INVESTIGATION OF THE RELATIONSHIPS BETWEEN THE THERMODYNAMIC
PHASE BEHAVIOR AND GELATION BEHAVIOR OF A SERIES OF TRIPODAL
TRISAMIDE COMPOUNDS

A Dissertation

Presented to

The Graduate Faculty of The University of Akron

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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August, 2012

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PHASE BEHAVIOR AND GELATION BEHAVIOR OF A SERIES OF TRIPODAL
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ABSTRACT

Low molecular weight organic gelators(LMOGs) are important due to potential applications in many fields. Currently, most of the major studies focus on the empirical explanation of the crystallization for gelator assembly formation and morphologies, few efforts have been devoted to the thermodynamic phase behaviors and the effect of the non-ideal solution behavior on the structure of the resultant gels. In this research, tripodal trisamide compounds, synthesized from tris(2-aminoethyl)amine (TREN) by condensation with different acid chlorides, were studied as model LMOGs due to the simple one-step reaction and the commercially available chemical reactants. Gelation of organic solvents was investigated as a function of concentration and solvent solubility parameter. It has been found that the introduction of branches or cyclic units have dramatically improves the gelation ability compared to linear alkyl peripheral units. Fitting the liquidus lines using the regular solution model and calculation of the trisamide solubility parameter using solubility parameter theory gave good agreement with the trisamide solubility parameter calculated by group contribution methods. These results demonstrate that non-ideal solution behavior is an important factor in the gelation behavior of low molecular mass organic gelators. Understanding and controlling the thermodynamics and phase behaviors of the gel systems will provide effective ways to produce new efficient LMOGs in the future.

ACKNOWLEDGEMENTS

First, I would like to thank my PhD advisor, Dr. Kevin Cavicchi, who has supported me throughout my Ph.D. study with his great enthusiasm, knowledge and patience. I attribute the level of my research to his encouragement and effort, none of this work would have been possible without him.

Many thanks to committee members in my dissertation defense: Dr. Thein Kyu, Dr. Mesfin Tsige, Dr. Matthew Espe, Dr. Avraam Isayev, I would like to thank them for their valuable criticism and time.

Special thanks to Rong Bai, who instructed me in the operation of many instruments.

I would also like to thank the group members, especially Yuqing Liu, Pengzhan Fei, Lei Feng and Maurice Wadley, who helped me greatly with my research and daily life.

Far too many people to mention individually have assisted me in so many ways during my work at the University of Akron. They all have my sincere gratitude.

A final thank-you goes to my wonderful parents and my husband for always being there for me.

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CHAPTER I

BACKGROUND

1.1 Introduction

Low molecular weight organic gelators(LMOGs) are important due to potential applications in many fields. There are numerous examples of gels and gelators.

1.1.1 What is a gel?

There are numerous examples of gels, such as in cosmetics, food, contact lenses, sea cucumbers, agarose gels for electrophoresis, and even living organisms which consist largely of hydrogels^{1,2}.

Flory defined that a substance is a gel when it has a continuous structure with permanent macroscopic dimensions on the time scale of an analytical experiment; its modulus is low; and its rheological properties are solid-like³. Many systems can be considered as gels based on this rather broad definition including chemically and physically crosslinked polymers and colloidal mixtures.

More recent work has emphasized that gels are formed from a combination of a fluid and gelator, where the fluid is immobilized by low concentrations of the gelator, mainly by surface tension and capillary forces by the formation of a three dimensional network of the gelator within the fluid⁴⁻¹⁰. A gelator could be a polymer, surfactant or other small

molecules. Rheologically, gels have been defined as having frequency independent storage modulus, G' , and loss modulus, G'' . Also, because gels are elastic G' should be larger than G'' ^{11,12}.

1.1.2 Types of gels

Gels are usually classified as being either chemically or physically crosslinked. In chemically crosslinked gels the network is covalently bonded and irreversible. Examples include inorganic oxides networks and cross-linked polymers¹⁰. Physical gels usually have networks composed small molecules or macromolecules that are held together by non-covalent interactions such as, London dispersion interactions, hydrogen bonding, aromatic (π - π) interactions, ionic or organometallic coordination bonding, or a combination of these. Physical gels are typically reversible between a gel and a solution. For example, this can driven by a change in temperature due to the disruption of the non-covalent bonding^{13,14}.

Gels can alternatively be divided into hydrogels and organogels. In hydrogels water is the gelled fluid¹⁵. Hydrogels usually consist of more than 99 percent of water and are superabsorbent. They have long been used for many applications. Because hydrogels resemble natural living tissue due to their high water content, they can be used as scaffold substrate in tissue engineering¹⁶. Silicone hydrogels are used for contact lenses². Hydrogels formed from cross linked polymers such as polyAMPS, polyethylene oxide, and polyvinylpyrrolidone are used as medical electrodes².

Organogels encompass systems where non-aqueous fluids are gelled. They have potential for use in a number of applications, such as in drug delivery, food processing, pharmaceuticals and cosmetics¹⁵.

1.2 What are low molecular mass organic gelators?

Low molecular weight organic gelators (LMOGs) are important due to potential applications in many fields. There are numerous examples of gelators.

1.2.1 General description

Low molecular mass organic gelators (LMOGs) are primarily organic in composition and the molecular mass is usually less than 2000 Da¹⁷. They can self-assemble to form fibers, strands, tapes, and helices via one dimensional growth of the molecules. Non-covalent cross-links between the nanofibers and/or mechanical entanglements create a three-dimensional network. When the solvents are entrapped within the three-dimensional network it forms a gel. It has been suggested that the solvent molecules are immobilized by capillary forces between the networks formed by the gelator molecules¹⁸.

Chemically crosslinked gels are formed by covalently cross-linked polymer networks. In these systems the covalent bonds must be broken if the system is to revert to a solution state, however, most gels of LMOGs are thermally-reversible, physical gels assembled through non-covalent interactions. These molecules self-assemble to form fibrillar networks including worm-like micelles or fibrous molecular crystals¹⁹. In the case of crystals, many times specific interactions like hydrogen bonding drive crystal formation. However, even simple Van der Waals interactions can also drive crystal formation, such as the cases of waxes in oil¹⁴. However, the secondary interactions should not be too large, or else a macro phase separation may occur and lead to crystal precipitation rather than network formation^{15,20,21}.

LMOG organogels are usually prepared by heating a solution of a gelator in an organic liquid until the mixture becomes a homogenous solution, and then cooling the solution

below a characteristic gelation transition temperature, T_{gel} . T_{gel} is the temperature below which flow is no longer discernible over long periods. T_{gel} depends on the concentration of the gelator, the properties of the solvents and the procedure of cooling the solution¹⁷. When the temperature increased above T_{gel} , the viscoelastic gel material reverts to a liquid. This thermal transition can be explained by lowering the network density and finally unable to support the gel phase.

Figure 1.1 Schematic view of gelation of an organic solvent by an LMOG.

1.2.2 Applications

Gels constructed from low molecular weight molecules have gained particular interest recently. The developments and applications of molecular gels are in a broad range of fields, such as viscosity modifiers for foodstuffs and cosmetics; nucleating agents for crystalline polymers; inorganic and porous material synthesis; stimuli responsive materials; and drug delivery^{10,22-24}. A few examples are given in the remainder of this section.

The LMOG 1,3:2,4-bis(3,4-dimethyldibenzylidene)sorbitol (DMDBS) was used as a clarifying agent in semi-crystalline polymers to improve their optical properties²⁵. Figure

1.2 illustrates the effect of the addition of different amounts of DMDBS on the macroscopic optical properties of injection-molded isotactic polypropylene (i-PP). By addition of only small amounts (~0.2 wt %) of DMDBS to i-PP, a highly clear/transparent polymer product is achieved, which is because of a reduction of the polymer spherulite size due to increase in the number of DMDBS nucleated spherulites. However, a loss of clarity was observed with increasing concentrations exceeding 1 wt %, and concentrations of 10 wt % and higher leads to complete absence of visible light transmittance. That is because DMDBS assembled into relatively large domains through liquid-liquid phase separation, which has large structures that significantly scatter visible light, leading to poor clarity and haze of the solid mixtures.

Figure 1.2. Optical properties of isotactic polypropylene (i-PP)/1,3:2,4-bis(3,4-dimethyldibenzylidene)sorbitol (DMDBS) for different compositions. [Reproduced from reference 25 with permission].

Jung *et al.* found that ultrastable mesoporous-sized silica structures can be template by organogel networks using a phenanthroline-appended cholesterol organogelator (Figure 1.3)²⁶.

Figure 1.3. Chemical structure of the phenanthroline-appended cholesterol organogelator 1.[Reproduced from reference 26 with permission].

The sol-gel polymerization of tetraethoxysilane (TEOS) was carried out using an acetic acid gel. The left SEM picture in Figure 1.4 shows the typical picture of the fibrous structure obtained from the xerogel of 1. The right SEM picture showed the mesoporous silica obtained from the acetic acid gel after calcination.

Figure 1.4. SEM picture of xerogel 1 obtained from the acetic acid gel(left), SEM picture of the silica (after calcination) obtained by sol-gel polymerization of TEOS in the 1+ acetic acid gel(right). [Reproduced from reference 26 with permission].

This result indicates that the xerogel structure of the 1 + acetic acid gel acts as a good template to obtain the mesoporous silica under the specific sol-gel polymerization conditions. This mesoporous-sized silica is created by the electrostatic interaction of the silica particles with the gelator fiber structure (Figure 1.5).

