The chain exchange kinetics between block copolymer micelles in solution is most commonly explained based on an unimer expulsion/insertion mechanism.\textsuperscript{2-4} According to this model, the chain exchange process is first order and yields a single-exponential decay function with a relaxation time ($\tau_{un}$) determined by the potential barrier for unimer expulsion, which is concentration independent and occurs considerably slower than unimer insertion.\textsuperscript{4} Unimer expulsion considerably slows down with an increase in the interfacial tension $\gamma$ between blocks (or between core-block and solvent) and core-block
length $N_A$: $\tau_{un} \sim \exp(N_A^{2/3} \gamma/kT)$ where $k$ is Boltzmann constant and $T$ is temperature.\textsuperscript{4} The dependence on corona-block length $N_B$ comes only in a pre-exponential factor with $\tau_{un}$ increasing with $N_B$ as a power-law function $\tau_{un} \sim N_B^{9/5}$, reflecting slower chain diffusion for longer corona blocks.\textsuperscript{4,5} There are also other theoretical models suggesting that despite micelle fission/fusion being slower than unimer expulsion/insertion, it may also contribute to the chain exchange process.\textsuperscript{5-8} Similar to unimer exchange, micelle fusion/fission slows down with an increase in incompatibility between blocks (or between core-block and solvent), core-block length and to less extent corona-block length. Micelle fusion/fission is expected to become more active with an increase of polymer concentration, as the probability of aggregate collision increases and the corresponding relaxation time $\tau_{mic}$ decreases with concentration. We note that theoretical approaches describing chain exchange kinetics in polymer micelles\textsuperscript{4, 5} consider the long chain(block) limit, i.e. $N_A >> 1$, $N_B >> 1$ and ignore the often observed dependence of micelle aggregation number (size) on corona-block length.\textsuperscript{9,10} The latter has to play a role in the kinetics of chain exchange between micelles, which will be discussed in this chapter.

Various experimental techniques, such as nonradiative energy transfer and fluorescence-quenching techniques, sedimentation velocity, transmission electron microscopy, time-resolved light and small angle neutron scattering have been applied to study the process of chain exchange between equilibrium micelles in solution.\textsuperscript{11-30} It has been found that the process of chain exchange between micelles can occur very quickly or slowly depending on the system and characteristic time scales vary from milliseconds to days or
even years for kinetically “frozen” solutions. In micelle hybridization experiment designed to study chain exchange kinetics, typically block copolymers are labeled by fluorescent tags or by hydrogen/deuterium (H/D) isotope substitution and micelle solutions containing chains with one label are mixed with solution of very similar micelles carrying a different label. Chain exchange (hybridization) is detected by the time-dependent change in the fluorescence of the label molecules in the presence of each other or the scattering contrast of the micelles. The chain-exchange kinetics is very sensitive to the properties of the micelle solution, such as the interaction between blocks (and/or solvent), temperature, chain length and system composition. The influence of interactions between the core- and corona-forming block or solvent has been studied by varying the solvent quality (by using co-solvent) or temperature. It was found that a reduction of the solvent quality for the core or a temperature decrease can significantly slow down the chain exchange process or even leads to “frozen” micelles exhibiting no chain exchange in days or months. In several cases an exponential dependence of the chain exchange relaxation time on the inverse temperature has been reported $\tau \sim \exp(E_a/kT)$, where $E_a$ is a constant. The influence of the core-forming block length $N_A$ has also been studied and it was shown that an increase in $N_A$ slows down the chain exchange process, in qualitative agreement with theoretical predictions. The effect of the corona-forming block length $N_B$ on chain exchange between micelles at equilibrium is more subtle and relatively few studies have addressed this problem. Underhill et al have found that an increase of the corona block length increases chain exchange between micelles, while Popelka et al report the opposite trend, i.e. a decrease in the chain exchange with an increase in $N_B$. In several micelle
hybridization experiments the chain exchange rate was found to be independent of polymer concentration.\textsuperscript{18, 28, 29} At the same time, often chain exchange can not be explained as a simple first-order process - a double-exponential fitting\textsuperscript{16,18,22,24,31} or a more complicated process with a distribution of relaxation times leading to logarithmic decay\textsuperscript{28-30} have been reported.

Monte Carlo and Stochastic Dynamics simulations have also been used to study chain exchange process between micelles at equilibrium.\textsuperscript{32-36} Various auto-correlation functions were designed to characterize different relaxation processes, such as chain insertion, expulsion and chain exchange. Similar to experimental observations and theoretical predictions, the increase in insoluble block length and repulsive interaction energy between core-and corona-blocks (or solvent) has been shown to slow down the chain exchange in simulations\textsuperscript{34,36} with an exponential dependence of the chain expulsion rate on inverse temperature reported for surfactant micelles.\textsuperscript{35} The influence of polymer concentration was found to be more complex. The chain expulsion relaxation time was found to be independent of the polymer concentration, while the chain insertion relaxation time decreases with increase of the polymer concentration.\textsuperscript{32} The chain exchange process was shown to be dominated by the unimer expulsion mechanism at lower polymer concentration, while as the polymer concentration increases micelle fission/fusion starts to contribute more and more to the chain exchange due to the higher probability of micelle collision\textsuperscript{34}. 

99
Despite a large body of data collected, a complete understanding of chain-exchange kinetics, especially the exchange mechanisms and influence of different factors on chain exchange, is still lacking. In this chapter, we apply dissipative particle dynamics (DPD) simulations to study chain-exchange in micelle solutions of short diblock-copolymers with different polymer concentrations, interaction energies and corona-block lengths.

5.2 Simulations and Data Analysis

5.2.1 DPD Simulations

To study the kinetics of micelle hybridization, we performed DPD simulations of dilute micelle solutions formed by short diblock copolymers (oligomers) upon self-assembly. In our simulations, a diblock copolymer (oligomer) was modeled as a coarse-grained linear bead-spring chain $A_mB_x$ with $m$ insoluble (A) beads and $x$ soluble (B) beads linked by a harmonic bond force with a force constant $k = 100 \frac{k_B T}{d_p^2}$ ($k_B$ is the Boltzmann constant, $T$ is temperature) and equilibrium bond length $b_0 = d_p$, where $d_p$ is the bead diameter. Solvent molecules were modeled as single beads identical to the soluble block bead (B) in a model chain. All beads in our simulations had the same mass $m_0$ and diameter $d_p$, which will be used as units of mass and length. All simulations were performed under periodic boundary conditions in a cubic box ($30d_p \times 30d_p \times 30d_p$) containing 81000 beads. The density of all beads including polymer monomers and solvent was equal to $3d_p^{-3}$ and the repulsive interaction parameters between the same type of beads were $a_{AA} = a_{BB} = 25 \left(\frac{k_B T}{d_p^2}\right)$, chosen to reproduce the compressibility of water at room temperature.\(^{37}\) (In the following $k_B T/d_p^2$ will be omitted when referring to values of the interaction parameter $a$). Based on the value of the $a_{BB}$ interaction parameter, the B-block is in a good solvent, as
the chain length dependence of the radius of gyration and diffusion coefficient for corresponding homopolymers follow scaling dependences with the Flory exponent of 0.6.\textsuperscript{38,39} The cutoff distance for all DPD forces, including conservative force, dissipative force and random force\textsuperscript{37} was the same $r_c = d_p$. The friction coefficient for dissipative force was $3.0 \left( k_B T / d_p^2 \right)$ and the noise amplitude for random force was $\sigma = (2 \gamma k_B T)^{1/2}$.\textsuperscript{37} In our simulations we considered two core-forming blocks $N_A = 2$ and $N_A = 4$. For micelle solutions of $A_2B_3$ chains, we varied the repulsive parameter ($a_{AB} = 47.5, 50, 52.5, 55$) and volume fraction of chains, $\varphi$, (which is equal to concentration as $d_p^3$ is a unit volume) from 0.02 to 0.05 to study the interaction energy and oligomer concentration effects on the chain exchange kinetics. For solutions of $A_4B_x$ chains, we kept the core block length ($N_A = 4$) and the volume fraction of chains ($\varphi = 0.05$) constant, and varied the soluble block length ($N_B = 4, 6, 8$) and repulsive parameter ($a_{AB} = 38, 40$) to study the chain length and interaction energy effects. In all simulations the NVT ensemble was adopted ($k_B T = 1$) and the equations of motion were integrated with a modified version of the velocity-Verlet algorithm\textsuperscript{40} with time step $\Delta t = 0.04 (m_0 d_p^2 / k_B T)^{1/2}$.\textsuperscript{37} We used the free-source code LAMMPS\textsuperscript{41} for the DPD simulations on the HPC computer cluster at Case Western Reserve University.

To obtain the equilibrium diblock copolymer micelle solution our DPD simulations were started from a random dispersion of model chains (obtained using $a_{ij} = 25$ for all pair interactions), and increased the interaction parameter $a_{AB}$ to the desired value to initiate micelle self-assembly.\textsuperscript{42} In the obtained equilibrium state aggregates were distinguished by a general distance criterion,\textsuperscript{42,43} in which any pair of chains within a certain cut-off
distance between the centers of mass of hydrophobic blocks belongs to the same aggregate. A cut-off distance of $1.2d_p$ was used to distinguish different aggregates for all systems with $A_2B_3$ chains, and cut-off distance of $1.5d_p$ was used for aggregates composed of $A_4B_x$ chains. All equilibrated micelles had a spherical form. The simulations for equilibrated micelle solutions were conducted for $t = 3.2 \times 10^5$ for solutions with $A_2B_3$ chains and for $t = 1.2 \times 10^6$ for systems with $A_4B_x$ chains. The movement trajectories were collected every 100 time steps for data analysis (discussed below). We used VMD for displaying movement trajectories and data analysis. The equilibrium properties of the micelle solutions, including aggregation number distributions and micelle structure, have been discussed in chapter 3. In Table 5.1, we summarize the equilibrium number-average aggregation numbers corresponding to the peak position of the aggregation number distributions and unimer volume fractions for the micelle solutions discussed in this study.
Table 5.1 Equilibrium aggregation numbers determined from number-average aggregation number distributions $M_{\text{peak}}$ and unimer volume fractions $\varphi_{\text{unimer}}$, for $A_2B_3$, $A_4B_4$, $A_4B_6$, and $A_4B_8$ micellar solutions for different interaction parameters $\alpha_{AB}$ (the corresponding $\chi_{AB}$ values$^{37}$ are listed as well) at $\varphi = 0.05$

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>$\alpha_{AB}$</th>
<th>$\chi_{AB}$</th>
<th>$M_n$</th>
<th>$\varphi_{\text{unimer}} (\times 10^{-4})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2B_3$</td>
<td>47.5</td>
<td>6.44</td>
<td>24±7</td>
<td>19.0±0.6</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>50</td>
<td>7.15</td>
<td>31±6</td>
<td>9.9±0.5</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>52.5</td>
<td>7.87</td>
<td>36±6</td>
<td>4.9±0.1</td>
</tr>
<tr>
<td>$A_2B_3$</td>
<td>55</td>
<td>8.58</td>
<td>43±8</td>
<td>2.8±0.4</td>
</tr>
<tr>
<td>$A_4B_4$</td>
<td>38</td>
<td>3.72</td>
<td>39±10</td>
<td>15.8±3.2</td>
</tr>
<tr>
<td>$A_4B_6$</td>
<td>38</td>
<td>3.72</td>
<td>26±7</td>
<td>24.7±3.5</td>
</tr>
<tr>
<td>$A_4B_8$</td>
<td>38</td>
<td>3.72</td>
<td>17±4</td>
<td>32.6±4.1</td>
</tr>
<tr>
<td>$A_4B_4$</td>
<td>40</td>
<td>4.29</td>
<td>51±6</td>
<td>4.9±2.9</td>
</tr>
<tr>
<td>$A_4B_6$</td>
<td>40</td>
<td>4.29</td>
<td>38±4</td>
<td>8.9±3.3</td>
</tr>
<tr>
<td>$A_4B_8$</td>
<td>40</td>
<td>4.29</td>
<td>31±4</td>
<td>12.9±4.3</td>
</tr>
</tbody>
</table>

* For all $A_2B_3$ micelle solutions $\varphi_{\text{unimer}}$ was calculated for a given $\alpha_{AB}$ by averaging over different volume fractions, while for $A_4B_x$ micelle solutions it was calculated by averaging over time.

5.2.2 Micelle Hybridization Analysis

To study the chain exchange kinetics at equilibrium, we performed in silico micelle hybridization experiments (Figure 5.1) inspired by previously reported experimental studies$^{28-30}$ using the movement trajectories generated from DPD simulations of
equilibrium micelle state. In the \textit{in silico} micelle hybridization experiment, at time $t=0$ chains were randomly labeled blue in the largest aggregate and red in the next largest micelle until all chains in aggregates were marked and this initial configuration was accepted if the disparity between the total number of red and blue chains was less than 10\%. Similarly, half of the unimers were labeled in red and other half in blue, so that the total number of red and blue chains was approximately equal to each other. As the time passes, chain exchange between micelles leads to a redistribution of red and blue chains between different micelles.