Figure 1.5. Transcription of the organogel superstructure as a template.[Reproduced from reference 26 with permission].

Huo *et al.* successfully employed 12-hydroxystearic acid in a 3-methoxypropionitrile (MePN) based liquid electrolyte as a LMOG to form a gel electrolyte for a dye-sensitized solar cell (Figure 1.6) and obtained 97% photoelectric conversion efficiency at full sunlight irradiation with good stability during illumination²⁷.

Figure 1.6. Photo of liquid and low molecular mass organogelator based gel (the bottle is upside down) electrolytes (from left to right). [Reproduced from reference 27 with permission].

In Figure 1.6 the left vial shows the pure ionic liquid 1,2-Dimethyl-3-propylimidazolium iodide (DMPPI) without the gelator. The ionic liquid rapidly flows to the bottom of the vial upon turning the vial upside down. The right vial contains 5 wt% of the organogelator. After complete dissolution of the organogelator at elevated temperatures, the gelator molecules build up nano-scale fibrils through hydrogen bonds and form a three-dimensional network (Figure 1.7) to gel and hinder the flow of the ionic liquid. It is possible to prepare stable quasi-solid-state dye-sensitized solar cells with this gelator. Above the sol–gel transition temperature (T_{gel}), the solar cell chamber can be efficiently filled with a low-viscosity liquid and upon cooling a mechanically stable quasi-solid electrolyte is obtained.

Figure 1.7. Transmission electron micrographs of low molecular mass organogelator based gel in MePN. [Reproduced from reference 27 with permission].

CHAPTER II

BASIC RESEARCH OBJECTIVES

Low molecular mass organic gelators have attracted considerable interest due to the broad spectrum of molecular structures and potential applications in a wide variety of fields. In recent years there has been a lot of research dedicated to LMOGs because of their potential applications in many fields. However, designing an organic gelator still remains a major challenge mainly because of the lack of information on the mechanism of formation of gels and the gel-network/solvent interactions. The goal of this thesis was to investigate the relationships between gel formation and the gel/solvent interactions including the relationships between the thermodynamic phase behavior and the gelation behavior and the effect of the non-ideality of the organogelator/liquid solutions on the supramolecular assembly and structure.

Here the study was narrowed to gelators that form molecular crystals. Since crystallization is a thermodynamic process, there should be connections between gelation and thermodynamic phase behavior, which is a very important aspect for understanding the inherent ability of a compound to act as an LMOG. The phase diagram provides a platform to explore other contributions to gelation, such as the propensity of a compound to form fibrous networks opposed to other crystal structures or the kinetic competition

with liquid-liquid phase separation. The rest of this thesis is organized as follows. The remainder of this chapter will discuss the current state of understanding of LMOG/solvent thermodynamics; an overview of amide and 12-hydroxystearic organogelators, which are the types of LMOGs studied in this thesis; and a review of the regular solution model and solubility parameter theory that are used extensively to interpret the solution behavior presented in the succeeding chapters.

The second chapter describes the experimental procedures for synthesis and characterization used in this research. The third chapter describes the gelation of common organic solvents with different tris(2-aminoethyl)amine (TREN) trisamide derivatives. The fourth chapter describes the solution behavior of 12-hydroxystearic (12-HSA), a common organogelator, in organic solution. In the fifth chapter the solution behavior of 12-HSA in polymeric fluids is presented. In this case polymeric solvents were used to vary the relative sizes of the solute and solvent to influence the entropy of mixing of the solutions. Finally the sixth chapter provides a summary of the work and recommendations for future research.

2.1 Current Understanding of LMOG/solvent Thermodynamics

In the cases where gelation is driven by the crystallization of the LMOG to form a three-dimensional fibrillar network the underlying thermodynamic phase behavior should be strongly linked to the bulk gelation behavior. The simplest phase diagram for this type of system is shown in Figure 2.1. Here the transition between a homogeneous liquid phase and a two phase liquid + solid is defined by the liquidus line. A number of studies have shown that there is a direct correlation between the gelation transition and the melting

temperature or solubility limit of the LMOG as a function of temperature²⁸. Another key factor is the level of undercooling or supersaturation achieved during gelation. As shown in Figure 2.1, if the melting point of the pure solid phase is T_m , the solubility of the solute at temperature T is x_s , for a solution of solute composition x_2 quenched to a temperature T , $T_m - T$ is the undercooling, and $(x_2 - x_s)$ is the supersaturation, which can be determined by the intersection of a horizontal line drawn from x_2 and a vertical line drawn from T with the liquidus line, respectively. Lescanne and coworkers presented a study of an organogel, formed by the gelator 2,3-di-*n*-decyloxyanthracene (DDOA) in propylene carbonate, it is shown that the number density of the fiber junctions depends on the cooling rate and a certain level of undercooling is needed to achieve good gelation²⁹.

Figure 2.1. Schematic of liquidus line and determination of undercooling and supersaturation.

2.2 Previous experiments examining phase behavior

Currently, most of the major studies focus on the empirical explanation of the crystallization for gelator assembly formation and morphologies, few efforts have been devoted to the thermodynamic phase behaviors and the effect of the non-ideal solution behavior on the structure of the resultant gels.

2.2.1 Schroeder-Van Laar and Vant Hoff equations

A number of investigations have tried to correlate the gel and melting transition with the thermodynamic parameters of the system. The most common approach is to use the or Schroeder-Van Laar (equation 2.1) or Vant Hoff (equation 2.2) equations³⁰ that describe the transition temperature as a function of composition in terms of the enthalpy and entropy of dissolution. The Schroeder-Van Laar equation is,

$$\ln x = \frac{\Delta H_f^o}{R} \left(\frac{1}{T_m^o} - \frac{1}{T} \right) \quad (2.1)$$

Where x is the solute concentration, ΔH_f^o is the heat of fusion and T_m^o is the melting temperature of the pure solute^{9,28,31-35}. This equation³⁶ is often used to fit the phase diagrams of LMOG/solvent systems and the gel-to-sol transition is interpreted as a melting or dissolution of gelator crystals^{9,31,37}.

Figure 2.2 shows the fit of the experimental data of the 2-*O*-(1-ethylpropylidene)- α -D-glucopyranose gelator concentration vs. the reciprocal absolute temperature of T_{gel}^{20} , the best fit is shown as the solid line.

Figure 2.2. Plot of the logarithm of gelator concentration vs. the reciprocal absolute temperature of T_{gel} . The solid line is the best fit of eq 2 to the experimental points. The correlation coefficient $\gamma = 0.98$ and the fitting parameter ΔH is equal to 72 kJ/mol. [Reproduced from reference 20 with permission].

Dastidar *et al.* also used Schroeder-Van Laar equation to fit their experimental gelation results, to calculate ΔH values of the gelators³⁸, as shown in Figure 2.3.

Figure 2.3. Semilog plot of mole fraction of the gelators against $1/T$; 1,2 Dichlorobenzene and nitrobenzene gels were used for DBAMC 6 and DBUAMC 3, respectively. [Reproduced from reference 38 with permission].

Two recent investigations have also stress the importance of solute solubility on gelation by using the Vant Hoff equation to obtain the enthalpy and entropy of dissolution of different solutes in organic solution^{39,40}.

$$\ln x = -\frac{\Delta H_{diss}}{RT} + \frac{\Delta S_{diss}}{R} \quad (2.2)$$

ΔH_{diss} is the enthalpy of dissolution and ΔS_{diss} is the entropy of dissolution. This equation gives the liquidus line in terms of the thermodynamic dissolution parameters. Hirst et al. found that ΔH_{diss} scales inversely with the minimum gelation concentration (MGC) concentration for a series of lysine-based LMOGs.⁴⁰ Muro-Small did not observe a correlation between ΔH_{diss} and MGC for a series of pyridine- and dipeptide-based compounds, but did observe that the ability of a compound to act as an LMOG was correlated with the dissolution parameters, where gelation typically occurs at larger ΔH_{diss} .³⁹

The Schroeder Van Laar equation arises from the ideal solution model. For an ideal solution, where there are no interactions between the solvent and LMOG, the liquidus line is given by Equation 2.3.

$$\ln x_s = \frac{\Delta H_f^o}{R} \left(\frac{1}{T_m^o} - \frac{1}{T} \right) \quad (2.3)$$

Where ΔH_f^o is the enthalpy of fusion of the pure LMOG.

However, real LMOG-solvent solutions display non-ideal behavior, because a single LMOG behaves differently in different solvents which might affect the liquidus line and ΔH_{diss} varies with the choice of solvent^{34,41,42}.

2.2.2 Correlation with solvent parameters

The choice of solvent influences the behavior of the LMOG. A number of studies have tried to correlate this with bulk solvent parameters. Different solvent parameters have been developed and applied to gel-phase materials, such as dielectric constant (ϵ)⁴³ which can reflect only very roughly the interactions between a solute and the solvent; Hildebrand solubility parameter (δ); Hansen solubility parameters ($\delta_H^2 = \delta_d^2 + \delta_p^2 + \delta_h^2$, where δ_H , δ_d , δ_p , and δ_h are the total Hansen, dispersive, polar and hydrogen bonding parameters, respectively)⁴⁴. Hanabusa and co-workers reported that the minimum gelation concentration of cyclo(dipeptide) gelators was dependent on Hildebrand's solvent polar solubility parameter⁴⁵. Boutellier and co-workers have noted that the steric demands of solvent molecules can be parameterized and have a direct influence on gel formation⁴⁶. Smith and co-workers used bis-urea gelators to gain a more detailed

understanding of the effect of solvent in terms of Kamlet–Taft parameters. There are three different Kamlet–Taft parameters, each of which accounts for a different way in which a solvent can interact with a solute: α (hydrogen bond donor ability), β (hydrogen bond acceptor ability) and π^* (dipolarity/polarizability). In particular, α , has strong predictive power for gelation processes in their gelator systems⁴⁷⁻⁴⁹.

Zhang and coworkers reported solvent effects driven by van der Waals interactions of a dicholesterol-linked azobenzene organogel by introducing Teas plots⁵⁰. Several solvents with different solubility parameters were added to cyclopentanone as mixed solvents for gelation experiment. The Hansen solubility parameters of the mixed solvents can be estimated from the following equation:

$$\delta_{average} = \sum \phi_i \delta_i \quad (2.4)$$

Where $\delta_{average}$ is the average solubility parameter of the mixed solvent and ϕ_i and δ_i are the volume fraction and solubility parameter of the component. The Hansen solubility parameters of the gelator DCAZO2 can be calculated by group contribution method. The Teas parameters of the mixed solvent can be estimated from the following equations,

$$\begin{aligned} f_d &= \delta_d / (\delta_d + \delta_p + \delta_h) \\ f_p &= \delta_p / (\delta_d + \delta_p + \delta_h) \\ f_h &= \delta_h / (\delta_d + \delta_p + \delta_h) \end{aligned} \quad (2.5)$$

Where f_d , f_p , and f_h are the dispersion component, polar component, and hydrogen bonding component of Teas parameters, respectively.

The solubility parameters of DCAZO2 and the mixed solvents are calculated and presented in the Teas plots to study the gelator-solvent interaction and explain the

gelation test in different mixed solvents. Each compound is represented by a single point in a ternary plot. The gelator-solvent interaction strength can be directly related to the difference of solubility parameters of a gelator and a solvent. Usually, with increasing difference the interactions between gelator and solvent decrease^{44,51,52}. When the solubility parameters of the solvents are very close to that of the gelator, the gelator-solvent interactions are strong enough to dissolve the gelator in the solvents. On the contrary, the solubility parameters of solvent far away from the solubility parameters of the gelator indicate that the gelator-solvent interactions are unfavorable so that the gelator precipitates. When the distance between the solubility parameters of the solvent and the gelator are moderate, the gelator-solvent interactions are appropriate to form stable gels. It can be concluded that gelation requires the gelator-solvent interaction be neither too favorable or unfavorable, otherwise solutions or precipitates are formed.

2.3 Classes of LMOGs

Several classes of low molecular mass organic gelators form stable thermally reversible gels with various organic solvents at low concentrations, from simple molecules such as long n-alkanes to complex molecules, polymers and gelators responding to external stimuli⁵³. Their discovery and development are particularly important due to potential applications in many fields such as food, medicine, materials science, cosmetics, and pharmacology¹⁵.

Figure 2.4 shows some examples of small molecular weight organogelators of different kinds, such as fatty acids (1)⁵⁴, anthracene(DDOA¹⁰) and anthraquinone (3)⁴, steroids(CAB, CAQ¹⁰), and amides (14)⁵⁵. The combination of structural fragments such

as ester, amino acid and peptide units was assumed to be favorable for gelation, the gel assemblies can be stabilized by the intermolecular hydrogen-bonding interactions between the peptidic and carboxylic acid units.

Figure 2.4. Various types of small molecular weight organogelators⁵⁶. [Reproduced from reference 10 with permission].

2.3.1 Amide based LMOGs

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Figure 2.5. Examples of gelators based on amide-amide interactions¹⁰. [Reproduced from reference 10 with permission].

Small molecular weight organogelators that act via amide-amide interactions are frequently used (Figure 2.5)^{48,57}, the thermoreversible gels are based on the amide-carbonyl hydrogen bonding. The compound in Figure 2.6 is capable of gelling both highly polar solvents such as water and DMSO, as well as highly lipophilic solvents such as gasoline and diesel, the common hydrocarbon fuels.

Figure 2.6. Example of amide gelator⁵⁸.

The gelator in Figure 2.7 ($n = 4, 6, 9$, and 11) with a carboxylic group and an amide group separated by a long polymethylene chain was synthesized by Vögtle *et al*⁵³, where R is an aliphatic chain or an aromatic group. When R is a photochromic naphthopyran group, gelation/de-gelation could be affected by light irradiation and heating treatments.

Figure 2.7. Example of amide gelator.

Many enantio-pure *trans* 1,2-diamidocyclohexanes (Figure 2.8) are able to gel a wide variety of liquids including hydrocarbons, alcohols, ketones, esters, ethers, polar aprotic solvents, mineral oils, and edible oils⁵⁷.

Figure 2.8. *trans*1,2-diamidocyclohexane.

Figure 2.9. TEM images of a loose acetonitrile gel by *trans* 1,2-diamidocyclohexanes.

Magnification: a) x 7000. b) x 30000. [Reproduced from reference 57 with permission]

Molecular modeling studies suggest that the two amide-NH and amide-CO of *trans* isomer can direct themselves perpendicular to the cyclohexyl ring and antiparallel to each other, two intermolecular hydrogen bonds between each molecule stabilize the tape like molecular aggregates. On the other hand, the *cis* isomer aggregates fail to form because the amide units in an axial position cannot form hydrogen bonds and were not able to gel any of the liquids.

Figure 2.10. Hydrogen bonding among the *trans*-1,2-diamidocyclohexyl groups.
[Reproduced from reference 57 with permission]

It has also been reported that simple diurea compounds form thermoreversible gels stable at temperatures of up to 100°C with several organic solvents⁵⁹. The urea-urea hydrogen-bonding interaction is highly directional and has limited conformational flexibility. It was

discovered that two urea groups in one molecule are sufficient enough to form aggregation in dilute solutions of a range of organic solvents^{7,60,61}.

2.3.2 12-hydroxystearic acid

The 12-hydroxystearic acid(HSA) is a saturated monobasic acid prepared by the hydrogenation of castor oil. The hydroxyl groups are responsible for various uses in different industrial fields, such as a firming agent in cosmetics, activator and internal lubricant in elastomers and resin intermediate in coatings^{2,62}.

12-Hydroxystearic acid is well known as a low-molecular weight gelator with the influence of chirality on the modes of self-assembly. Most of the time, low concentrations of HSA form a thermoreversible gel with a fibrous associated network in organic solvents, which transforms into solution by raising temperature.

Figure 2.11. Structure of 12-hydroxystearic acid

Grahame and coworkers studied the chirality effects on the gelation behavior of HSA⁶². In their study, 2.0 wt % racemic DL-12HSA was required to gel mineral oil effectively,

however, only less than 1.0 wt % of optically pure D-12HSA was needed to form an organogel. Time-dependent synchrotron IR measurements and optical microscopy were used to determine the nucleation phenomena. It was proved that optically pure D-HSA molecules were organized as head-to-head dimers with hydroxyl hydrogen-bonding along the transverse axis promoting longitudinal growth. The racemic HSA mixture is more likely to form single, in-plane hydrogen-bonded acyclic dimers which allow additional H-bonding of the 12-hydroxyl groups within each dimer to promote the growth of platelets and limit the ability of the longitudinal growth.

2.4 Relationships between phase behavior and gelation

Understanding and controlling the thermodynamics and phase behaviors of the gel systems is an important factor in understanding the gelation behavior of low molecular mass organic gelators. And it will provide effective ways to produce new efficient LMOGs in the future.

2.4.1 The regular solution model

The regular solution model is a thermodynamic solution model to describe the non-ideal solution behavior of many solutions. In a regular solution the entropy of mixing is due to the combinatorial entropy of mixing. For two components the entropy of mixing is,

$$\Delta S_m = -nR(x_1 \ln x_1 + x_2 \ln x_2) \quad (2.6)$$

Where R is the gas constant, n is the total number of moles and x_i is the mole fraction of each component.

In contrast to the ideal solution model, regular solutions have a non-zero enthalpy of mixing. The non-ideality of the solution is assumed entirely due to the interactions between the solvent and solute which is described by the interaction parameter χ ^{28,30,63}. The basic assumptions in regular solution theory are that the components have equal molar volume, the local concentration is equal to the bulk concentration, and there are no volume changes due to mixing^{30,64}. The free energy of mixing of a regular solution is,

$$\frac{\Delta G_m}{RT} = x_1 \ln x_1 + x_2 \ln x_2 + x_1 x_2 \chi \quad (2.7)$$

For a system where one component is able to crystallize when cooled from the homogeneous state two transitions may occur, (1) liquid-liquid phase separation or (2) liquid-solid phase separation. The simplest temperature dependence of the interaction parameter is $\chi = A/T$. The binodal line separating the homogeneous liquid from the two phase liquid is found numerically. The spinodal line denoting the boundary of absolute instability of a solution to decomposition into multiple liquid phases is given by,

$$T_s = \frac{2A}{\frac{1}{x_1} + \frac{1}{x_2}} \quad (2.8)$$

The liquidus line separating the homogeneous liquid and the two phase liquid + solid is given by the following equation^{30,65},

$$T_{gel} = \frac{\frac{\Delta H_f^o}{R} + A(1-x_2)^2}{\frac{\Delta H_f^o}{R} \left(\frac{1}{T_m^o} \right) - \ln x_2} \quad (2.9)$$

where ΔH_f° is the latent heat of fusion of the pure organogelator, R is the gas constant, x_2 is the mole fraction of the organogelator and T_m° is the melting temperature of the pure gelator.⁶⁶ This equation assumes the following about the system. First, the liquid is completely excluded from the solid crystal. Second, ΔH_f° is independent of temperature over the range T_m to T_m° . Third, the heat capacity difference between the solid and the liquid is negligible. Fourth, the solid has the same crystal structure as the pure solute.