![Hybridization](image)

Figure 5.1 Schematic representation of the micelle hybridization process.

To evaluate the time-dependent progress of micelle hybridization, the following autocorrelation function $I(t)$ was used$^{28,29}$:

$$I(t) = 4 \left< \sum_{n} \left( \frac{N_r(t)}{N(t)} - \frac{1}{2} \right)^2 \frac{N(t)}{N_{total}} \right>$$  \hspace{1cm} (5.1)

where $N_r(t)$ and $N(t)$ are the number of red chains and the total number of chains in a micelle at time $t$ and $N_{total}$ denotes the total number of chains in the solution. The summation is performed for all aggregates in the solution and $\langle \ldots \rangle$ denotes averaging over different initial starting states. $N_r(t)/N(t)$ represents the extent of hybridization for an
individual micelle, while $N(t)/N_{\text{total}}$ is the weighting factor of the micelle, i.e. $I(t)$ is a weight average quantity, such as measured by a scattering experiment. At $t=0$, there are no hybridized micelles (i.e. micelles containing both red and blue chains), $N_r(t)/N(t)=1$ for red micelles and $N_r(t)/N(t)=0$ for blue micelles, thus $4^*(N_r(t)/N(t)-1/2)^2=1$ for all micelles and $I(t)$ is practically 1. As hybridization proceeds, the fraction of blue and red chains in micelles become more equal and $I(t)$ decays with time, approaching 0 for the perfectly hybridized state (with exactly half red and half blue chains per aggregate). We note that due to the slight initial mismatch in the number of red and blue chains and some statistical effects of chain distribution between micelles (discussed below) the hybridization function $I(t)$ never reaches precisely zero.

5.3. Results and Discussions

In this section, we present the results on chain exchange dynamics and discuss the influence of oligomer concentration, interaction energy, and corona block length on the kinetics of equilibrium chain exchange kinetics.

5.3.1 Oligomer Concentration Effect

We have performed micelle hybridization simulations and calculated autocorrelation function $I(t)$ using eq.5.1 for $A_2B_3$ micelle solutions with different interaction energies and concentrations. Figure 5.2 shows the hybridization curves $I(t)$ obtained at the same interaction energy ($a_{AB}=50$) for different oligomer concentrations. As is seen, for all concentrations the initial slope of hybridization curves is rather similar and in all cases $I(t)$ decreases quickly, reaching different plateau levels at longer times. The plateau level
originates from a) the initial slight mismatch in the number of red and blue chains and b) statistical deviations of the probability of finding a particular color chain in a given micelle from the average probability for the whole system. The latter is the main reason for the non-zero plateau level.

To estimate the plateau level, we calculated it in two different ways for comparison. The first is by averaging over the last $t = 1 \times 10^4$ of the plateau level. The second is to perform the following simulations. In our simulations, each chain is numbered consequently, for example, for $A_2B_3$ micelle solution at $\varphi = 0.05$, there are 810 chains in total, and the chain index varies from 1 to 810, correspondingly. To calculate the plateau level, chains with index from 1 to 405 (i.e. half of the chains) were labeled as red and the rest as blue. Since in the simulation, the distribution of red and blue chains in micelles is independent of the chain index, the distribution of red or blue chains should be random at the end of hybridization process. Using such random labeling, the plateau level then can be calculated using eq.5.1. As is seen from Table 5.2, the plateau level calculated from random labeling chains (discussed above) is practically identical to the plateau level obtained by averaging over the plateau level (Figure 5.2).
Table 5.2 Plateau level of the hybridization correlation function $I(t)$ calculated from Figure 5.2 (main text) in comparison with the value obtained by random labeling of chains in micelles for $A_2B_3$ micelle solutions with interaction energy $a_{AB}=50$ at different oligomer concentrations.

<table>
<thead>
<tr>
<th>plateau φ</th>
<th>from Figure 2</th>
<th>from random labeling</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>0.03</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>0.04</td>
<td>0.06</td>
<td>0.06</td>
</tr>
<tr>
<td>0.05</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

To eliminate the influence of such statistical effects, which depend on the micelle size distribution, we normalized the autocorrelation function $I(t)$ and calculated the following contrast function\textsuperscript{28}\textsuperscript{-30}:

$$C(t) = \left[ \frac{I(t) - I(\infty)}{I(0) - I(\infty)} \right]^{1/2}$$

(5.2)

where $I(\infty)$ is the plateau level, calculated by averaging $I(t)$ over the last $t = 1 \times 10^4$. We note that the contrast function is proportional to the average fraction of red (blue) chains in an average aggregate. By normalizing the original $I(t)$ curves shown in Figure 5.2, we found that all “contrast” function $C(t)$ curves are practically the same, i.e. fall into a single line in a semi-log plot of Figure 5.2 (inset). The obtained $C(t)$ dependence can be
well-fitted by a single-exponential decay function with the corresponding characteristic relaxation time $\tau_c \approx 7.5 \times 10^3$. Similar analysis has been performed for $A_2B_3$ micelle solutions with different interaction energies for different concentrations and in all cases contrast functions $C(t)$ were found to be independent of concentration. The effect of interaction energy $a_{AB}$ on the behavior of the contrast function $C(t)$ will be discussed in the next section. A single-exponential decay of the contrast function indicates that there is one dominant relaxation process or there might be several processes with similar relaxation times that govern the chain exchange kinetics.

Figure 5.2 Hybridization autocorrelation function $I(t)$, eq.1, and contrast function $C(t)$, eq.5.2, (inset) for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ at different oligomer concentrations: $\varphi = 0.02, 0.03, 0.04, 0.05$ (from top to bottom curves in the main plot, color scheme is the same for the inset).
To understand which kinetic process or processes contribute to the chain exchange reflected in the contrast function (eq. 5.2, Figure 5.2), we first consider unimer expulsion/insertion, which is usually regarded as the dominant mechanism of chain exchange between block copolymer micelles at equilibrium. Following a previous study on surfactant self-assembly\textsuperscript{35}, we calculated the correlation function for unimer formation, $E(t)$. At time $t=0$ chains in all aggregates were labeled. Whenever a labeled chain leaves a micelle and remains as a free chain for at least two consecutive time intervals, the chain was unlabeled. The time evolution of the number of labeled chains $N(t)$ was monitored and the ratio of $N(t)$ to the initial number of labeled chains $N(0)$ was calculated:

$$E(t) = \langle \frac{N(t)}{N(0)} \rangle$$

(5.3)

Where $\langle \ldots \rangle$ denotes averaging over different initial states. Assuming that only unimer expulsion contributes to the formation of free chains in the solution, the correlation function $E(t)$ is expected to follow a single exponential decay and be concentration independent.\textsuperscript{35} Figure 5.3 shows in a semi-logarithmic plot the correlation function of unimer formation $E(t)$ for $A_2B_3$ micelle solutions with interaction energy $a_{AB}=50$ calculated for different oligomer concentrations. As is seen, all curves indeed follow single-exponential decay, but there is an obvious dependence on oligomer concentration: unimer formation occurs slower for the micelle solutions with higher oligomer concentration. A similar concentration dependence is also seen for $A_3B_3$ micelle solutions with different interaction energies (not shown).
Figure 5.3 Unimer formation $E(t)$, eq.5.3 and native chain expulsion $F(t)$, eq.5.4 (inset) correlation functions for $A_2B_3$ micelle solution with interaction energy $a_{AB}=50$ for different oligomer concentration ($\phi = 0.02, 0.03, 0.04, 0.05$, from bottom to top, color scheme is the same for the inset).

By fitting the $E(t)$ curves in Figure 5.3 with a single-exponential decay function ($f(t) = \exp(-t/\tau)$), we obtained the characteristic relaxation times for unimer formation, listed in Table 5.2. Comparing relaxation times for unimer formation, one can see a systematic increase of $\tau$ with an increase in oligomer volume fraction $\phi$. As is seen from Table 5.2, the characteristic time for unimer formation is slightly smaller (for the lowest $\phi$) or larger (for the higher $\phi$) to that for contrast function $C(t)$.

To calculate the chain insertion correlation function, all unimers were marked at time $t=0$. When a unimer joins an aggregate and remains assembled for at least two time intervals, the chain is unmarked. The unimer insertion correlation function $U(t)$ is calculated as:
where \( N(0) \) is the number of unimers at \( t=0 \) and \( N(t) \) is the number of labeled unimers at time \( t \), \( <\ldots> \) denotes averaging over different initial configurations. Figure 5.4 shows the unimer insertion correlation function for \( A_2B_3 \) micelle solutions \( (a_{AB}=50) \) at different oligomer concentrations. As is seen, unimer insertion follows a single-exponential decay process with a characteristic time decreasing with an increase in concentration.

![Figure 5.4 Unimer insertion correlation function U(t), eq. 5.4, for A\(_2\)B\(_3\) micelle solutions with interaction energy \( a_{AB}=50 \) at different oligomer concentrations (\( \phi = 0.02, 0.03, 0.04, 0.05 \) from top to bottom).](image)

In Table 5.3, the unimer insertion relaxation times obtained by fitting \( U(t) \) correlation function with a single-exponential decay function are given for \( A_2B_3 \) micelle solutions for different interaction energies and oligomer concentrations. As is seen, the increase in the interaction energy slows down unimer insertion while an increase in concentration speeds it up.
Table 5.3 Unimer insertion time \( \tau_{\text{insertion}} \) obtained by a single-exponential decay fitting of unimer insertion correlation function \( U(t) \) for \( A_2B_3 \) micelle solutions with different interaction energies and oligomer concentrations.

<table>
<thead>
<tr>
<th>( \alpha_{AB} )</th>
<th>50</th>
<th>52.5</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \varphi )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>280</td>
<td>475</td>
<td>832</td>
</tr>
<tr>
<td>0.03</td>
<td>235</td>
<td>395</td>
<td>525</td>
</tr>
<tr>
<td>0.04</td>
<td>212</td>
<td>328</td>
<td>459</td>
</tr>
<tr>
<td>0.05</td>
<td>179</td>
<td>273</td>
<td>359</td>
</tr>
</tbody>
</table>

To understand the observed dependence of unimer insertion time \( \tau_{\text{insertion}} \) on oligomer concentration and interaction energy, we estimated the average distance between two aggregates in solution: \( d = (L^3/n)^{1/3} \), where \( L \) is the simulation box size and \( n \) is the average number of aggregates (counting all aggregates starting from dimers, i.e. \( P > 1 \)) in the box. In Figure 5.5 we plotted unimer insertion time \( \tau_{\text{insertion}} \) vs. the square of the average distance between aggregates \( d^2 \). As is seen, \( \tau_{\text{insertion}} \) linearly increases with \( d^2 \) in agreement with Einstein relation: \( \tau \sim d^2/D \), with \( D \) being a diffusion coefficient, which is about 0.1 for a homopolymer of the same length as \( A_2B_3 \) chain. With an increase in oligomer concentration the number of aggregates in the solution increases (for a given interaction energy) and the average distance for a unimer to travel before insertion into an aggregate decreases leading to a decrease in \( \tau_{\text{insertion}} \). Similarly, with an increase in the
interaction energy the average aggregation number increases and the number of micelles decreases (for a given polymer concentration) resulting in an increase of the average distance for a unimer to travel to enter a micelle and therefore increasing $\tau_{\text{insertion}}$.

Figure 5.5 The unimer insertion time $\tau_{\text{insertion}}$ vs. the square of average distance $d^2$ between aggregates ($P>1$) for A$_2$B$_3$ micelle solutions with different interaction energies ($a_{AB}=50, 52.5, 55$), and oligomer concentrations ($\phi = 0.02, 0.03, 0.04, 0.05$).

In general, as seen in Table 5.4, the unimer insertion time is more than one order of magnitude smaller than unimer formation time, which implies that unimer escape is the rate-determining step for unimer exchange in agreement with analytical considerations.$^4$
Table 5.4 Characteristic times obtained by a single-exponential decay fitting of contrast function (eq.5.2), unimer formation (eq.5.3) and native chain expulsion (eq.5.4) for A₂B₃ micelle solution with interaction energy \( a_{AB} = 50 \) at different oligomer concentrations.

<table>
<thead>
<tr>
<th>Contrast function, ( a )</th>
<th>Unimer Formation, ( C(t) )</th>
<th>Unimer Insertion, ( E(t) )</th>
<th>Native Chain Expulsion, ( U(t) )</th>
<th>Native Chain Expulsion, ( F(t) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02</td>
<td>6748</td>
<td>280</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.03</td>
<td>7733</td>
<td>235</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.04</td>
<td>7531±214</td>
<td>8685</td>
<td>212</td>
<td>6340±210</td>
</tr>
<tr>
<td>0.05</td>
<td>9032</td>
<td>179</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\( a \) the error-bars are obtained by averaging over corresponding different relaxation times obtained for different oligomer concentrations.