Figure 2.12 plots the liquidus line and spinodal line as both a function of A and T_m° using Equation 2.8 and 2.9 from regular solution model.

Figure 2.12. Liquidus (solid lines) and spinodal lines (dotted lines) for LMOG/solvent systems with varying χ ($A = 0$, black; $A = 200$, red; $A = 400$, blue; $A = 600$, green)

Figure 2.12 shows the calculation results of the temperature-composition phase diagram for the solvent/LMOG systems. Here $\Delta H_f^\circ/R$ is set to 8835.7K and T_m° is set to 459K. The temperature-composition phase diagram is calculated with three different χ parameters ($A = 0, 200, 400$ and $600, \chi \sim A/T$). As expected, when χ is increased this metastable miscibility gap moves towards the liquidus line, an equilibrium miscibility gap would appear above the liquidus line over a range of composition if χ were increased even more. Different χ parameters could be obtained by varying the solvent. If T_m° is lowered, the entire liquidus line will shift to lower temperatures.

The assumption that the solvent is always excluded from the gelator crystal is not always observed experimentally. When the solvent molecules are incorporated into the gel fiber, the gel can be classified as a “wet gel”, different from “dry gels” where the solvent is excluded from the solid phase. X-ray patterns were observed in comparison of 4,6-O-benzylidene-R-D-mannopyranoside/p-xylene gels, freeze-dried gels, and the pure gelator, as shown in Figure 2.13. Results indicate that the molecular assembly in the gel state is different from that in the crystalline state⁶⁷.

Figure 2.13. (A) Comparison of WAXD profiles between solvent (a), gel (b), and crystalline powder (c). (B) SAXS profile for the powder and freeze-dried samples. All measurements were carried out at room temperature. The arrows indicate the identical peak. [Reproduced from reference 67 with permission].

WAXD shows that the gel sample shows only amorphous peaks and no trace of crystalline peak at all; on the other hand, the pattern from the powder shows a typical crystalline powder solid feature. This result indicates that the gelator molecules in the gel are in a disordered state and do not give a diffraction peak, quite different from those obtained for the “dry gels”. In SAXS the spacing of the gelator molecules in the gel is larger than the gelator molecular size, indicating solvent incorporation. In terms of the thermodynamic phase behavior, for wet gels there should be an additional solidus line extending from T_m^0 at $x_2 = 1$ below the liquidus line to delineate the solid + liquid region and the one-phase solid solution.

Amorphous, low glass transition temperature polymers could be used as model liquids for the LMOG/liquid system. By changing degree of polymerization, N , to change the size of the solvent molecules and interaction parameter, χ , we can finely tune the phase behavior that would be difficult to control in LMOG/solvent systems.

The Flory diluent theory gives a mathematical relationship between the melting temperature of the LMOG and its volume fraction for the mixture of a polymer and low molecular weight crystalline solvent, assuming equal molar volumes of the LMOG and polymer repeat unit³⁰. The liquidus lines are described by

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H^0} \left[(\ln \phi_2 + (1 - \frac{1}{N})\phi_1 + \chi \phi_1^2) \right] \quad (2.10)$$

Where T_m is the melting temperature of the LMOG at volume fraction ϕ_2 and R is the gas constant. The spinodal line for the liquid-liquid miscibility gap is given by,

$$\frac{1}{\phi_1} + \frac{1}{N \phi_2} - 2\chi = 0 \quad (2.11)$$

Figure 2.14 shows the calculation results of the temperature-composition phase diagram for the polymer/LMOG systems. $\Delta H_f^\circ/R$ is set to 8835.7K, T_m° is set to 459K, and degree of polymerization of the polymer N is set to 10, the temperature-composition phase diagram is calculated with three different χ parameters ($A = 140, 240$, and 340 , $\chi \sim A/T$). As expected, when χ is increased this metastable miscibility gap moves towards the liquidus line, an equilibrium miscibility gap would appear above the liquidus line if χ were increased even more. Different χ parameters could be obtained by varying the solubility parameter of the polymer by changing the chemistry of the polymer. In Figure 2.14b, χ is constantly set to $240K/T$ but degree of polymerization N increases from 1 to 5 to 10. Here, a shift of the metastable miscibility gap towards the liquidus line is also observed. This fine tuning of the phase behavior is difficult to accomplish in common organic solvent systems, and it is very useful for investigation of the relative driving forces for liquid-liquid and liquid-solid phase separation.

(a)

(b)

Figure 2.14. Liquidus (solid lines) and spinodal lines (dotted lines) for LMOG/polymer systems with (a) varying χ ($A = 140\text{K}$, navy; $A = 240\text{K}$, blue; $A = 340\text{K}$ purple) and (b) varying molecular weight ($N = 1$, black; $N = 5$, red, $N = 10$, Navy).

The regular solution model has found wide application in metallurgy, polymers, coatings, and pharmaceuticals, however, it has not been as much applied in the LMOG field^{10,30}.

Fahrlander *et al.* have measured gel formation temperatures for poly(propylene

glycol)(PPG) /dibenzylidene sorbitol(DBS) organogels in which the molecular weight of the PPG was varied. They have adopted a regular solution model to extract a value of δ_{DBS} from temperature, strain, and frequency dependent rheological measurements data. The magnitude of this value is reasonable given the apparent solubility of DBS in various organic solvents⁶⁸.

Takeno et al. obtained the binodal curve for the mixture of 12-Hydroxystearic Acid (12-HSA) and polybutadiene(PB) by the fit of the melting point depression equation derived from Flory-Huggins theory to the cloud point data and determined the interaction parameter between 12-HSA and PB⁶⁹. This interaction parameter was then used to calculate the melting curve from the melting point depression equation derived from Flory-Huggins theory with the heat of fusion from the DSC result for the HSA powder. The calculated PB gel curve agrees with the experimental melting data. For the gels prepared in toluene, dodecane and PB oligomer, the calculated melting curves by using the solvent solubility parameters and solubility parameter of 12-HSA calculated from the group contribution method can qualitatively explain the experimental values. The calculated curves are quantitatively inconsistent with the data because factors such as the excess volume of the solution and the excess entropy of mixing are neglected. The broken curves in Figure 2.15 represent the ones calculated.

Figure 2.15. Phase diagram of D,L-12-HSA and D-12-HSA gels in PB oligomer, toluene and dodecane. The upper solid line represents the one obtained by equating the chemical potentials of two components in the two coexisting phases. The lower solid line represents the one calculated by using the χ parameter obtained in the above fit. Broken lines represent the melting curves calculated by substituting the solubility parameter of each component into the melting point depression equation derived from Flory-Huggins theory. [Reproduced from reference 69 with permission].

2.4.2 Prediction of χ from solubility parameters

The constant A in the interaction parameter ($\chi = A/T$) can be estimated from the solubility parameters of the solvent and gelator by,

$$A = \frac{V}{R}(\delta_1 - \delta_2)^2 \quad (2.12)$$

where V is the average molar volume of the solvent and gelator and δ_1 and δ_2 are the solubility parameters of the organogelator and solvent, respectively.⁶⁶ Both T_m° and ΔH_f° can be determined calorimetrically, experimental liquidus lines can be fit to measure χ and calculate the solubility parameter of the solute. Furthermore, since solubility parameters can also be calculated using group contribution methods⁴⁴, the regular solution model could potentially be used to predict the thermodynamic phase behavior of LMOG/solvent systems.

2.4.3 Implication of phase behavior on gelation

Understanding and controlling the thermodynamics and phase behaviors of the gel systems is an important factor in understanding the gelation behavior of low molecular mass organic gelators. And it will provide effective ways to produce new efficient LMOGs in the future.

2.4.3.1 Phase separation

There are two main processes for network formation upon cooling of the gelator/solvent solution. One of them is the solid-liquid phase separation where the assembly of the

LMOG molecules forms nanofibers, which branch and entangle to form a three-dimensional molecularly connected network (Figure 2.16a). The second process is the liquid-liquid phase separation of the molten LMOG and solvent; the network is formed of the LMOG-rich phase and stabilized by the phase separation process. The network structure composed of the mixture of both cases can also occur; depending on the relative thermodynamic driving-forces for molecular level self-assembly and liquid-liquid phase separation (Figure 2.16c, d).

Figure 2.16. Schematic morphologies of molecular gels: (a) molecularly connected. (b) phase-connected, (c, d) mixed molecularly- and phase-connected.

If equilibrium phase behavior of LMOG/solvent systems obey standard thermodynamic laws^{67,70}, three possible phase diagrams are shown in Figure 2.17.

Figure 2.17. Possible phase diagrams of LMOG/liquid systems: (a) ideal solution behavior, (b) liquid-liquid miscibility gap, and (c) metastable miscibility gap.

Figure 2.17a displays ideal solution behavior, where the liquidus line separating the L and L+S regions can be described by Schroeder-Van Laar equation. However, most of the time, the LMOG/liquid systems are actually non-ideal solutions with solvent-gelator interactions.

The phase diagram becomes complicated if the systems are non-ideal. When the total free energy of the two phase liquid is less than that of the homogeneous liquid, liquid-liquid phase separation of LMOG-rich and LMOG-poor phases could occur. This results in a liquid-liquid miscibility gap. This miscibility gap can either occur as an equilibrium phase at temperatures above the liquidus line (Figure 2.17b) or as a metastable state in the supercooled solution (Figure 2.17c).

CHAPTER III*

EXPERIMENTAL METHODS

3.1 Materials

Materials include chemicals used as received and chemicals synthesized; the polymers are synthesized by Raft-polymerization.

3.1.1 Chemicals used as received

Tri-n-ethylamine (Acros, HPLC grade), benzene (Alfa Aesar, HPLC grade), o-xylene (Aldrich, reagent grade), chloroform (Fisher Scientific), hexane (EMD), toluene (EMD, ACS grade), methanol (MeOH, Fisher Scientific, reagent grade), tetrahydrofuran (THF, EMD, ACS grade), N,N-dimethylformamide (DMF, Aldrich 99.9%), cyclohexane (Fisher Scientific, ACS), 2-ethyl butyryl chloride(Aldrich, 97%), valeryl chloride(Aldrich, 98%), hexanoyl chloride(Aldrich, 99%),* heptanoyl chloride(Aldrich, 98%), octanoyl chloride(Aldrich, 97%), nonanoyl chloride(Aldrich, 96%), decanoyl chloride(Aldrich, 98%), cyclohexanecarbonyl chloride(Aldrich, 98%), ethanol(EMD, ACS grade), tris(2-aminoethyl)amine(Fisher Scientific, 96%), decane(Fisher Scientific, 99%), 2-propanol (EMD, HPLC grade), sec-butylbenzene(Aldrich, 99%), methyl ethyl ketone(MEK, Fisher Scientific, reagent grade), dioctyl phthalate(Fisher Scientific, 99%), carbon disulfide

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(CS₂, Aldrich, ACS reagent, > 99.9%), cesium carbonate(Fisher Scientific, 99.5%), *N,N*-dimethylacetamide(Fisher Scientific, ACS grade), benzyl chloride(Aldrich, 99%), methylacrylate(MA, Aldrich 99%), deuterated chloroform (CDCl₃, 99.8%D, Cambridge Isotope laboratories), *N*-butyl acrylate (99%, stabilized, Aldrich), hydroxystearic Acid(Aldrich, 99%).

3.1.2 Purification

N-butyl acrylate (99%, stabilized, Aldrich), methyl acrylate (MA, Aldrich 99%) were purified by passing through a column of basic alumina.

Azobisisobutyronitrile (AIBN) was purified by recrystallization in methanol, dried in a vacuum oven at room temperature and stored in a refrigerator.

Hydroxystearic Acid(HSA) was purified by recrystallization in acetone, dried in a vacuum oven at 50 °C for 16 hours and stored at room temperature.

3.1.3 Synthesis of tripodal trisamide compounds

Figure 3.1. Synthesis of tripodal trisamide compounds. Here $R = \text{CH}(\text{CH}_2\text{CH}_3)_2$ for TREN-EB, $(\text{CH}_2)_n\text{CH}_3$, $n=3,4,5,6,7,8$, for TREN-C $n+2$, cyclohexyl for TREN-CH.

The synthesis of TREN-EB was as follows. 1 mL (6.68mmol) tris(2-aminoethyl)amine (TREN) 3 mL (21.5mmol) triethylamine, and 40 mL anhydrous dimethylformamide (DMF) were mixed in a 250 mL 3-neck round bottomed flask under nitrogen and placed in an ice bath. 3.2 mL (23.38mmol) 2-ethyl butyryl chloride was added drop-wise with constant stirring. The resulting solution was stirred for 15 min in the ice bath and 2 hours at room temperature. The mixture was poured into 400 mL saturated aqueous sodium bicarbonate solution. The white precipitate that formed was filtered and washed twice with deionized water. The collected product was dried under vacuum at 60°C for 12 hours. For TREN-C5 (valeryl chloride), TREN-C6(hexanoyl chloride), TREN-C7 (heptanoyl chloride), TREN-C8(octanoyl chloride), TREN-C9 (nonanoyl chloride) TREN-C10(decanoyl chloride), TREN-CH(cyclohexanecarbonyl chloride), 20 mL of ethanol was used in place of the DMF. For each reaction 1 mL of TREN and a molar ratio of acid chloride to TREN of 3.5: 1 was used. The TREN-C5 did not immediately precipitate in water, but was recrystallized at 4 °C. ^1H NMR, ^{13}C -NMR and ESI/HRMS

characterization results of tripodal trisamide compounds are listed in the appendix.

3.1.4 Synthesis of RAFT agent dibenzyl trithiocarbonate (DBTC)

DBTC was prepared by a previous reported method as follows (Figure 3.2).⁷¹ Carbon disulfide (50.0 mmol) was added to a suspension of cesium carbonate (50.0 mmol) in *N,N*-dimethylacetamide (40 mL, DMAc), and the resulting mixture was stirred vigorously at 25 °C. The colorless mixture changed to a red solution within a few minutes, indicating the formation of trithiocarbonate anion (CS_3^{2-}). After stirring for 15 minutes, benzyl chloride (50.0 mmol) in DMAc (10 mL) was added to the mixture. The color of the mixture immediately changed from red to pale yellow. After stirring for 16 hours, the reaction was quenched by pouring into ice-water. The product was extracted with ethyl acetate, dried over anhydrous sodium sulfate, filtered, and evaporated to give pure DBTC as a yellow oil. Further purification is achieved by silica gel column chromatography eluted with hexane to yield the pure DBTC as a pale yellow crystal.

Figure 3.2. RAFT polymerization of polyacrylates.

3.1.5 Raft Polymerization of poly (methyl acrylate)

In an example polymerization 1g of RAFT agent (3.45mmol), 4 mL of MA(44.4mmol), and 120 mg (0.73mmol) of 2,2'-azobisisobutyronitrile (AIBN) as the initiator, were mixed together in a 10mL round bottom flask. The mixture was thoroughly deoxygenated by purging with nitrogen gas for 15 minutes. Polymerizations were carried out for 3.5 hour

at 60 °C in N₂ atmosphere. The viscous solution was then dissolved in 10mL THF, and polymer was precipitated by dripping the solution in THF into hexane. The polymer PMA was collected by filtration, and then dried in vacuum oven at 80 °C for 12 hour.

3.1.6 Raft Polymerization of poly (butyl acrylate)

15g butylacrylate monomer, RAFT agent dibenzyl trithiocarbonate (DBTC), AIBN (1:5 molar ratio to DBTC) were added to make a monomer solution. The solution and a stir bar were added to a round bottom flask sealed with a rubber septum. The solution was sparged with nitrogen for 25min, and then the flask was fit with a reflux-condenser and heated at 80°C under nitrogen. 16 hours later, the reaction was terminated by quenching in a water bath. To remove unreacted monomers from the polymer, the solution were concentrated on a rotary evaporator and dried under vacuum at 80°C for 24h. Four polymerizations were run with the target PBA molecular weights of 2.5 kDa, 5 kDa, 10 kDa, and 20 kDa. The average molecular weight and molecular weight distribution were characterized by gel permeation chromatography using polystyrene standards.

3.2 Characterization techniques

Different characterization techniques are used to characterize the products, including Nuclear magnetic resonance (NMR) characterization, Size Exclusion chromatography (SEC) characterization and so on.

3.2.1 Nuclear magnetic resonance (NMR) characterization

¹H NMR spectra of tripodal trisamide compounds were measured on a Varian Mercury-300MHz spectrometer. Samples were dissolved in deuterated chloroform (CDCl₃,

99.8%D, Cambridge Isotope laboratories) at concentrations of 10 mg/mL. The ^1H NMR spectra were referenced to the peak of CDCl_3 at 7.27ppm. The relaxation time was 5s. ^{13}C -NMR spectra were measured on a Varian Mercury-300MHz spectrometer. Samples were dissolved in deuterated chloroform (99.8%D, Cambridge Isotope laboratories) at the concentration of 10mg/mL.

3.2.2 Size Exclusion chromatography (SEC) characterization

The molecular weight and molecular weight distribution were obtained using size exclusion chromatography (SEC) with THF as the eluent at a flow rate of 0.5mL/min at 35°C. These measurements were taken on a Waters 1515 HPLC instrument equipped with three Styragel columns, a differential refractometer. A mixture of polymer and THF at the concentration of 2mg/mL was injected. The molecular weights were determined by the universal calibration method, which was calibrated by polystyrene standards.

3.2.3 Differential Scanning Calorimetry (DSC)

All the measurements were done using a Q200 differential scanning calorimeter (TA Instruments) under nitrogen atmosphere. Two heating cooling cycles were carried out for each sample under the following protocol: samples were heated from room temperature to 250°C at a rate of 10°C/min, held at 250°C for 5 minutes, cooled to 20°C at a rate of 10°C/min, held at 20°C for a 5 minute period, heated to 250°C again at a rate of 5°C/min, held for 5 minutes at 250°C, then cool the sample to 20°C at a rate of 10°C/min.

3.2.4 Calibration of Heating Block

Thermal measurements of trisamide solutions were conducted using an anodized aluminum thermostated heating block (Chemglass) regulated with a magnetic stir plate with a temperature probe (IKA RCT basic). The temperature controller was calibrated by measuring the temperature of a stirred solution of n-diocylphthalate from 25 to 200°C with a digital thermometer. This thermometer was independently verified by simultaneously measuring the temperature of a heated oil bath using an immersion thermometer and the digital thermometer and controlling the temperature with the stir plate temperature probe. These two thermometers were within $\pm 1^{\circ}\text{C}$ of the setpoint of the stir plate from 25 to 140°C. Using the aluminum heating block the solution temperature was found to systematically lower than the set-point temperature especially at higher temperature. A calibration curve was constructed by fitting a third order polynomial to a plot of the measured solution temperature (T_{measure}) vs. the set point temperature of the stir plate (T_{setpoint}) (Figure 3.3).

$$Y = -103 + 1.9 \cdot X - 0.0026 \cdot X^2 + 2.33 \cdot 10^{-6} \cdot X^3$$

Figure 3.3. Calibration curve of the aluminum heating block.