The observed concentration dependence of unimer formation function \( E(t) \) (Figure 5.3, Table 5.4) indicates that in addition to direct unimer expulsion, there are other mechanisms which contribute to unimer formation process. In particular micelle fusion/fission is known to be concentration dependent: the higher the concentration the larger is the probability of these events. In the calculation of the unimer formation correlation function \( E(t) \) a chain was unmarked only when it becomes a free chain regardless of its history. For instance, a marked chain could escape the initial micelle as a part of a small aggregate (e.g. a fission process) and be transported to another micelle before the chain finally escapes, become a free chain and be unmarked. To investigate the contribution of different mechanisms to the overall chain exchange process, we
calculated the relative occurrence frequency as well as the overall contributions of different mechanisms including unimer expulsion/insertion, small aggregate (from dimers to tetramers) escape/formation and micelle (containing more than 5 chains) fission/fusion for A$_2$B$_3$ micelle solution (Table 5.5). A kinetic event was defined as the process of merging/splitting of two reactants (including unimers). The relative frequency is defined as the ratio of a number of events of a given type to the total number of events calculated averaging over the entire simulation and the contribution denotes the fraction of chains exchanged during the given kinetic event compared to the total number of chains exchanges.

Table 5.5 Relative frequency and contribution (fraction of chains exchanged) of different kinetic events, and corresponding relaxation times for native chain escaped by these mechanisms for A$_2$B$_3$ micelle solution with interaction energy $a_{AB}=50$ at two different oligomer concentrations.

<table>
<thead>
<tr>
<th>Processes</th>
<th>0.02</th>
<th>0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Frequency (%)</td>
<td>Contribution (%)</td>
</tr>
<tr>
<td>Unimers</td>
<td>71±1</td>
<td>40±1</td>
</tr>
<tr>
<td>Small aggregates</td>
<td>24±2</td>
<td>33±2</td>
</tr>
<tr>
<td>$(2 \leq P \leq 4)$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Micelles $(P \geq 5)$</td>
<td>5±1</td>
<td>27±1</td>
</tr>
</tbody>
</table>

As is shown in Table 5.5 for two oligomer concentrations, the unimer expulsion/insertion occurs more frequently (70%) than other two kinetic events, as expected. At the same
time, the overall contribution of unimer exchange is about 30-40%, while the rest of the chains are exchanged via small aggregates expulsion/insertion or micelle fusion/fission. The contribution of unimer or small aggregates exchange decreases with an increase of concentration and corresponding contribution of micelle fusion/fission increases (Table 5.5). As a result, the process of unimer formation considered in Figure 5.3 is more likely to involve small aggregate exchange between micelles or micelle fission/fusion at higher oligomer concentration than at lower $\phi$. Since such chain transport between the micelles directly contributes to the contrast function $C(t)$ but would delay the appearance of a free chain, the relaxation time for the correlation function $E(t)$ would increase with an increase of concentration, as is seen in Figure 5.3 and Table 5.5.

To test the hypothesis that the observed concentration dependence for $E(t)$ correlation function for unimer formation originates from contribution of other kinetic mechanisms besides direct unimer expulsion, we obtained correlation function for native chain fraction $F(t)$. At $t=0$, all the chains in a given micelle (with the number of chains larger than 10) were marked as native chains, $N_{\text{native}}(0)$. The chain is unmarked if it leaves the micelle by any kinetic mechanism, either as a single chain or as part of an aggregate. During the simulation, the identity of the micelle during the time step $t$ is traced as the micelle that contains more than half the chains comparing to the preceding time step. The native chain correlation function $F(t)$ is calculated as:

$$F(t) = \langle \frac{N_{\text{native}}(0) - N_{\text{leave}}(t)}{N_{\text{native}}(0)} \rangle$$

(5.5)

where $N_{\text{leave}}(t)$ is the accumulating number of native chains that have left the micelle and the averaging occurs over different original micelles and different initial states. The
native chain correlation function $F(t)$ is shown in the inset of Figure 5.3 for $A_2B_3$ micelle solutions with interaction energy ($a_{AB}=50$) calculated for different oligomer concentrations. As is seen, all curves practically follow the same single exponential dependence with characteristic time $\tau_{\text{esc}} \approx 6340$, which is somewhat smaller than that for unimer formation or the contrast function $C(t)$. Comparing the unimer formation and native chain correlation functions, one can conclude that concentration dependence of the former is due to unimer transport between micelles by small aggregates or micelle fusion/fission processes, which become more active with a concentration increase. Another perhaps even more interesting conclusion, which can be made by comparing all three correlation functions and the corresponding characteristic times is that single exponential decay for the contrast and native chain correlation functions does not imply that chain exchange is dominated by a single kinetic process. Indeed, as is seen from Table 5.5 the contribution of small aggregate escape/insertion or micelle fusion/fission is comparable to that by unimer exchange for these short diblock copolymer micelle solutions. This implies that the characteristic times for unimer expulsion, small aggregate escape or even micelle fission should be comparable for this system to observe a single exponential dependence for the contrast and native chain correlation functions.

To validate this point, we calculated the characteristic time for a native chain to be expelled from a micelle by three different mechanisms. In order to determine the contribution of different kinetic mechanisms into the process of chain expulsion we monitored the chains which escaped from a selected micelle via direct unimer expulsion, released as a part of a small aggregate ($2 \leq P \leq 4$) or as part of micelle fission (with an
aggregation number of the smallest aggregate \( P \geq 5 \). For each of the kinetic processes we calculated a native chain escape correlation function \( F(t) \), eq. 5.5, in which \( N_{\text{native}}(0) \) was the total number of the native chains that escaped by this kinetic process. Figure 5.6 shows the native chain expulsion functions for \( A_2B_3 \) micelle solution (\( \phi = 0.05, \ a_{AB}=50 \)) for different kinetic mechanisms: unimer expulsion/insertion, small aggregate splitting/merging and micelle fission/fusion. As is seen, all three curves are practically indistinguishable and show single-exponential decay with nearly the same slope. Thus the characteristic times for a native chain escape by different kinetic mechanisms are very close to each other, as shown in Table 5.4. The physical origin for this behavior is a small difference in the energy barrier for a chain or a group of chains to leave a micelle due to a short length of the core-forming block, as discussed below.

![Figure 5.6](image)

Figure 5.6 Native chain expulsion correlation function \( F(t) \) via unimer expulsion/insertion (black), small aggregate splitting/merging (red) and micelle fission/fusion (blue) for \( A_2B_3 \) micelle solution (\( \phi = 0.05, \ a_{AB}=50 \)).
5.3.2 Interaction Energy Effect

The interaction energy between blocks or between core block and solvent plays an important role in thermodynamics and kinetics of micelle self-assembly. We have performed micelle hybridization simulations for $\text{A}_2\text{B}_3$ micelle solutions with different interaction energies $a_{AB}$ at different oligomer concentrations. As discussed in the previous section, oligomer concentration does not influence the obtained contrast correlation functions $C(t)$. The interaction energy has very strong effect, as is seen from Figure 5.7, where contrast functions are shown for $\text{A}_2\text{B}_3$ micelle solutions with different interaction energies $a_{AB}$. All curves follow a single exponential decay. With an increase in $a_{AB}$ the exchange of chains between micelles considerably slows down and the characteristic time increases, as seen in Table 5.6.

![Figure 5.7 Contrast function C(t), eq.2, obtained for A2B3 micelle solutions with different interaction energies (aAB=47.5, 50, 52.5, 55) at the oligomer concentration φ = 0.03.](image)
Table 5.6 Characteristic times obtained by a single-exponential decay fitting of contrast correlation function $C(t)$ for $A_2B_3$ micelle solutions with different interaction energies at $\varphi =0.03$.

<table>
<thead>
<tr>
<th>$a_{AB}$</th>
<th>47.5</th>
<th>50</th>
<th>52.5</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau$ from $C(t)$</td>
<td>2703</td>
<td>7517</td>
<td>19390</td>
<td>44172</td>
</tr>
</tbody>
</table>

The increase in the interaction energy leads to a higher surface tension at the core-corona interface which increases the aggregation number, decreases the critical micelle concentration (cmc), and hence unimer volume fraction, as listed in Table 5.1 and increases the potential barrier for chain expulsion (and aggregate escape or micelle fission)$^{4,5}$ Indeed, the free energy barrier for a block copolymer with a short core block $N_A$ to escape from a micelle is defined primarily by the volume interaction energy of the block in solution$^{45,46}$:

$$\tau_{un} \sim \exp(c\chi_{AB}N_A)$$

(5.6)

where $\chi_{AB}$ is the Flory-Huggins interaction parameter between monomers A and B and $c$ is coefficient close to unity.$^{45,46}$ As has been shown by Groot and Warren$^{37}$, in DPD simulations the interaction energy parameter $a_{AB}$ can be related to the Flory-Huggins interaction parameter $\chi_{AB}$, as

$$\chi_{AB} = 0.286\Delta a_{AB} = 0.286(a_{AB} - a_{BB})$$

(5.7)

where $\Delta a_{AB} = a_{AB} - a_{BB}$. To investigate whether the relationship displayed in eq. 5.6 holds for the characteristic time for chain exchange obtained from hybridization simulations we plotted the corresponding data in Figure 5.8 as a function of reduced interaction energy.
\( \chi_{AB} N_A = 0.286 N_A \Delta a_{AB} \). As is seen, the data follow linear dependence in the semi-logarithmic scale of the Figure in agreement with eq. 5.6. We have also performed simulations and data analysis for native chain expulsion correlation function \( F(t) \) for \( A_2B_3 \) and \( A_4B_x \) micelle solutions with different interaction energies and unimer formation correlation function \( E(t) \) for \( A_2B_3 \) micelle solutions. The obtained characteristic times follow very similar dependence on reduced interaction energy \( \chi_{AB} N_A \) (Figure 5.7) and were fitted together with the characteristic times for corresponding contrast functions \( C(t) \), leading to \( \tau \sim \exp(0.67 \chi_{AB} N_A) \). Thus, the obtained characteristic times for different correlation functions for both \( A_2B_3 \) and \( A_4B_x \) micelle solutions closely follow the dependence of eq. 5.6 that indicates that energy barrier for chain escape or exchange is primarily defined by volume interactions between the core block and solvent (or corona block). As will be discussed below, there is an additional effect of corona block length \( N_B \) on chain exchange kinetics (which is responsible for some spreading of the data for \( A_4B_x \) micelle solutions in Figure 5.8).
As discussed in the preceding section, the characteristic times for different correlation functions for A$_2$B$_3$ micelle solutions are not associated with a single kinetic process as unimer escape/exchange, but rather a reflection of several processes such as small aggregate escape/insertion or even micelle fusion/fission occurring at comparable time scales. For unimer escape with the short core block as considered in our simulation study, the potential barrier is defined by volume interactions experienced by each A-type monomer surrounded by B-monomers, as described by eq 5.6. For a small aggregate that has escaped from a micelle, core-block monomers will be able to reduce volume

\[ \tau \sim \exp(0.67 \chi_{AB} N_A) \]
interaction to surface interactions with corona blocks or solvent solution\textsuperscript{4, 5}, which will reduce the corresponding potential barrier. Thus, for an aggregate for 10 or fewer monomers (which is the typical size of aggregates exchanged between A\textsubscript{2}B\textsubscript{3} micelles even for micelle fission/fusion events) the potential barrier for small aggregate escape/exchange will be very comparable with that for single chain escape.

### 5.3.3 Corona block length effect

As discussed in the previous section, the potential barrier for chain exchange follows the dependence of eq.5.6 which implies that chain exchange considerably slows down with an increase in interaction energy $a_{AB}$ or core-block length, $N_A$. The influence of the corona block length $N_B$ on the chain exchange dynamics is normally considered to be a rather minor factor (at least in the limit of large $N_B$) and is primarily associated with the slower chain diffusion for a longer corona blocks\textsuperscript{4, 5}. We have performed hybridization simulations and calculated the contrast function for A\textsubscript{4}B\textsubscript{x} micelle solutions with different corona block lengths, which is shown in Figure 5.9. As is seen, an increase in the corona block length leads to a quicker chain exchange for micelle solutions with the same core block in both cases ($a_{AB}$=38,40).
We have also calculated for A_{4}B_{x} micellar solutions the native chain expulsion correlation functions and observed very similar dependence on the corona-block length $N_B$ as for the contrast function. As is seen from Figure 5.10, the characteristic times for both correlation functions systematically decrease with an increase in corona block length implying that in all cases chain exchange becomes quicker with an increase in $N_B$. 

Figure 5.9 Contrast correlation function $C(t)$ for A_{4}B_{x} micelle solutions with different corona block lengths ($N_B=4, 6, 8$) for (a) $a_{AB}=38$ and (b) $a_{AB}=40$, $\varphi=0.05$. 

124
Figure 5.10 Characteristic times for contrast $C(t)$ (squares) and native chain expulsion $F(t)$ (triangles) correlation functions for $A_4B_4$, $A_4B_6$, and $A_4B_8$ micelle solutions with different interaction energies at $\phi = 0.05$ as functions of corona block length $N_B$.

The obtained results indicate that there are other more important factors than decreasing the diffusion coefficient with an increase of corona-block length, which result in a quicker overall chain exchange in our $A_4B_x$ micelle solutions. Similar to $A_2B_3$ micelle solutions, the characteristic time scale for unimer insertion into a micelle is one or even two orders of magnitude smaller than chain expulsion time for $A_4B_x$ micelle solutions, and therefore this is not a factor determining the chain exchange rate. As it has been shown in experimental, simulation and analytical studies, the increase in the corona-block length (for a given core-forming block) leads to a decrease of the average micelle aggregation number,\(^9\,10\,47-49\) and perhaps more importantly increases the critical micelle concentration (cmc).\(^49-54\) The main reason is that by having a longer soluble block a
diblock copolymer has higher compatibility with solvent and a somewhat weaker tendency to form micelles compared to a diblock with shorter soluble block (and the same core block). We note that this effect will be especially noticeable for diblocks with a small mismatch between the core and corona block lengths and shorter overall chain length, as considered in our simulations. Indeed, as is seen from Table 5.1, the increase in B-block length results in a considerable decrease in the micelle aggregation number and an increase in unimer concentration. Furthermore, the area per chain in the micelle corresponding to the most probable aggregation number, increases with an increase in the corona-block length, as is seen in Figure 5.11, making it easier for a chain to escape from a micelle.

![Area per Chain vs. $N_B$](image)

**Figure 5.11** The average area per chain for the micelle corresponding to the maximum of the aggregation number distribution for $A_4B_x$ micelle solutions ($a_{AB}=38, 40$) at oligomer concentration $\varphi=0.05$.

Besides an increase in the cmc for diblocks with a longer soluble block, there is also a decrease in cmt (critical micelle temperature). Indeed, comparing the unimer fraction (i.e.
fraction of free chains to the total number of chains) for different corona-block lengths, we observe that unimer fraction for $A_8B_8$ micelle solution significantly increases with a decrease in $\Delta a_{AB}$ (which is linearly proportional to $\chi_{AB}$, and hence inversely proportional to temperature) and remains consistently higher than that for $A_4B_4$ case, as seen in Figure 5.12. Having a higher cmc and lower cmt for micelles formed by diblock copolymers with longer corona-block length, indicates that there is a higher penalty for chain transfer from the bulk to a micelle and therefore a lower potential barrier for a chain escape from the micelle\textsuperscript{12, 55}, which translates into more rapid chain exchange kinetics as shown in Figures 5.8 and 5.9.

![Fraction of unimers in $A_8B_4$ and $A_8B_8$ micelle solutions with different interaction energies $\Delta a_{AB} = a_{AB} - a_{BB}$ ($a_{BB}=25$) at oligomer concentration $\varphi=0.05$.](image)

Figure 5.12 Fraction of unimers in $A_8B_4$ and $A_8B_8$ micelle solutions with different interaction energies $\Delta a_{AB} = a_{AB} - a_{BB}$ ($a_{BB}=25$) at oligomer concentration $\varphi=0.05$.

In terms of the influence of corona-block length on the chain exchange mechanisms, an increase in B-block length leads to the decrease in frequency and contribution of micelle fission/fusion, (since a thicker corona makes it more difficult for the cores of two
micelles to come into contact) and in an increase in the contribution of unimer exchange and small aggregate escape/insertion, as is seen in Table 5.7.

Table 5.7 Relative frequency and contribution (fraction of chains exchanged) of different kinetic events for A₄B₄, A₄B₆ and A₄B₈ micelle solutions with interaction energy aₐ₃₈=38 at at φ = 0.05.

<table>
<thead>
<tr>
<th>Event (%)</th>
<th>Contribution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A₄B₄</td>
</tr>
<tr>
<td>Unimers</td>
<td>60±1</td>
</tr>
<tr>
<td>Small aggregates</td>
<td>34±1</td>
</tr>
<tr>
<td>(2≤P≤4)</td>
<td>Micelles (P≥5)</td>
</tr>
</tbody>
</table>

5.4 Conclusions

In this chapter, we have studied the kinetics of chain exchange between diblock copolymer micelles in solution at equilibrium using DPD simulations. In our in silico micelle hybridization experiments inspired by previously reported experimental studies, approximately half the micelles and chains were randomly labeled red and another half blue and chain exchange between micelles has been observed and analyzed in terms of the contrast function. To gain insights on the process of chain exchange at the molecular level we also obtained correlation functions for unimer formation (starting from marked
chains located in micelles) and native chain escape. We found that for all micelle solutions studied all correlation functions follow a single exponential decay. The corresponding relaxation times for contrast function, unimer formation and native chain correlation functions were found to follow an exponential dependence on the interaction energy $\chi_{AB}$ (which is related to the difference in the interaction parameters $a_{AB} - a_{BB}$) and core block length $N_A$: $\tau \sim \exp(0.67\chi_{AB}N_A)$. The decrease in chain exchange rate with an increase in core block length and incompatibility between blocks (or between the core block and solvent) is a result of a higher potential barrier for chain (or small aggregate) expulsion\textsuperscript{4,5}. For a short core blocks as considered in our simulation study, the potential barrier is defined by volume interactions experienced by each A-type monomer in surroundings of B-monomers, $\sim\chi_{AB}N_A$. For a small aggregate core-block monomers will be able to reduce volume interactions to surface interactions with corona blocks or solvent in solution which will define the corresponding potential barrier $\sim N_A^{2/3}/kT$.\textsuperscript{4,5}

Thus, for an aggregate for 10 or less monomers (which is the typical size of aggregates exchanged between $A_2B_3$ micelles even for micelle fission/fusion events) the potential barrier for small aggregate escape/exchange will be very comparable to that for single chain escape. As a result, despite the fact that there is more than one kinetic mechanism that contributes to chain exchange, the overall chain exchange kinetics follow first order kinetics with a single relaxation time.

Comparing the results obtained for $A_2B_3$ micelle solutions at different polymer concentrations, we found that chain exchange process is independent of concentration and is dominated by unimer (small aggregate) expulsion. Unimer insertion, which occurs more rapidly for micelle solutions with higher oligomer concentration occurs at a
noticeably shorter time scales than chain expulsion and hence does not significantly influence the chain exchange kinetics. At the same time, the correlation function for unimer formation (from chains being originally part of micelles) shows a strong concentration dependence – unimers form more slowly in the micelle solutions with higher oligomer concentration, where the contribution of micelle fusion/fission is higher. Since the characteristic time for native chain expulsion from micelles $F(t)$ does not exhibit concentration dependence, it is the transport of chains between micelles via fusion/fission mechanism, which slows down unimer formation, that is responsible for the concentration dependence of $E(t)$.

We also studied the influence of the corona block length on the chain exchange kinetics in $A_xB_x$ micelle solutions and found that chain exchange and native chain expulsion both occur more rapidly for diblock copolymers with longer corona blocks. These results are in contrast to theoretical predictions made in the limit of long chain length$^{4,5}$ that chain exchange kinetics slow down with corona block length due to the decrease in the chain diffusion through the corona for longer corona lengths. The decrease in diffusion coefficient in solution with an increase in corona block length does not have an appreciable effect on the observed chain exchange as unimer insertion occurs much quicker than chain expulsion. More importantly for reasonably short diblock copolymers, as considered in our study, the micelle average aggregation number decreases and cmc increases with an increase in corona block length, which implies a higher compatibility with solvent and a somewhat weaker tendency to form micelles compared to a diblock with a shorter corona block (and the same core block). This factor was not considered in the theoretical models for the kinetics of chain exchange between polymer micelles.$^{4,5}$
Having a higher cmc and lower cmt for micelles formed by diblock copolymers with longer corona-block length, indicates that there is a higher penalty for chain transfer from the bulk to a micelle and therefore a lower potential barrier for a chain escape from the micelle\textsuperscript{12,55}, which translates into more rapid chain exchange kinetics.

In summary, in this chapter, using DPD simulations, we studied systematically the influence of the oligomer concentration, interaction energy and corona block length on the chain exchange kinetics between copolymer micelles in solutions. The obtained results provide new insights on the time scales and mechanisms of chain exchange in block copolymer micelle solutions, which will be useful for future development of analytical models and experimental research on polymer self-assembly.
5.5 Bibliography


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Chapter 6

Rheology of Supramolecular Polymers by MD Simulation

In this chapter, Molecular Dynamics simulation has been applied to study the dynamics and rheological properties of reversible associated supramolecular polymers solution. We first review previous studies on the dynamic and rheological properties of supramolecular polymers. Then we describe the reversible association model and MD simulation details. In the results section, we will discuss the equilibrium properties, shear-thinning behavior and equilibrium viscosity of the supramolecular polymer solution in our simulations. Finally, we summarize our main findings in the conclusion section.

6.1 Introduction

The equilibrium properties of supramolecular polymers have been actively studied both experimentally and theoretically and a reasonable level of understanding of the self-assembly process has been achieved. While we are aware of only a few experimental studies on the rheological response of linear supramolecular polymers to shear or external force fields. Mejer and coworkers have studied the complex viscosity of hydrogen
bonding-based supramolecular polymers in solution as a function of angular frequency for different oligomer concentrations, temperature, spacer lengths and binding strength. Using dynamic light scattering and rheological measurements, Buhler et al.\textsuperscript{9} studied the shear modulus and viscosity of hydrogen-bonded supramolecular polymers as a function of angular frequency and shear stress. Cohen Stuart and co-workers\textsuperscript{10} investigated the influence of concentration and chain length on the viscosity, relaxation time and elastic modulus of wormlike hydrogen bonded polymers (based on 2,4-bis(2-ethylhexylureido) toluene (EHUT) monomers) subjected to shear.

To interpret the experimental rheological results obtained for supramolecular polymers, analytical predictions for living polymers\textsuperscript{11,12} and (Monte Carlo (MC) or MD) computer simulation results for wormlike micelles\textsuperscript{13-18} are most commonly used. While these models can often be helpful in the experimental data analysis, especially if supramolecular polymers are structurally similar to wormlike micelles, it is important to keep in mind the differences between two systems. For instance, in contrast to wormlike micelles, supramolecular polymers usually contain homopolymer spacers of different length, which are chemically different from the associating units. As a result, the association or disassociation can occur only at specific locations along the chains and there might be some additional volume interactions between the spacers and associating groups and/or solvent. Additionally the rigidity of the spacer and associating groups can be different, as the interactions between hydrogen bonded arrays or metal-ligand complexes acting as associating units can be highly orientationally specific. Head-to-tail associating polymers do not exhibit branching, which is known to occur in wormlike
micelles. These properties of supramolecular polymers may lead to a somewhat different dynamic and rheological behavior compared to wormlike micelles.

On the computational side, the main challenge for large-scale molecular dynamics simulations is to model correctly the specific and possibly orientation-specific binary reversible interactions such as exist between a donor and an acceptor. This interaction differs from the two basic interaction types in conventional bead-spring MD simulations: bond interaction or non-bonded pair-wise interaction. The only simulation study of supramolecular polymer dynamics we are aware of is the combined MD/MC simulations by Hoy et al.\textsuperscript{18} of reversibly associating polymer networks in the melt. In their simulations, the reversible association was represented as a “sticky bond” which is created/updated based on a MC protocol. One-to-one (binary) binding is achieved by limiting to one the number of bonds that can form between sticky groups. In the current work, we present a MD model for linear (or ring-like) head-to-tail reversibly associated polymers where the specific reversible interactions between oligomer ends were implemented by using a combination of pseudo-Coulombic and repulsive interactions, without employing a MC protocol. Using this model, we studied the different rheological properties of supramolecular polymer solutions under shear flow.

An important property of supramolecular polymers which can be extracted from rheological measurements is the equilibrium viscosity. Solution viscosity is routinely used as an indication of self-assembly and even for quantification of the extent of polymerization.\textsuperscript{3, 19, 20} As for other dynamic or rheological properties of supramolecular
polymers, the concentration dependence of solution viscosity ($\eta$) is normally interpreted using either models for non-associating polymers or wormlike micelles. In dilute solutions in the absence of reversible association solution viscosity increases linearly with concentration ($c$), i.e. $\eta \sim c^{21-23}$. In semi-dilute solutions above the overlap concentration when different chains start to feel presence of their neighbors, Cates’ model predicts a $\eta \sim c^{3.5}$ dependence for the viscosity of living polymer solutions.\textsuperscript{12} While for some supramolecular polymer solutions the Cates model seems to work well,\textsuperscript{3,10} in other cases a somewhat weaker dependence of the supramolecular solution viscosity on the oligomer concentration is reported for metallo-supramolecular, DNA- and hydrogen-bonding-based supramolecular solutions: $\eta \sim c^{\alpha}$ with $\alpha$ in the range 1.3-1.8 for the exponent.\textsuperscript{19,20,24,25} These results show that solution viscosity of supramolecular polymers often exhibits a weaker dependence than expected for semi-dilute solutions of wormlike micelles\textsuperscript{12}, but stronger than the linear dependence expected for non-associating polymers.