3.2.5 Minimum Gelation Concentration

Gelation of organic solvents by the trisamide compounds was tested by dissolving 20 mg of the compound in 1 mL of solvent in a 20 mL scintillation vial at elevated temperature to form a homogeneous, clear solution followed by quenching the solution to room temperature for five minutes using a 25°C water bath. Gels were identified as solutions that exhibited no flow when inverted. If a gel was formed the minimum gelation concentration for a particular gelator/solvent pair was determined by adding solvent in 0.5 mL increments and repeating the heating-quenching experiment until a portion of the solution flowed upon inversion of the cooled sample.

3.2.6 Gel Transition Temperature

TREN-EB was mixed with 1 mL of selected organic solvent in a 4 mL vial and heated to completely dissolve the gelator, then cooled to 20 °C in a water bath to form gels. Then the vial was annealed in an thermostated heating block. Starting at 30 °C the temperature was increased in increments of 2 °C and left to equilibrate for 15 minutes at each new setting. The gel transition temperature was defined as the temperature at which a gel visibly flowed upon tilting the sample 90°.

3.2.7 Freeze Drying of Gels

Organogels of TREN-EB and solvent were formed by mixing a known amount of TREN-EB and 1 mL of solvent in a 4 mL vial, heating the solution at elevated temperature and then quenching the vials in a water bath. These organogels were freeze-dried using a Schlenk line, the vials containing the gels are dipped inside a liquid N₂ bath for 2 hours under vacuum.

3.2.8 Scanning Electron Microscopy

The xerogels were examined by scanning electron microscopy. Carbon double-sided tape was used as a conductive mounting adhesive. Sample pieces were mounted onto aluminum SEM stubs (diameter 12 mm). Samples were coated with silver with thickness around 10 nm using EMITECH K575X Turbo Sputter Coater. Samples were then examined in a JEOL JSM5310 scanning electron microscope.

3.2.9 Polarized Optical Microscopy

Gels were sealed inside glass fibers by heating and melting the ends using a propane torch. Bright birefringent patterns were observed in optical microscopy (Olympus BX51) under cross-polarized light. The samples then were heated with a hot plate. The temperature was increased in increments of 5°C and left to equilibrate for 10 minutes at each new setting. The gel transition temperature was defined as the temperature at which birefringent patterns disappeared.

3.2.10 Wide Angle X-ray Scattering

The crystalline structure of the samples were analyzed through wide-angle X-ray diffraction scanning (WXDS) using a 40 mA–40 kW Bruker AX8 diffractometer with Cu K-alpha1 radiation. The scan speed was 1 degree/min and scan time was 10 minutes.

3.2.11 Spincoating and Atomic Force Microscopy

3mg (2wt%) tren-EB and 0.15g PMA were dissolved in a solvent mixture of CHCl_3 and methanol(5:2 in volume), the solvent was removed by rotary evaporation and dried in vacuum oven at 80 °C for 12 hour. This TREN-EB/PMA polymer gel was then dissolved at concentration of 50 mg/mL in three different solvents: chloroform, toluene and benzene. The solutions were spin coated onto cleaned Si substrates(1cm*1cm) using a spin time 15 s and spin speed 1500 rpm. A spin coater Laurell Technologies WS-400B-6NPP/Lite was used. Atomic force microscopy profiles were obtained with AFM Digital Instrument Nanoscope IIIa using tapping mode.

3.2.12 Rheometry

The rheological measurements were performed using a ARES-LS rotational rheometer (Rheometrics) with parallel plate geometry (plate diameter of 25 mm, gap of 1 mm). Frequency, temperature, and strain sweeps were performed to monitor the modulus change of the gels.

3.2.13 Electrochemical Impedance Spectroscopy (EIS)

The TREN-EB/EMIMS gels were prepared by heating the mixture to 180°C to form a homogenous solution, followed by cooling in water bath at room temperature. EIS was done using the CH 604 Impedance Analyzer at room temperature. The EIS measurements were performed with 10 mV perturbation amplitude in the range from 100 kHz to 0.1 Hz from high to low frequencies. The impedance spectra were recorded allowing at least 5 minutes for equilibration after each frequency change. The electrodes were aluminum plates 0.64 cm² and the electrochemical measurements were performed with gel of 0.046 cm thickness filled in between of the two electrodes. The impedance (Z) was obtained in the form of $Z = Z' + iZ''$, where i is the imaginary unit, and Z' and Z'' are the real and imaginary parts of the impedance.

3.2.14 Cavitation rheology measurement

The cavitation rheology technique involves inducing a cavitation event at the tip of a syringe needle inserted in 1 mL gel in a 4 mL sample vial. 22 gauge syringe needles were purchased from Hamilton Scientific. Cavitation is induced by increasing the pressure of an air bubble via a syringe pump (Braintree Scientific BS-8000 Programmable Digital

Syringe Pump) and monitoring the pressure via a pressure sensor (Omega CX136-4) in conjunction with a personal computer to record the pressure and cavity growth as a function of temperature. The pressure acquisition is controlled by DATAQ Instruments Hardware Manager program software.

CHAPTER IV[†]

TRIPODAL TRISAMIDE ORGANOGELEATORS

4.1 Introduction

This chapter describes the solution behavior of a series of tripodal trisamide compounds. The general solution behavior of eight compounds was investigated and qualitatively interpreted using the regular solution model and solubility parameter theory. The phase behavior of one trisamide in dioctylphthalate and aromatic solvents, where gels were formed, was investigated in more detail. The gel network morphologies were investigated by scanning electron microscopy (SEM) and X-ray scattering methods were used to characterize the crystal structures. Scanning force microscopy (SFM) was used to characterize the LMOG/low T_g polymer systems. The gelation of TREN-EB organic solvent solutions has also been characterized by polarized optical microscopy to check for birefringence as a proof of self-assembly of the LMOG.

4.2 Synthesis and characterization of tripodal trisamide compounds

A series of tripodal trisamide compounds have been synthesized from tris(2-aminoethyl)amine (TREN) by condensation with different acid chlorides. The chemical

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structures were characterized by ESI/MS and NMR. The ^1H and ^{13}C NMR spectra of tripodal trisamide compounds are shown in Appendix.

Figure 4.1. Synthesis of the tripodal trisamide compounds.

The peak melting temperature and heat of fusion of each compound were measured by differential scanning calorimetry and are listed in Table 4.1 as T_m° and ΔH_f° . The DSC curves are shown in Figure 4.2. The solubility parameters of the tripodal trisamide compounds are calculated from the group contribution method⁴⁴,

$$\delta = \sqrt{\frac{\sum E_i}{\sum V_i}} \quad (4.1)$$

Where E_i and V_i are the contribution from each chemical unit to the cohesive energy density and the molar volume, respectively.

Figure 4.2. DSC 2nd-heating traces of the tripodal trisamide compounds.

Table 4.1. Thermal properties measured by differential scanning calorimetry measurement and solubility parameters of the tripodal trisamide compounds.

Compound	T_m° (°C)	ΔH_f° (kJ/mol)	V (cm ³ /mol)	δ (MPa ^{1/2})
TREN-C5	102	32.0	362	23.1
TREN-C6	108	28.5	410	22.3
TREN-C7	104	42.3	458	22.0
TREN-C8	111	47.2	506	21.7
TREN-C9	109	49.3	555	21.3
TREN-C10	115	74.1	603	21.0
TREN-CH	212	53.2	403	23.5
TREN-EB	186	62.2	411	22.2

4.3 Solution Behavior of Trisamides

The gelation behaviors of the trisamides were tested with regard to their gelation properties and minimal gelation concentration (MGC) in a range of selected organic solvents. 20mg tripodal trisamide compound was mixed into 1mL of the selected solvent and heated to 150°C, then cooled to 20°C by a water bath. If a gel formed, the MGC was then measured by incrementally decreasing the amount of gelator in the solvent. The results and the total Hansen solubility parameter for each solvent are listed in Table 4.2.

Table 4.2. Solution Behavior of Trisamide Compounds

GELATOR (TREN-X)		C10	C9	C8	C7	EB	C6	C5	CH
Solvent	T _m (°C)	115	109	111	104	186	108	102	212
	δ (MPa ^{1/2})	21.0	21.3	21.7	22.0	22.2	22.5	23.1	23.5
PDMS 770	15.3	I→P	I→P	I→P	I→P	I→1.8(c)	I→P	I→P	I→P
<i>n</i> -Decane	15.8	P	P	P	I→20(c)	I→9.1(c)	I→3.1(c)	N/A	I→P
Dodecane	16.0	P	P	P	I→8.3(c)	I→9.1(c)	I→2.9(c)	N/A	I→P
Squalane	15.9	I→12.5(c)	I→10(c)	I→P	I→20(c)	I→0.3 (c)	I→P	I→P	I→P
Cyclohexane	16.7	P	P	20(c)	P	E	5.6(c)	10(c)	E
<i>sec</i> -Butylbenzene	17.0	P	P	P	P	4.4	P	P	3.6(c)
<i>o</i> -Xylene	18.1	P	P	S	P	3	S	P	4.5(c)
Toluene	18.2	P	S	S	S	4.4	S	P	8.3(c)
Benzene	18.5	S	S	S	S	6.7	S	S	12.5(c)
Methyl ethyl ketone	19.1	S	P	S	S	20 (c)	S	S	P
Chlorobenzene	19.5	S	S	S	S	8	S	S	S
Acetic acid	21.4	S	S	S	S	S	S	S	S
Isopropyl alcohol	23.6	S	S	S	S	S	S	S	S
Dimethylformamide	24.9	S	S	S	S	S	S	S	S
Ethanol	26.5	S	S	S	S	S	S	S	S
Dimethylsulfoxide	26.7	9.1(c)	S	S	S	S	S	S	S
Methanol	29.8	S	S	S	S	S	S	S	S
Ethylene Glycol	32.9	P	10(c)	P	P	S	S	N/A	S

Key: δ - solubility parameter, I – forms insoluble droplets elevated temperature, E – solvent evaporates before dissolution, S – soluble at room temperature, P – precipitates at room temperature, # - minimum concentration for gelation in mg/mL, (c) cloudy gel.