As discussed above, a complete understanding of dynamics and rheological properties of supramolecular polymers is still lacking. There is an evident need for theoretical and computational studies, which would help to understand the dynamics and rheological properties of supramolecular polymers. In this chapter, we apply Molecular Dynamics (MD) simulations to study the rheological properties of head-to-tail associating polymer solutions.
6.2 Model and simulation details

6.2.1 Reversible association model

One important structure feature of supramolecular polymers is the complementary reversible association between the end-groups. For MD simulation, it is difficult to model a reversible association as a single type of interaction because in conventional MD simulation, a bonding interaction is specific one-to-one interaction, but not reversible, while a pairwise interaction is reversible but not specific. In previous MD simulations involving complementary reversible associations, the one-to-one association was usually achieved by regulating the maximal number of bonds an bead can form.\textsuperscript{7, 13, 14, 18} For example, Kröger \textit{et al.} developed a modified FENE potential which was applied to associating beads to model wormlike micelles.\textsuperscript{13, 14} In this approach, a reversible bond is formed (or broken) between two beads when they come closer (or further away) than the cutoff distance with the maximum of two reversible bonds per bead allowing formation of chains or loops of reversibly bonded beads. Recently, Hoy \textit{et al.} developed a hybrid MD/MC simulation protocol to model associating polymer networks.\textsuperscript{18} Formation and breaking of reversible bonds was handled by a Metropolis MC algorithm, which was also used to select the most probable bond pair in case there is more than one possible associating pair. A modified covalent FENE potential was imposed between any two reversibly bonded beads. In our simulations, we explored the possibility of achieving spontaneous (unregulated) complementary reversible associations. To this end we designed a one-to-one reversible association model employing combination of a pseudo-Coulombic potential and Leonard-Jones potential.
In our MD simulations, an oligomer (as shown in Figure 6.1) in a supramolecular polymer solution was modeled as a linear coarse-grained bead-spring chain containing 8 or 20 beads linked by a harmonic potential:

$$U_{\text{bond}} = \frac{1}{2}k(b - b_0)^2$$

(6.1)

with a force constant $k=100\ \epsilon/\sigma^2$ and equilibrium bond length $b_0=\sigma$, where $b$ is the distance between two bonded beads. The oligomer contained one donor (D) and one acceptor (A) end-groups, which were capable of reversible attractive interactions. Solvent molecules were represented as single beads. Unless otherwise specified, the default pairwise interactions between non-bonded beads were represented by a shifted, truncated Lennard-Jones (LJ) potential:

$$U_{ij}^{\text{LJ}} = 4\epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{1}{4} \right] \quad (r_{ij} \leq 1.12\sigma)$$

(6.2)

where $r_{ij}$ is the distance between beads $i$ and $j$, $\epsilon$ is the potential well depth (which will be used as a unit of energy) and $\sigma$ is the value of $r_{ij}$ at which the unshifted potential is zero ($\sigma$ will be used as a unit of distance). All beads in our simulations had the same LJ mass $m=1$.

To introduce reversible association between two end-groups, we first applied a potential similar to truncated pseudo-Coulombic potential $U_{ij}^{\text{Coul}} = E_0q_iq_j/\sigma/r_{ij}$ between the donor and acceptor groups (which were assumed to carry opposite “charges”) in addition to $U_{ij}^{\text{LJ}}$:

$$U_{ij}^{\text{LJ}} + U_{ij}^{\text{Coul}} = \begin{cases} 
4\epsilon \left[ (\sigma / r_{ij})^{12} - (\sigma / r_{ij})^{6} + 1/4 \right] + E_0q_iq_j/\sigma/r_{ij} & (r_{ij} \leq 1.12\sigma) \\
E_0q_iq_j/\sigma/r_{ij} & (1.12\sigma < r_{ij} \leq 2.5\sigma) \\
0 & (r_{ij} > 2.5\sigma) 
\end{cases}$$

(6.3)
where $E_0$ is a (positive) association energy parameter and $q_i, q_j$ are the “charges” of $i$ and $j$ beads: $q_D=1$ and $q_A=-1$ for the donor and acceptor, respectively. As is seen from Figure 6.1, showing the potential for $E_0=30$ (in units of $\varepsilon$, which will be omitted below), the pairwise interaction between the donor and acceptor is attractive and tunable by adjusting $E_0$.

The pairwise interaction between the same type of end groups (i.e. donor/donor or acceptor/acceptor) is repulsive, which promotes complementary reversible donor-acceptor associations. To introduce directional specificity of reversible interactions and minimize the occurrence of associations involving multiple donor-acceptor pairs, we introduced a shifted long-range LJ interaction between a donor or an acceptor and an acceptor neighbor (AN) or a donor neighbor (DN) on an oligomer:

$$U_{ij}^{LJ'} = 4 \varepsilon \left[ (2\sigma/r_{ij})^{12} - (2\sigma/r_{ij})^6 + 1/4 \right] \quad (r_{ij} \leq 2.24\sigma) \quad (6.4)$$

In Figure 6.1, all potentials contributing to the reversible association were shown. As is seen, the cut-off distance for this potential is larger than the cutoff distance for the standard LJ potential. This longer range repulsion diminishes the occurrence of multiple donor-acceptor aggregates (e.g. for solution of 8-bead associating oligomers the fraction of multiple donor-acceptor aggregates was 3.6% for $E_0=30$ with an oligomer volume fraction $\phi=0.2$). It renders some level of orientational specificity of donor-acceptor complexation.
Figure 6.1 The combined LJ and truncated pseudo-Coulombic potential (Eq.(6.3)) for donor/acceptor (D/A) and donor/donor (D/D) or acceptor/acceptor (A/A) interactions (solid curves, $E_0=30$) and shifted, long-range LJ potential (Eq.(6.4), dashed curve). Donor (D), acceptor (A), donor neighbor (DN) and acceptor neighbor (AN) are identified in the schematic representation of reversibly bonded donor-acceptor complex in 8-bead oligomer.

Figure 6.2 shows the distribution of the angles formed by NA-A-D and A-D-ND beads. In the absence of long-range LJ repulsive interactions the angle distribution reaches a maximum around 90°, as can be expected from simple geometric considerations. With the long-range LJ interaction the angle distribution is noticeably more narrow with a maximum centered at around 150°, indicating enhancement of the orientational specificity of donor-acceptor reversible interactions.
Figure 6.2 Average distribution of angles between a donor (D)-acceptor (A) reversible bond and acceptor-acceptor neighbor (AN) chemical bond (as shown in the schematic presentation) or donor-donor neighbor (DN) chemical bond in the absence (squares) and in the presence (circles) of the long-range LJ repulsive interactions in an associating oligomer solution ($\phi = 0.2$, $k_B T=1$, $E_0=30$).

As a note of caution, for reasonably short oligomers containing a considerable fraction of donor/acceptor groups the existence of multiple long-range interactions can result in a decrease in the overall degree of association or formation of clusters of multiple donor-acceptor pairs, therefore limiting the applicability of this model for studying head-to-tail self-assembly of oligomers in concentrated solutions or melts.

6.2.2 MD simulations

In our simulations, the system is comprised of a given number of oligomers and solvent molecules placed in a cubic simulation box maintained at a constant volume and temperature under periodic boundary conditions. The supercell size for an (associating)
oligomer solution of 8-bead oligomers was \((26.7\sigma)^3\) with a total number of beads inside being 16,000. For a solution of 20-bead oligomers the box size was \((22.8\sigma)^3\) with 10,000 beads inside. Thus the bead density in all simulations was 0.84 and the selected range of parameters represents good solvent conditions for the modeled associating oligomer solutions.

Since we were interested in behavior or dilute or semi-dilute solutions of associated oligomers, we varied the volume fraction of oligomers \(\phi\) (which is equivalent to concentration in this case as the volume of a bead \(\sigma^3\) corresponds to a unit volume) between 0.01 and 0.2 for systems with 8-bead oligomers and 0.02-0.3 for systems with 20-bead oligomers. We have also varied the temperature \((k_BT=0.75, 1, 1.5)\) and association energy \((E_0=20, 25, 30)\) to explore their impact on the molecular weight of self-assembling oligomers and viscosity of the solution. For all EMD simulations the time step of integration was \(0.004(m\sigma^2/\epsilon)^{1/2}\). Units of time, \((m\sigma^2/\epsilon)^{1/2}\), will be omitted below. Initially, all oligomers were randomly dispersed in the solution LJ and bead-spring potentials (Eqs. (6.1) and (6.2)) were applied and the solution was allowed to equilibrate for up to \(t=1.6\times10^4\). After that, the truncated pseudo-Coulombic and extended LJ potentials (Eqs. (6.3) and (6.4)) for the donor, acceptor groups and their bonded neighbors were turned on and reversible self-assembly between oligomers was monitored: simulations for up to \(t=4\times10^4\) were performed to achieve equilibrium and additional simulations for another \(t=4\times10^3\) were used to collect the movement trajectories for data analysis. All simulations were performed on the High Performance Computing
cluster of Case Western Reserve University using LAMMPS, an open-source MD simulation software.\textsuperscript{26}

Besides EMD simulations, we also employed NEMD simulations to study associating oligomer solution under shear and to analyze the shear-rate-dependent viscosity $\eta$ (in units of $(m\epsilon)^{1/2}/\sigma^2$, which will be omitted below). Shear flow was introduced by deforming the simulation box in the $x$ direction with a constant shear strain rate $\dot{\gamma}$. The SLLOD thermostat was applied to maintain the temperature and volume of the system.\textsuperscript{27}

To study the shear-thinning behavior and extrapolate the zero-shear viscosity of associating oligomer solution, we varied the shear strain rate over a wide range from $\dot{\gamma}=0.0005\ (m\sigma^2/\epsilon)^{1/2}$ to $1\ (m\sigma^2/\epsilon)^{1/2}$. The units of shear rate $((m\sigma^2/\epsilon)^{1/2})$ will be omitted below. Starting from a configuration obtained from the equilibrium MD simulation, NEMD simulations were performed over $t=2\times10^4$ to achieve a steady-state shear flow, and additional simulations over $t=2\times10^4$ were conducted to collect the data. The shear-rate-dependent viscosity $\eta$ was calculated using the equation

$$\eta = -\frac{\langle P_{xy} \rangle}{\dot{\gamma}},$$

(6.5)

where $P_{xy}$ is the time-average X-Y pressure tensor component, which was obtained directly from MD simulations using LAMMPS and $\dot{\gamma}$ is the shear strain rate. The standard deviation was calculated by averaging of 10 equal time intervals of the data collection runs. Using the viscosity for different shear strain rates, the zero-shear viscosity $\eta_0$ can be obtained by extrapolation of the data to zero shear rate using various fitting or averaging strategies depending on the nature of the data, i.e. the analysis of
viscosity data for pure solvent or dilute oligomer solutions was different from that for semi-dilute solutions of associating oligomers. The specific viscosity $\eta_{sp}$ was calculated as $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$, where $\eta_s$ is the zero-shear viscosity of pure solvent.

6.2.3 Data Analysis

VMD$^{28}$ was used for visualization and data analysis of MD simulations. For the structural analysis of the solution of associating oligomers, the positions of donors and acceptors were evaluated against a cutoff distance criteria of $r_c = 1.5\sigma$, so that any donor and acceptor pair satisfying the distance criteria were considered to form a reversible bond. In the relatively rare case of multiple donor and acceptor groups inside the cutoff distance, a D-A pair with the shortest separation distance was chosen or a history of the association was taken into account: if a reversible association existed during the previous time step it was given a preference compared to other possible reversible bonds satisfying the same separation distance criterion. The degree of association, $p$, i.e. the ratio of the number of reversible bonds to the maximum possible (which is equal to the number of donors or acceptors) was calculated as well as the number-average ($M_n$) and weight-average ($M_w$) molecular weight (in unit of oligomer weight):

$$M_n = \frac{\sum_i n_i N_i}{\sum_i n_i}, \quad M_w = \frac{\sum_i n_i N_i^2}{\sum_i n_i N_i}$$  \hspace{1cm} (6.6)

where $n_i$ is the number of chains or rings containing $N_i$ oligomers.

6.3 Results and Discussions$^1$

In this section, we first discuss the equilibrium properties of the supramolecular polymer solution in our EMD simulations, including the ring/chain equilibration and molecular
weight distribution. Studies on the associating structure help us to understand the macroscopic properties of the solution such as the solution viscosity, which is the main topic discussed thereafter.

6.3.1. Equilibrium Properties

6.3.1.1 Ring-Chain Equilibrium

Solutions of head-to-tail associating oligomers are inherently polydisperse as a result of reversible self-assembly into rings and chains. As shown in Figure 6.3, at low volume fraction of 8-bead oligomers reversible association between donor and acceptor groups leads predominantly to formation of rings since intramolecular reversible bonding is favorable when oligomers are far apart from each other. Depending on the association energy ($E_0$) the fraction of rings, defined as the ratio of the number of intramolecular reversible bonds to the total number of reversible bonds, can approach values close to 1. As the oligomer volume fraction increases the fraction of rings quickly decreases as the solution undergoes a change from a ring-dominated to chain-dominated regime. At higher oligomer volume fractions ($\phi=0.2$) ring fraction decreases to about 0.25 (for $E_0=30$) with the corresponding chain fraction reaching 0.75 indicating that at this oligomer volume fraction intermolecular bonding is dominant and the solution consists of mainly linear chains with only a few rings present. These observations agree well with results of Monte Carlo simulations for head-to-tail associated polymer solutions.$^5-7, 29$
Figure 6.3 Fraction of reversible bonds in rings (open symbols) and chains (solid symbols) for solutions of 8-bead oligomers as a function of oligomer volume fraction for different association energies $E_0=20$ (squares), $E_0=25$ (circles) and $E_0=30$ (triangles) at $k_BT=1.0$.

With an increase in the association energy the fraction of rings at low $\phi$ increases, which results in a corresponding decrease in the chain fraction and shifts the upper boundary of ring-dominated regime to a higher oligomer volume fraction in qualitative agreement with previous MC simulation results.\(^7\) We note that the increase in the association energy $E_0$ results in the overall increase of association, as expected. Thus the percentage of reversible bonds formed compared to the maximum possible (defined by the number of donor or acceptor groups) increases from about 74% to 95% when $E_0$ increases from 20 to 30, as is seen from Table 6.1. The fraction of reversible bonds in rings is also larger for larger association energies (see Figure 6.3 and Table 6.1).
Table 6.1  Equilibrium properties of head-to-tail associating polymers at different temperatures \((T)\) and association energies \((E_0)\) for oligomer volume fraction \(\phi=0.2\): number-average \((M_n)\) and weight-average \((M_w)\) molecular weight (in units of oligomer weight), polydispersity index \((PI=M_w/M_n)\), degree of association \((p)\), fraction of reversible bonds in rings \((f_{ring})\) and zero-shear viscosity \((\eta_0)\).

<table>
<thead>
<tr>
<th>(k_BT)</th>
<th>(E_0)</th>
<th>(M_n)</th>
<th>(M_w)</th>
<th>(PI)</th>
<th>(p)</th>
<th>(f_{ring})</th>
<th>(\eta_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>25</td>
<td>7.1</td>
<td>31.4</td>
<td>4.42</td>
<td>96%</td>
<td>0.21</td>
<td>6.51±0.16</td>
</tr>
<tr>
<td>1.0</td>
<td>20</td>
<td>3.0</td>
<td>5.6</td>
<td>1.87</td>
<td>74%</td>
<td>0.14</td>
<td>4.12±0.14</td>
</tr>
<tr>
<td>1.0</td>
<td>25</td>
<td>4.7</td>
<td>12.3</td>
<td>2.61</td>
<td>88%</td>
<td>0.17</td>
<td>5.08±0.02</td>
</tr>
<tr>
<td>1.0</td>
<td>30</td>
<td>6.4</td>
<td>29.7</td>
<td>4.64</td>
<td>95%</td>
<td>0.21</td>
<td>5.84±0.21</td>
</tr>
<tr>
<td>1.5</td>
<td>25</td>
<td>2.4</td>
<td>4.0</td>
<td>1.67</td>
<td>65%</td>
<td>0.13</td>
<td>3.52±0.05</td>
</tr>
</tbody>
</table>

The degree of association and ring-chain equilibrium also depends on temperature. Higher temperature favors higher entropy states leading to a lower overall degree of association (65% for \(k_BT=1.5\) compared to 96% for \(k_BT=0.75\) for \(\phi=0.2\)) and a smaller fraction of intramolecular bonds \((f_{ring} =0.13\) for \(k_BT=1.5\) compared to \(f_{ring} = 0.21\) for \(k_BT=0.75\) for \(\phi=0.2\)) as is seen from Table 6.1 and Figure 6.3. A lower fraction of reversible bonds in rings at higher temperature results also in the decrease of the lower boundary of chain-dominated regime (Figure 6.3), as has been previously predicted.\(^7\)
Figure 6.4 Fraction of reversible bonds in rings (open symbols) and chains (solid symbols) for solutions of 8-bead oligomers as a function of oligomer volume fraction at different temperatures, $k_B T=1$ (squares) and $k_B T=1.5$ (triangles), for association energy $E_0=25$.

The fractions of reversible associations in rings and chains are shown in Figure 6.5 as functions of oligomer number density for solutions of 20-bead and 8-bead head-to-tail associating oligomers. An increase in oligomer length increases the conformational entropic penalty for ring closure leading to a smaller fraction of rings and a correspondingly larger fraction of chains (at the same oligomer number density) compared to 8-bead oligomers. Consequently the lower boundary of chain-dominating region noticeably decreases (nearly by half in units of oligomer number density) compared to shorter associating oligomers.
Figure 6.5 The fractions of reversible associations in rings (open symbols) and chains (filled symbols) vs. oligomer number density in solutions of 8-bead (squares) and 20-bead associating oligomers (triangles) for $k_B T=1$, $E_0=30$. The horizontal dashed line indicates equal fraction of chains and rings and the vertical dashed lines mark the corresponding oligomer number density defined as the ring/chain transition point.

### 6.3.1.2 Molecular Weight

To characterize the molecular weight distribution of self-assembled rings and chains, we considered the average number density of rings and chains of different molecular weights (in units of oligomer weight), which are shown in Figure 6.6. As is seen, linear chains have a wide distribution, while the distribution of rings is relatively narrow. The distribution of rings can be fitted with the power-law decay function $M^{-2.5}$ in agreement with predictions by mean field theory\cite{11,12} and MC simulation,\cite{14} for a semi-dilute living polymer solution. The molecular weight distribution of linear chains is found to follow exponential dependence (Figure 6.6), as expected.\cite{6,11,12,30,31} and can be fitted with...
$6.2 \times 10^{-5} \exp(-M/17.5)$, where 17.5 corresponds to the average molecular weight of linear chains (in units of oligomer weight). Oligomer volume fraction, the association energy and temperature all influence of molecular weight distribution. The number- ($M_n$) and weight-average ($M_w$) molecular weight, calculated using Eq.(6.5) as well as the polydispersity index ($PI$) are shown in Table 6.1 for different association energies and temperatures. As is seen, an increase in $E_0$ or decrease in $k_BT$ results in an increase in the average molecular weight and polydispersity.

Figure 6.6 Number density distribution of rings (squares) and chains (circles) in the associating solution of 8-bead oligomers ($\phi=0.2, E_0=30, k_BT=1.0$). The molecular weight is shown in units of oligomer weight.

The weight-average molecular weight ($M_w$) for the associating oligomer solutions with different association energies is shown in Figure 6.7 as a function of oligomer volume fraction. As is seen, with an increase in oligomer volume fraction $M_w$ for both 8-bead and 20-bead associating oligomer solutions noticeably increases, especially for high association energy, following the transformation from the ring-dominated to chain-
dominated regimes. In the chain-dominated regime further increase of molecular weight with an increase in oligomer volume fraction $\phi$ is associated with an increase of chain length and according to the mean field theory, $M_w$ of living polymers in a theta solution scales as $M_w \sim \phi^{0.5}$ in both semi-dilute and concentrated regimes\textsuperscript{11,12}. In our simulations, which correspond to a good solvent condition, we obtained by fitting data in chain-dominated regime (solid symbols in Figure 6.7), $M_w \sim \phi^x$, with $x \approx 0.6$, in agreement with the results of MC ($x = 0.6$)\textsuperscript{29,31} and MD simulations ($x$ in the range 0.5–0.8)\textsuperscript{13} for semi-dilute living polymer solutions.

![Figure 6.7](image)

Figure 6.7 Weight-average molecular weight of associating solution of 8-bead oligomers for $E_0=20$ (circles), $E_0=25$ (triangles) and $E_0=30$ (squares) as a function of oligomer volume fraction. Weight-average molecular weight of associating solution of 20-bead oligomers for $E_0=30$ is shown in the inset. Solid symbols correspond to the chain-dominated regime and open symbols describe the ring-dominated regime.
Thus, the obtained results for ring-chain equilibrium, the molecular weight distribution and its dependence on oligomer volume fraction all agree well with previous predictions of mean field theory and MC simulations, indicating that our model successfully reproduces the equilibrium behavior of head-to-tail reversibly associating polymers.

6.3.2 Rheological Properties

6.3.2.1 Shear-thinning Behavior

It is well-known that solutions of associating polymers, such as wormlike micelles, telechelic or supramolecular polymers experience shear-thinning under flow.\(^{3, 4, 9, 32-37}\) The structural origin of shear-thinning behavior of associating polymer solution can be attributed to dissociation of the reversible bonds, in addition to the chain stretching and orientation that also occurs in conventional chemically bonded polymer solutions. To analyze the shear-thinning behavior of head-to-tail associating polymer solution, we performed NEMD simulations and calculated (using Eq.(6.6)) the shear-rate-dependent viscosity over a wide range of shear strain rates.

In Figure 6.8, the viscosity of associating solution of 8-bead oligomers is shown as a function of shear strain rate for different association energies \(E_0\) and temperatures \(k_B T\). At small shear strain rates, as the shear strain rate increases, the viscosity decreases slowly indicating that the associated polymer structure is not significantly affected by the external shear force. Because the degree of association increases with an increase in the association energy or with the decrease of temperature (as is shown in Table 6.1) the viscosity of the corresponding solutions is higher at low shear rates (Figure 6.8). As the
shear strain rate increases the apparent shear-thinning starts first for the solution with a higher degree of association (i.e. with larger \( E_0 \) or lower temperature \( k_B T \)) as longer associated chains start to orient along the flow. In all cases the viscosity decreases rather sharply following the dissociation of supramolecular structure, as discussed below. At very high shear strain rates the solution viscosities of associating oligomers with different temperatures or association energies become nearly the same (Figure 6.8) and approach the solution viscosity for non-associating oligomers at about shear strain rate 1.0, where the degree of association becomes rather small and the number-average molecular weight approaches that of a single oligomer. Qualitatively similar rheological behavior has been observed experimentally for supramolecular polymers and wormlike micelles at different temperatures.\(^3, 34, 36\)
Figure 6.8 Solution viscosity of head-to-tail associating 8-bead oligomers for different a) association energies $E_0$ and b) temperatures as a function of shear-strain-rate for $\phi=0.2$. Shear-strain-rate dependent viscosity for non-associating oligomer solution (open symbols) and pure solvent are shown for comparison.

Solution viscosity of head-to-tail associating oligomers at different oligomer volume fractions show rather similar shear-thinning behavior, as shown in Figure 6.9. The higher the oligomer volume fraction, the higher is the initial zero-shear rate viscosity. As the shear strain rate increases the viscosity starts to decrease for solutions with high oligomer volume fractions, finally reaching a similar level for all $\phi$ at very high shear strain rates.
Similar observations have been made for wormlike micelles experimentally and in MD simulations.\textsuperscript{14, 35}

![Graph showing viscosity of solution of 8-bead associating oligomers as a function of shear strain rate for different oligomer volume fractions at $k_B T=1.0$, $E_0=25$.]

**Figure 6.9** Viscosity of solution of 8-bead associating oligomers as a function of shear strain rate for different oligomer volume fractions at $k_B T=1.0$, $E_0=25$.

As we consider in this thesis dilute and semi-dilute solutions of associating oligomers, the solvent contribution $\eta_s$ to the overall solution viscosity $\eta$ is significant, as is seen from Figure 6.8, so it is appropriate to subtract the solvent viscosity in order to analyze the polymer contribution to solution viscosity, similar to what is done for conventional chemically bonded polymer solutions.\textsuperscript{38, 39} Figure 6.10a shows the normalized reduced viscosity $(\eta-\eta_s)/(\eta_0-\eta_s)$ (where $\eta_0$ is viscosity at zero shear rate) for 20-bead and 8 bead associated oligomer solutions (inset) as a function of the reduced shear rate $\beta = \dot{\gamma}(\eta_0-\eta_s)/k_B T \rho_p$ (where $\rho_p$ is the polymer number density).\textsuperscript{38,39} As is seen, the viscosity data obtained for different oligomer volume fractions of 20-bead associating oligomers fall into one single curve in a double logarithmic scale of the Figure. Similarly, the results for
8-bead associating oligomer solutions ($\phi=0.2$) obtained at different temperatures or different association energies presented in Figure 6.8 also collapse into one single curve shown in the inset of Figure 6.10a. In both cases the normalized reduced viscosity exhibits a plateau at low shear rates followed by the noticeable decrease with a slope around -0.55 with an increase in $\beta$. We note that this slope is rather similar to what has been previously reported (-0.5) for conventional chemically bonded polymer solutions under shear.$^{39, 40}$ At even higher shear rates the decrease of the normalized reduced viscosity becomes even stronger with slope -0.9 and -0.8 for 20-bead and 8-bead associating oligomer solutions, respectively (Figure 6.10.a). We note that a similar value (-0.8) has been previously observed for solutions of supramolecular polymers,$^3$ as well as for wormlike micelle solutions (-0.94,-1.0,-0.9)$^{33-35}$ and telechelic polymer solutions (-1.0).$^{37}$
Figure 6.10 (a) Normalized reduced viscosity of 20-bead head-to-tail associated oligomer solution at different oligomer volume fractions ($\phi=0.07$ squares; $\phi=0.1$ circles; $\phi=0.2$ upper triangle; $\phi=0.3$ down triangle), (b) the average molecular weight of chains $<M_{\text{chain}}>$ (in units of oligomer weight) and the number of free oligomers $<N_{\text{free}}>$ for $\phi=0.2$, $E_0=30$ as functions of reduced shear rate for $k_B T=1$. The inset in (a) shows the normalized reduced viscosity of 8-bead associating oligomer solution for different association energies and temperatures (symbols are the same as in Figure 8) for $\phi=0.2$, $E_0=30$ as a function of reduced shear rate.
To correlate the observed shear-thinning behavior with the structural evolution of head-to-tail associating oligomer solutions, we analyze the change in the average molecular weight of chains and number of free oligomers with an increase of reduced shear rate $\beta$, as shown in Figure 6.10.b, for 20-bead associating oligomer solution with oligomer volume fraction $\phi=0.2$. As is seen, at low shear rates when the normalized viscosity exhibits a plateau (Figure 6.10.a), the average molecular weight of chains (in units of oligomer weight) remains practically unaffected by flow, whereas the number of free oligomers slightly decreases as chain orientation by flow promotes some association. With an increase of $\beta$, the average molecular weight of chains starts to decline. At the same time the number of free oligomers remains practically the same, implying reorganization of self-assembled chain (or rings) rather than their dissociation into oligomers.