A good gelator should gel as many kinds of solvent as possible. In Table 4.2 the solutions with minimum gel concentration numbers are the ones that form a gel, which is desired. From Table 4.2 we can see that compounds made with linear alkyl chains were poor gelators, while TREN-EB was an excellent gelator for many organic solvents, while TREN-CH with a cyclohexane end group can also gel several organic solvents with moderate solubility parameters. This may be explained by their different thermal properties. From Table 4.1 we can see that TREN-EB and TREN-CH have much higher crystallization temperatures than the other linear tripodal trisamide compounds, which

will provide larger undercoolings and larger driving forces for crystallization. It has been found that gelation was more favorable at larger undercoolings attributed to greater nucleation of LMOG crystals and a crossover to dendritic crystal growth¹. The branching density of the LMOG network also increases with increasing undercooling^{24,72-74}. When the solutions are quenched to room temperature from elevated temperature there will be a greater chance that the crystal fibers will be formed and aggregate to form a 3-dimensional network favorable for gelation. To further demonstrate the importance of extent of undercooling on gelation, TREN-EB/aromatic solvent solutions (20 mg/mL) were quenched to different temperature from elevated temperature and the solution states are listed in Table 4.3. As the quench temperature was increased a transition was seen from gelation to a homogeneous solution due to smaller undercooling, with precipitate formation at intermediate temperatures in some cases.

Table 4.3. Effect of quench temperature on TREN-EB solutions.

	Quench Temperature			
Solvent	20°C	40°C	60°C	80°C
<i>sec</i> -butyl benzene	G	G	G	S
<i>o</i> -xylene	G	P	S	S
Toluene	G	G	P	S
Benzene	G	G	P	S
methyl ethyl ketone	G	S	S	S
chlorobenzene	G	S	S	S

Key: (G) gelation, (P) precipitate, (S) remains soluble

Second, since 3D-crystallization of the self-assembled aggregates must be avoided, a balance between order and disorder has to be found. Although it is obvious that a certain degree of (one-dimensional) order is required to achieve self-assembly in one direction, the packing in the other directions should be far from ideal. The branched alkyl end chain of TREN-EB and bulky cyclo end group of TREN-CH can suppress the aggregation in directions other than the fiber direction, which may lead to large scale 3D-crystallization then eventually precipitation. This also explains why TREN-EB and TREN-CH work better as LMOGs than the compounds with linear alkyl chains, which form precipitates most of the time^{10,75}.

The formation of an organogel is also a result of the gelator-solvent interactions, from Table 4.2 we can see that different solvents act differently towards the same gelator. Polar solvents such as methanol interact with the gelators strongly and thus weaken the H-bonding between the gelators, which is the main driving force for all the above organogels. When the solvent-gelator interaction is too strong, the fibrous structure disappeared and the gelator dissolves in the solvent such as in alcohols where H-bonding substantially contributes to the overall solvent-gelator interaction. This compromises gelator-gelator H-bonding interactions, which lead to poor gelation. In the aromatic solvents, which are far less potent H-bonding solvents compared to alcohols, nonspecific forces dominate solvent-gelator interactions; therefore, the minimum gelation concentrations are relatively high. When the gelator-solvent interaction is very weak such as in some poor solvents with low polarity, cyclohexane for example, gelator-gelator self-interactions are highly preferred, the gelator either would not dissolve or precipitated through 3D-crystallization⁷⁶.

Solvent solubility parameter serves as a useful indicator of the solvation power of the solvent toward the gelators and therefore, impacts gelation. The gelator-solvent interaction strength can be directly related to the difference of solubility parameters of a gelator and a solvent. Usually, with increasing difference the interactions between gelator and solvent decrease^{44,51,52}. When the distance between the solubility parameters of solvent and the solubility parameters of the TREN-EB, $(\delta_1 - \delta_2) \geq 6.3$, is large. In PDMS, decane and squalane for example, the unfavorable gelator-solvent interaction is very strong, gelator-gelator self-interactions are highly preferred, the gelator either would not dissolve or precipitated through 3D-crystallization. When the distance between the solubility parameters of solvent and the solubility parameters of the TREN-EB, $3.1 \leq (\delta_1 - \delta_2) \leq 5.2$, is moderate, the aromatic solvents for example, the gelator-solvent interaction are appropriate to form stable gels. Indeed, clear trends were obtained for both of the branched alkyl end chain gelators. It can be concluded that gelation requires that the gelator-solvent interaction be neither too strong nor too weak, otherwise solution or precipitate are formed. However, the use of solubility parameter theory to quantify solute-solvent interactions is less accurate when specific solute-solvent attractive interactions exist, such as solvent-solute hydrogen bonds existing in polar alcohol and glycol solutions. Although large values of $(\delta_1 - \delta_2)$ are observed at the bottom of Table 4.2, these solvents are strongly polar and likely to form specific interactions with the trisamides, such as hydrogen bonds which will enhance liquid-liquid solubility.⁷⁷

($\delta_1 - \delta_2$) of TREN-EB and MEK is only 3.1 and should be able to gel the solvent easily, but solvent-solute hydrogen bonds are likely to form due to the carbonyl group in MEK, which will enhance liquid-liquid solubility and thus requires more TREN-EB for self-aggregation into networks.⁷⁷ This can explain the large MGC in MEK.

4.4 Investigation of gel morphology and crystal structures

The gel morphologies are observed by scanning electron microscopy (SEM), Wide angle X-ray scattering measurement and Optical polarizing microscopy measurement.

4.4.1 The gel network morphology

The gel network morphologies are observed by scanning electron microscopy (SEM).

Figure 4.3. organogels of TREN-EB and benzene were formed by mixing a known amount of TREN-EB and benzene, heating the solution at elevated temperature and then quenching the vials in a water bath at 20°C. Self-supporting gels were formed.

These organogels were freeze-dried using a Schlenk line and the xerogels were examined by scanning electron microscopy. As shown in Figure 4.5, 4.6, 4.7, TREN compounds formed a nanofibrillar network structure during gelation. The higher the concentration of the gelator, the denser the fiber networks are.

Figure 4.4. Freeze-dry of TREN-EB/benzene organogels(40 mg/mL).

Figure 4.5. SEM images of the freeze-dried TREN-EB/benzene gel, the concentration of TREN-EB in benzene is a) 20mg/mL. b) 80mg/mL c) 130mg/mL

Figure 4.6. SEM images of the freeze-dried TREN-C6(left), TREN-C8(right)/cyclohexane gel, the concentration is 40mg/mL.

Figure 4.7. SEM images of the freeze-dried TREN-CH/benzene gel, the concentration is 20mg/mL.

4.4.3 Wide angle X-ray scattering measurement

The molecular packing arrangements of the TREN-EB gelator in the gel and other phases are investigated by X-ray diffraction. Wide angle X-ray scattering (WAXS) is used here to compare the crystal structure of the gelator in the LMOG/liquid systems to the pure gelator crystal.

Figure 4.8. Azimuthally averaged WAXS patterns for (a) TREN-EB powder, (b) freeze dried 70 mg/mL TREN-EB/toluene gel, (c) freeze-dried 70 mg/mL TREN-EB/benzene gel, and (d) 70 mg/mL TREN-EB/toluene gel. The curves have been shifted vertically for clarity.

Azimuthally averaged wide angle X-ray patterns of the pure TREN-EB, freeze-dried xerogels from TREN-EB/benzene and TREN-EB/toluene gels, and a TREN-EB/toluene gel are shown in Figure 4.8. Good overlap between the neat TREN-EB and the freeze-dried gel peak positions indicate the same ordered structure. The broader peaks in the freeze dried gel indicate a more defective crystal structure than the pure gelator. XRD

studies demonstrate that the self-assembled fibrillar networks and the neat solid have the same packing, regardless the morphological changes during freeze drying due to capillary forces¹⁴. Only a broad peak with a shoulder was observed in the TREN-EB/toluene gel.

4.4.2 Optical polarizing microscopy measurement

The gelation of TREN-EB organic solvent solutions has also been characterized by polarized optical microscopy to check for birefringence as a proof of self-assembly of the LMOG.

Figure 4.9. Cross polarizing optical microscope picture of: TREN-EB/Toluene gel, 20mg/mL, in flat microscope cover glass.

Figure 4.10. TREN-EB/o-xylene gel(30mg/mL) tube under cross polarizing optical microscope. Phase changes observed took place at the gel-liquid transition temperature.