This can also be seen from the molecular weight distribution change at different shear rate, as shown in Figure 6.11. The molecular weight distribution of associated linear chains becomes noticeably more narrow with an increase in the shear rate. The population of longer chains considerably decreases giving rise to shorter associating rings as well, as shown in Figure 6.12.
Figure 6.11 Weighted chain length distribution in 8-bead head-to-tail associating oligomer solution ($\phi=0.2$, $E_0=30$) obtained at different shear strain rates and in the absence of shear. The inset shows the chain length probability distribution plotted in log-linear scale. The molecular weight is shown in units of oligomer weight.

Figure 6.12 Number density distribution of rings in the associating solution of 8-bead oligomers under different shear strain rates for $\phi=0.2$, $k_B T=1.0$, $E_0=30$. 
The overall chain distribution still follows an exponential dependence, but decays more rapidly with increased \( \dot{\gamma} \) (Figure 6.11, inset). Similar observations have been previously made in MD simulations of wormlike micelles.\(^{14-17}\) Thus in the intermediate range of reduced shear rates associating chains become oriented (similar to wormlike micelles\(^{17,33,35}\)) and the longest chains (which are most oriented and stretched) start to break into smaller associated chains. The decrease of viscosity at this stage is mainly due to the chain orientation and chain length redistribution from longer to shorter chains.

At larger reduced shear strain rates the average chain length continues to decline, while the number of free oligomers starts to increase, signifying the beginning of a different stage of shear-thinning, as is seen in Figure 6.10b. Now even short chains become strongly stretched and start to dissociate into free oligomers. A sharp increase in the fraction of free oligomers indicates that this process is very active and involves dissociation of shorter and shorter chains as \( \beta \) increases. As a result it comes as no surprise that at the high shear rates the normalized reduced viscosity \( (\eta-\eta_s)/(\eta_0-\eta_s) \) decreases at larger rate with an increase \( \beta \) (slope \(-0.9\) or \(-0.8\)) compared to that at the intermediate shear rates (slope \(-0.55\)), as is seen in Figure 6.10a.

### 6.3.2.2 Equilibrium Viscosity

The equilibrium viscosity of head-to-tail associated polymer solution, \( \eta_0 \), has been obtained by extrapolating the shear-rate-dependent viscosity data obtained in NEMD simulations to zero-shear rate. We have used different strategies of extrapolation. For pure solvent and dilute polymer solutions (with polymer volume fraction below or equal
to 0.05) with different association energies at different temperatures the shear-rate-dependent solution viscosity was fitted using scaling dependence $\eta \sim \gamma^{0.5}$ and $\eta_0$ was calculated by extrapolation to zero shear strain rate. In Figure 6.13 and Table 6.2, we show the fitting curves and determined equilibrium solvent viscosity.

![Figure 6.13 Viscosity of pure solvent at different temperatures fitted as a function of $\gamma^{0.5}$.](image)

Table 6.2 Equilibrium viscosity of pure solvent at different temperatures determined from the data shown in Figure 6.13.

<table>
<thead>
<tr>
<th>$k_B T$</th>
<th>0.75</th>
<th>1.0</th>
<th>1.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$</td>
<td>2.42 ±0.01</td>
<td>2.31±0.01</td>
<td>2.22±0.001</td>
</tr>
</tbody>
</table>

For solutions with oligomer volume fraction exceeding 0.05 the solution viscosity exhibits a plateau at low shear rates, as is seen in Figure 6.8. The higher the oligomer volume fraction, the higher is the initial zero-shear rate viscosity. The equilibrium
solution viscosity was calculated by averaging several data points in the plateau region.

The results corresponding to Figure 6.8 are presented in Table 6.3.

Table 6.3 Equilibrium viscosity of a solution of 8-bead associating oligomers at different oligomer volume fractions $\phi$ for $k_B T = 1.0$, $E_0 = 25$, determined from the data shown in Figure 6.8.

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>0.075</th>
<th>0.1</th>
<th>0.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\eta_0$</td>
<td>2.97±0.04</td>
<td>3.30±0.03</td>
<td>5.06±0.02</td>
</tr>
</tbody>
</table>

With the equilibrium viscosity, the polymer contribution to solution viscosity can be assessed by calculating the specific viscosity $\eta_{sp} = (\eta_0 - \eta_s)/\eta_s$ or intrinsic viscosity $[\eta]$. For a given concentration, $[\eta]$ can be replaced by the ratio $\eta_{sp}/\phi$.

Figure 6.14 shows the ratio $\eta_{sp}/\phi$ as a function of weight-average molecular weight $M_w$ (in units of oligomer weight) for the solutions of 8-bead and 20-bead head-to-tail associated oligomers for the chain-dominated regime. As is seen, all data points for a given association energy follow the scaling dependence $\eta_{sp}/\phi \sim M_w^\alpha$ with the exponent $\alpha \approx 0.8$, as expected for dilute polymer solutions in a good solvent ($[\eta] \sim M_w^{0.8}$). A similar scaling dependence has been reported for relatively dilute solutions of wormlike micelles ($\alpha=0.8, 1$) and rigid DNA-based supramolecular polymers ($\alpha=1.2$).
Figure 6.14 $\eta_{sp}/\phi$ in the chain-dominated regime for 8-bead head-to-tail associating oligomer solutions with different association energies ($E_0=20$ circles, $E_0=25$ triangles and $E_0=30$ diamonds) and 20-bead associating oligomer solution for $E_0=30$ (squares) as a function of the weight average molecular weight (in units of oligomer weight).

The equilibrium viscosity of associating oligomer solution is also strongly influenced by oligomer volume fraction, $\phi$. For a non-associated oligomer solution the viscosity increases in a linear manner with oligomer volume fraction in the studied composition range, as shown in Figure 6.15 for the equilibrium specific viscosity of solution of non-associating oligomers as a function of oligomer volume fraction, $\phi$. 

165
Figure 6.15 Specific viscosity $\eta_{SP}$ of 8-bead (squares) and 20-bead (triangles) oligomer solutions as a function of oligomer volume fraction for $k_B T=1.0$, $E_0=0$. Error bars are of the symbol size.

In a very dilute solution of head-to-tail associating oligomers, where isolated small rings are dominant, the increase of viscosity is also linearly proportional to oligomer volume fraction. As $\phi$ increases, more and more rings transform into linear chains, which start to feel each other’s presence, leading to a more rapid increase in viscosity. Indeed, as is seen from Figure 6.16, the specific viscosity for 8-bead and 20-bead associating oligomer solutions increases following a $\eta_{SP} \sim \phi^{1.5}$ scaling dependence in the chain-dominated regime. A similar scaling dependence has been observed experimentally in several dilute or semidilute solutions of supramolecular polymers.$^{19,20,24,25}$ For a hydrogen bonded supramolecular polymer solution, Shikata et al.$^{25}$ reported a 1.5 exponent for the apparent viscosity in the concentration range 1–100g/l. For a series of metallo-supramolecular
polymers Rowan and co-workers\textsuperscript{20} found the exponent for specific viscosity being between 1.37 and 1.65 for the concentration range between 0.001 and 0.06 g/ml and Lahn \textit{et al.}\textsuperscript{24} reported the exponent between 1.6 and 2.0 for copper(I) and silver(I)-based coordination polymers at low monomer concentrations (0.0025-0.01 mg/l). Craig and coworkers\textsuperscript{19} found a 1.8 exponent for the specific viscosity of dilute solutions of DNA-based supramolecular polymers.

![Graph showing specific viscosity vs. oligomer volume fraction](image)

Figure 6.16 Specific viscosity, ($\eta_{sp}$), for 8-bead head-to-tail associating oligomer solutions with different association energies ($E_0=20$ circles, $E_0=25$ triangles and $E_0=30$ diamonds) and 20-bead associating oligomer solution for $E_0=30$ (squares) in the chain-dominated regime as a function of oligomer volume fraction.

The scaling dependence obtained in our simulations (Figure 6.16) and reported in experimental studies on supramolecular polymers in dilute and semidilute solutions\textsuperscript{19,20,24,25} is noticeably smaller than the prediction of Cates’ model, $\eta \sim \phi^{3.2-3.5}$, for solutions of worm-like micelles\textsuperscript{12}, which is often used for interpretation of experimental
data for supramolecular polymer solutions. The dilute and semi-dilute solutions of supramolecular polymers are very polydisperse, but may not be sufficiently entangled to follow predominantly reptation dynamics. Additionally, other relaxation mechanisms may exist such as bond-interchange or end-group-interchange,\textsuperscript{12, 25, 42} which can alter the relaxation pathway thereby yielding a lower exponent value. In general for unentangled polydisperse polymer solution in a good solvent the specific viscosity satisfies the following relation\textsuperscript{21, 22}:

\[ \eta_{sp} \sim \phi M_w^{0.8} \]  

(6.7)

similar to what is seen in Figure 6.16. Taking into account that weight-average molecular weight \( M_w \) of supramolecular polymers changes with oligomer volume fraction as \( M_w \sim \phi^{0.6} \) as shown in Figure 6.7 or \( M_w \sim \phi^{0.5} \) as expected for living polymers\textsuperscript{11}, we arrive at

\[ \eta_{sp} \sim \phi^{1.4-1.5} \quad \text{(for } M_w \sim \phi^{0.5-0.6}) \]  

(6.8)

which agrees well with our current results shown in Figure 6.16 and experimental observations for dilute and semi-dilute solutions of supramolecular polymers.\textsuperscript{19, 20, 24, 25} At higher oligomer concentration the reptation mechanism is expected to become active for some components of the polydisperse solution (long chains) leading to an increase of the exponent. At even higher concentration the reptation mechanism will dominate leading to a \( \eta \sim \phi^{3.2-3.5} \) Cates scaling dependence, as observed for hydrogen-bonded supramolecular polymers.\textsuperscript{3}
6.4 Conclusions

To summarize, in this chapter, we have studied the dynamic and rheological properties of dilute and semi-dilute supramolecular polymer solutions using equilibrium and non-equilibrium molecular dynamics simulations. In our model spontaneous complementary reversible association between donor and acceptor groups at the ends of oligomers was achieved by introducing a combination of a truncated pseudo-Coulombic attractive potential acting between the donor and acceptor groups and a LJ repulsive potential between donor, acceptor and neighboring (along the chain) groups.

This model was tested by analyzing the equilibrium properties of head-to-tail associating polymers in our Equilibrium MD simulations. We considered ring-chain equilibrium and found that the lower the temperature, the higher the association energy, and the shorter the spacer length, the higher is the oligomer volume fraction where the chain and ring fraction become equal to each other. These observations agree well with previous results of computer simulations of supramolecular polymers\textsuperscript{5} and wormlike micelles\textsuperscript{14, 29}. We also analyzed the molecular weight distributions for chains and rings, which were found to follow an exponential decay and a power-law distribution, respectively. In the chain-dominated regime, the average molecular weight was found to scale with the oligomer volume fraction as $M_w \sim \phi^{0.6}$ for different associating energies and oligomer lengths in agreement with computer simulation results for living polymers. These results indicate that our model successfully reproduces the equilibrium behavior of head-to-tail associating polymers.
NEMD simulations were performed to study the shear-thinning behavior of dilute and semi-dilute solutions of reversibly associated polymers. At low shear rate the solution viscosity exhibits a plateau, which is influenced by the temperature, association energy and oligomer volume fraction. The normalized reduced viscosity data $(\eta-\eta_s)/(\eta_0-\eta_s)$ for a given oligomer length collapses into one master curve when plotted against the reduced shear rate $\beta = \dot{\gamma}(\eta_0-\eta_s)/k_BT_p$. The normalized reduced viscosity exhibits two regions of shear-thinning behavior: $(\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.55}$ for the intermediate range of reduced shear rate and $(\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.9}$ for 20-bead oligomers (or $(\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{0.8}$ for 8-bead oligomers) for higher $\beta$. Further investigation of the evolution of supramolecular polymers under shear flow revealed that the first region of shear-thinning is primarily accompanied by the orientation and redistribution of associating structure from larger to smaller ones with the number of free oligomers remaining unchanged. The following stage of shear-thinning involves the dissociation of associating structure with formation of free oligomers, which accelerates the viscosity decrease: $(\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.9}$. We note that a similar slope (-0.8) has been previously observed for solutions of supramolecular polymers\textsuperscript{3}, as well as for wormlike micelle solutions (-0.94,-1.0,-0.9)\textsuperscript{33-35}.

The equilibrium viscosity of supramolecular solutions was obtained by extrapolation of the shear-rate-dependent viscosity data to zero shear rate and its dependence on the molecular-weight of supramolecular polymers and oligomer volume fraction was analyzed. The reduced specific viscosity $\eta_{sp}/\phi$, which is equivalent to the intrinsic viscosity $[\eta]$ for a given oligomer volume fraction, was found to follow a $\eta_{sp}/\phi \sim M_w^{0.8}$ scaling dependence, as expected for relatively dilute polymer solutions in a good solvent.
([η] \sim M_w^{0.8}). A similar scaling dependence has been reported for solutions of wormlike micelles (\alpha=0.8, 1) and DNA-based supramolecular polymers (\alpha=1.2). The oligomer volume fraction dependence of the specific viscosity was found to obey \eta_{sp} \sim \phi^{1.5} for the chain-dominated regime, which is lower than the predictions of the Cates model for semi-dilute solutions of wormlike micelles (\eta_{sp} \sim \phi^{3.5}), but in agreement with experimental observations for several dilute or semi-dilute solutions of supramolecular polymers\textsuperscript{19,20,24,25}. This scaling dependence can be explained considering the relation of viscosity to molecular weight of a polydisperse solution \eta_{sp} \sim \phi M_w^{0.8} and accounting for the increase of molecular weight of supramolecular polymers with oligomer volume fraction \bar{M}_w \sim \phi^{0.6}. This implies that dilute and semi-dilute solutions of supramolecular polymers exhibit high polydispersity, but may not be sufficiently entangled to follow the reptation mechanism of relaxation considered in Cates’ model\textsuperscript{12}.
6.5 Bibliography


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Chapter 7
Summary and Outlook

7.1 Summary

In this work, we have represented an extensive study of the self-assembly dynamics of two polymeric systems: block copolymer micelles and supramolecular polymers.

Using DPD simulation technique we studied systematically the static and dynamic properties of dilute block copolymer micelle solution, including the equilibrium properties, and the kinetics of micellization and equilibrium chain exchange in chapter 3,4,5. In our simulations, the diblock copolymer micelle solutions were composed of linear bead-spring $A_2B_3$ and $A_xB_x$ ($x=4,6,8$) chains immersed in an explicit solvent environment. The hydrophobic interaction between the hydrophobic blocks and the hydrophilic blocks (as well as the solvent) was introduced by a repulsive parameter which is larger than the repulsion between identical blocks.

The equilibrium properties of block copolymer micelles, (Chapter 3) including critical micelle concentration, micelle aggregation number distribution and micelle structure were found to agree well with previous experimental and theoretical studies. We found that the CMC exceeds the unimer concentration at equilibrium due to the contribution of small aggregates (dimers, trimers, etc.). In all cases the aggregation number distribution
was rather smooth and exhibited one minimum and one maximum, indicating equilibrium
between unimers (and small aggregates) and larger micelles. We found, as is expected,
that increasing the polymer concentration does not change the average aggregation
number, while increasing the hydrophobic interaction energy causes the unimer
concentration to decrease and the average aggregation number to increase. Increasing the
hydrophilic chain length causes the unimer volume fraction at equilibrium to increase and
average aggregation number to decrease. For micelles with same core block length and
aggregation number, while different corona block length, the density profiles for the core
monomers are practically the same. The main difference seen in the density profiles is
that as the hydrophilic block length increases, the monomer density in the corona extends
to a larger distance. The density profiles of $A_2B_3$ micelles of the same aggregation
number with different interaction energies $a_{AB}$ do not show obvious difference.

The kinetics of block copolymer micellization (Chapter 4) was analyzed by monitoring
the time-evolution of the average aggregation number and fraction of aggregates of
different sizes. We find that micellization can be characterized as a three-stage process.
At the earliest stage the unimer concentration decreases sharply to a constant value due to
the rapid coupling of unimers into small aggregates. During the second stage, micelles
grow mainly by fusion of sub-micelles with intermediate aggregation numbers, in
agreement with an earlier analytical model by Dormidontova. Analysis of the frequency
of different events indicates that the processes involving small aggregates (dimers,
trimers, etc.) play an important role in the micelle growth process as the fraction of
chains exchanged by this mechanism is comparable to the fraction of unimers exchanged
between micelles, in agreement with recent experimental data for pyrene end-labeled diblock copolymers studied via a combination of stopped-flow light scattering and fluorescence techniques.\textsuperscript{2} During the third stage the weight average aggregation number continues to increase very slowly due to the adjustment of the aggregation number distribution. The weight-average aggregation number distribution, which still exhibits a bimodal shape in the earlier times of the final stage of micellization, gradually becomes unimodal with the peak position corresponding to the final equilibrium aggregation number. Statistical analysis of different events occurring during stage three shows that exchange of unimers and small aggregates with micelles becomes more dominant and the probability of micelle fission/fusion declines, although the contribution of micelle fusion to the overall chain redistribution remains significant as these multi-oligomer events are rather effective.

We found that increasing the polymer concentration speeds up not only the initial stage of unimer coupling, but also the whole micellization process due to an increase of the probability of micelle fusion/fission events. An increase in the hydrophobic interaction energy $\alpha_{AB}$ dramatically slows down the micellization process: while micelle growth at early times follows nearly the same pathway independent of the interaction energy, more events are required to achieve the larger final equilibrium aggregation number. With an increase in the interaction energy, we found that the overall process proceeds via the same stages, but the time windows for the different stages noticeably expand with an increase of oligomer length; micelle fusion/fission becomes somewhat less frequent during the second stage of micellization, although the fraction of chains exchanged via
micelle fusion increases. With an increase in the hydrophilic block length, the overall micellization process becomes slower. Statistical analysis of the micelle evolution reveals that the frequency and contribution of unimer exchange increases and probability of micelle fusion/fission decreases with increased chain length.

The kinetics of equilibrium chain-exchange between block copolymer micelles (Chapter 5) were studied by in silica micelle hybridization experiments inspired by previously reported experimental studies. The corresponding relaxation times for contrast function, unimer formation and native chain correlation functions were found to follow an exponential dependence on the interaction energy $\chi_{AB}$ and core block length $N_A$: $\tau \sim \exp(0.67\chi_{AB}N_A)$, despite the fact that there is more than one kinetic mechanism that contributes to chain exchange. The decrease in chain exchange rate with an increase in core block length and incompatibility between blocks (or between the core block and solvent) is a result of a higher potential barrier for chain (or small aggregate) expulsion.$^{1,3}$

We found that chain exchange process is independent of polymer concentration and is dominated by unimer (small aggregate) expulsion. Unimer insertion, which occurs more rapidly for micelle solutions with higher oligomer concentration occurs at a noticeably shorter time scales than chain expulsion and hence does not significantly influence the chain exchange kinetics. At the same time, the correlation function for unimer formation (from chains being originally part of micelles) shows a strong concentration dependence – unimers form more slowly in the micelle solutions with higher oligomer concentration, where the contribution of micelle fusion/fission is higher. Since the characteristic time for
native chain expulsion from micelles $F(t)$ does not exhibit concentration dependence, it is the transport of chains between micelles via fusion/fission mechanism, which slows down unimer formation, that is responsible for the concentration dependence of $E(t)$.

We also found that chain exchange and native chain expulsion both occur more rapidly for diblock copolymers with longer corona blocks, in contrast to theoretical predictions made in the limit of long chain length\textsuperscript{1,3} that chain exchange kinetics slow down with corona block length due to the decrease in the chain diffusion through the corona for longer corona lengths. Having a higher cmc and lower cmt for micelles formed by diblock copolymers with longer corona-block length, indicates that there is a higher penalty for chain transfer from the bulk to a micelle and therefore a lower potential barrier for a chain escape from the micelle\textsuperscript{4,5}, which translates into more rapid chain exchange kinetics.

In chapter 6, we have studied the dynamic and rheological properties of dilute and semi-dilute supramolecular polymer solutions using equilibrium and non-equilibrium molecular dynamics simulations. In our model spontaneous complementary reversible association between donor and acceptor groups at the ends of oligomers was achieved by introducing a combination of a truncated pseudo-Coulombic attractive potential acting between the donor and acceptor groups and a LJ repulsive potential between donor, acceptor and neighboring (along the chain) groups. The equilibrium properties of head-to-tail associating polymers, including ring-chain transition, molecular weight were found to agree well with previous results of computer simulations of supramolecular polymers\textsuperscript{6}.
and wormlike micelles\textsuperscript{7,8}, indicating that our model successfully reproduces the equilibrium behavior of head-to-tail associating polymers.

The shear-thinning behavior of supramolecular polymer solutions were found to exhibit two regions of shear-thinning behavior: \((\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.55}\) for the intermediate range of reduced shear rate and \((\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.9}\) for 20-bead oligomers (or \((\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{0.8}\) for 8-bead oligomers) for higher \(\beta\) in a unified master curve for oligomer of the same length. Further investigation of the evolution of supramolecular polymers under shear flow revealed that the first region of shear-thinning is primarily accompanied by the orientation and redistribution of associating structure from larger to smaller ones with the number of free oligomers remaining unchanged. The following stage of shear-thinning involves the dissociation of associating structure with formation of free oligomers, which accelerates the viscosity decrease: \((\eta-\eta_s)/(\eta_0-\eta_s) \sim \beta^{-0.9}\).

The equilibrium viscosity viscosity was found to follow a \(\eta_{sp}/\phi \sim M_w^{0.8}\) scaling dependence, as expected for relatively dilute polymer solutions in a good solvent (\(\eta \sim M_w^{0.8}\)). The oligomer volume fraction dependence of the specific viscosity was found to obey \(\eta_{sp} \sim \phi^{1.5}\) for the chain-dominated regime, which is lower than the predictions of the Cates model for semi-dilute solutions of wormlike micelles (\(\eta_{sp} \sim \phi^{3.5}\)), but in agreement with experimental observations for several dilute or semi-dilute solutions of supramolecular polymers\textsuperscript{9-12}. This scaling dependence can be explained considering the relation of viscosity to molecular weight of a polydisperse solution \(\eta_{sp} \sim \phi M_w^{0.8}\) and accounting for the increase of molecular weight of supramolecular polymers with

180
oligomer volume fraction $M_w \sim \phi^{0.6}$. This implies that dilute and semi-dilute solutions of supramolecular polymers exhibit high polydispersity, but may not be sufficiently entangled to follow the reptation mechanism of relaxation considered in Cates’ model$^{13}$.

### 7.2 Outlook

With the completion of this thesis, we’ve gained new insights on the static properties as well as the self-assembly dynamics of block copolymer micelles and supramolecular polymers. It is our hope that our results will be useful for future development of analytical models and experimental research on polymer self-assembly. At this point, we’d like to purpose several potential research directions related to this thesis.

1. For study of equilibrium properties of block copolymer micelles, our results indicate that DPD simulation is very efficient for sampling block copolymer micelle at equilibrium. It would be feasible and very interesting to investigate the equilibrium properties of block copolymer in a more systematic manner. For example, one can study the dependence of the CMC, micelle aggregation number and structure on the chain length as well as the interaction energy. With longer oligomer length, it would be possible to obtain quantitative results for comparison with predictions of scaling and mean field theories of spherical block copolymer micelles$^{14,15}$, as shown in one previous effort$^{16}$ in this direction.

2. For study of micellization and chain-exchange kinetics, it is interesting to study the two elementary mechanisms: unimer expulsion/insertion and micelle fission/fusion using
DPD simulation. For example, with longer oligomer, one can study the process of chain expulsion for validation of the chain geometrical restraint hypothesis responsible for the observed logarithmic decay observed in micelle hybridization experiments.\textsuperscript{17-19} It is also possible to study the effect of the polydispersity on the micelle dynamics.\textsuperscript{19}

(3) For further investigation of the dynamics and rheological properties of supramolecular polymers, it is always desirable to develop a better model for the reversible association interaction. Our current reversible association model was found to work well for dilute and semi-dilute regime, while it is less likely to work for concentrated solution or melt due to the limitation introduced by the repulsive interactions. It would be a very useful effort to develop a reversible association model that is applicable to all concentration regime and supramolecular network.
7.3 Bibliography


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