The TREN-EB/o-xylene gel sealed in capillary glass tube displayed birefringence under cross polars in an optical microscope and the birefringence disappeared at certain elevated temperature when the gelator crystals disassembled. The melting temperature (118°C) coincided with the T_{gel} measured by the heat & tilt method. This demonstrates that the gel transition corresponds to the disordering of the LMOG. Cross polarizing optical microscope provides another efficient method to measure the gel-liquid transition temperatures.

4.4.4 Gel Transition Temperatures

If gelation is driven by the solidification of the LMOG there should be a direct correlation between the gel transition temperature (T_{gel}) and the melting temperature (T_{m}) of the solid phase. Dioctylphthalate (DOP) is one of the most widely available and cost effective commonly used plasticizers for many resins, especially PVC⁷⁸. DOP is a high boiling point liquid and its low volatility allowed a measurement of the melting temperature of TREN-EB as a function of concentration by differential scanning calorimetry (DSC), where T_{m} was assigned to the peak position of the DSC traces are shown in the Appendix.

Figure 4.12 shows T_{gel} and T_{m} vs. mole fraction of gelator, T_{m} comes from the DSC traces indicating the melting temperature of the gelator, while T_{gel} was measured by heat & tilt method, it is the temperature at which the sample first flowed when inverted, corresponding to the bulk rheological transition from a gel to a free-flowing solution, as shown in Figure 4.11.

Figure 4.11. 'Heat & Tilt' method to measure T_{gel}

Figure 4.12 shows T_m (open symbols) from DSC and T_{gel} (closed symbols) from the Heat & Tilt measurement for gels of TREN-EB in DOP. T_m detected by calorimetry measured the dissolution of individual gelator strands microscopically. On the other hand, T_{gel} corresponds to the temperature at which the gel loses its structural integrity and some of the compound may still be aggregated, however those aggregates are too small to sustain a network. That is why T_m is consistently higher than T_{gel} as shown in Figure 4.12. Given the relatively small difference of T_{gel} and T_m for TREN-EB in DOP, the simplifying assumption was made that $T_{gel} \approx T_m$. DSC measurements of TREN-EB in aromatic solvent gels were also attempted, however, solvent evaporation even with hermetically sealed DSC pans generated multiple peaks in the DSC curve, it is difficult to identify the LMOG melting peak itself.

Figure 4.12. T_m (open symbols) and T_{gel} (closed symbols) for TREN-EB in DOP. The inset shows $T_m - T_{gel}$ vs. x_2 . The solid line is the predicted liquidus line from Equation 2.9 using zero free parameters.

The solid line in Figure 4.12 is the liquidus line predicted from Equation 2.9,

$$T_{gel} = \frac{\frac{\Delta H_f^o}{R} + A(1 - x_2)^2}{\frac{\Delta H_f^o}{R} \left(\frac{1}{T_m^o} \right) - \ln x_2}$$

using no free parameters. ΔH_f^o and T_m^o of TREN-EB can be found in

. The interaction parameter coefficient A was calculated from Equation 2.12 with the solubility parameters of DOP and TREN-EB from Table 4.1,

$$A = \frac{V}{R}(\delta_1 - \delta_2)^2$$

The molar volume V is set as the geometric mean of the molar volume of TREN-EB and DOP calculated by the group contribution method. This prediction gives the shape of the T_{gel} vs. composition liquidus line. The inexact matching with the experimental data may be due to the simple assumptions of χ , which ignored more complex temperature dependence and excess entropy of mixing^{30,79}.

shows a plot of T_{gel} vs. composition for TREN-EB in different organic aromatic solvents which can be gelled, including 50:50 mixtures by volume of *sec*-butylbenzene: *o*-xylene and *o*-xylene: chlorobenzene. The solubility parameter of a mixture solvent is the volume average of the solubility parameters of the two component solvents⁸⁰. For the mixtures the liquidus lines lay in between the liquidus lines of the constituent solvents. This is as expected as the mixture solubility parameter is in between of the solubility parameters of the two separate components. In **Error! Reference source not found.**, A_{fit} is from the fitting of T_{gel} vs. composition data to Equation 2.9. A_{predict} values were calculated using the solubility parameters in Table 4.1 and 4.2 with Equation 2.12. A_{fit} is larger than A_{predict} due to a number of assumptions. First, it is assumed that $T_m \approx T_{\text{gel}}$, which is not accurate as discussed previously, T_m should be slightly higher than T_{gel} , this assumption leads to the underestimation of A . Second, the size of the LMOG fibers is assumed to be infinite thus the Gibbs–Thomson effect³⁰ referring to the observation that small crystals of a liquid melt at a lower temperature than the bulk is not included, which leads to the underestimation of A . Another deficiency in the regular solution theory resides in the inherent assumption that solvent is completely rejected from the gelator crystal, i.e., the chemical potential of the liquid solution was equated to that of the pure gelator crystal⁸¹. This deficiency in the regular solution theory overestimated A . To further describe the complete phase diagrams of the binary crystalline gelator solvent systems, the anisotropic interaction such as the repulsive crystal–solvent interaction should be included in the enthalpic contribution term. A fourth assumption was that the crystal structure of the LMOG in solution is the same as the bulk solid. This is not always true as polymorphs which have different bulk melting temperature (T_m^0) and heat of fusion (ΔH_f^0) have been

observed in other LMOG solvent systems.^{82,83,84} On the basis of the fitting results, it implies that if a polymorphic crystal was formed it would have a similar T_m° and ΔH_f° as bulk TREN-EB.

Figure 4.13. T_{gel} vs. composition for TREN-EB in different organic solvents, chlorobenzene (circles), toluene (upward triangles), o-xylene (downward triangles), and sec-butyl benzene (diamonds), o-xylene+chlorobenzene(squares), o-xylene+sec-butyl benzene (stars).

Takeno et al. previously found that using only $\chi = A/T$ under-predicted the experimental

liquidus lines, however when an interaction parameter of $\chi = A/T + B$, determined from the binodal line of the polymer/LMOG system was used, a good agreement between the predicted and experimental liquidus lines was achieved⁶⁹. The T_{gel} vs. composition data in Figure 4.12 and 4.13 were also fit using $\chi = A/T + B$, where B is the parameter to describe the excess entropy of mixing due to volume changes and solvent-solute packing⁶⁹,

$$T_m = \frac{\frac{\Delta H_f^o}{R} + A(1 - x_2)^2}{\frac{\Delta H_f^o}{RT_m^o} - \ln x_2 - B(1 - x_2)^2} \quad (4.2)$$

Where the $A_{predict}$ in Table 4.4 were used, $A_{predict}$ are calculated using the solubility parameters in Table 4.1 and 4.2 with Equation 2.12 and B was set as the varied fitting parameter. The fittings are shown in the Appendix (Figure A. 10) and the result B values are listed in Table 4.4. These fits are reasonable as B is found to typically be in the range from 0.2 – 0.6 empirically.⁵¹

Table 4.4. Fitting results of liquidus lines to Equation 2.9 and 4.2.

Solvent	δ_{solvent} (MPa ^{1/2})	A_{fit} (K)	A_{predict} (K)	B
<i>s</i> -bb	17.0	919	824	0.24
<i>o</i> -xyl	18.1	743	449	0.77
Tol	18.2	600	401	0.54
Cl-bz	19.5	335	180	0.43
<i>s</i> -bb: <i>o</i> -xyl	17.6	844	619	0.58
Cl-bz: <i>o</i> -xyl	18.8	510	296	0.58
DOP	19.4	534	390	0.35

Key: *s*-bb – *s*-butylbenzene, *o*-xyl – *o*-xylene, tol – toluene, -Cl-bz – chlorobenzene. A_{fit} from fitting T_{gel} vs. composition data to Equation 2.9. A_{predict} calculated with Equation 2.12.

In Figure 4.14, T_m was calculated for TREN-EB and TREN-CH at the minimum gelation concentration at 25°C listed in Table 4.2 using Equation 4.2. ΔH_f° and T_m° from Table 4.1, A_{predict} and B from

Table 4.4 were used. $B = 0.4$ was used for solutions where no gel transition temperatures were measured. The level of undercooling required for gelation by TREN-CH is consistently higher than TREN-EB. This indicates that TREN-EB has a greater inherent ability to self assemble into three-dimensional fibrillar structures. Larger undercoolings are required in both TREN-EB and TREN-CH to gel *sec*-butylbenzene compared to other aromatic solvents; it may be due to the influence of liquid-liquid phase separation as liquid-liquid immiscibility becomes increasingly favourable as the solvent solubility parameter decreases. TREN-CH was found to be soluble in chlorobenzene at 20 mg/mL at 25 °C. The T_m of TREN-CH in chlorobenzene was calculated to be 368K At 20 mg/mL and is plotted as an open symbol. At this concentration and temperature the system is close to the minimum undercooling needed for gelation explaining why gelation was not observed here.

Figure 4.14. Calculated T_m vs. δ_s at the minimum gel concentration for TREN-EB (squares) and TREN-CH (circles). The open circle is the T_m for TREN-CH in chlorobenzene at 20 mg/mL concentration.

This calculation of the melting temperature at the minimum gelation concentration demonstrates predictive capability of the regular solution model for LMOGs. Here the MGC is linked to the minimum level of undercooling needed for gelation after a thermal quench from elevated temperature and consistent data is obtained for systems where the liquidus line was directly measured or predicted from the thermodynamic parameters of the individual components. The predictive capability of the regular solution model should be useful for the design of new LMOGs. This includes predicting the range of the undercooling and gel transition temperatures in different solvents; the minimum gelation concentration if the minimum undercooling for gelation is known; and more complex

phase behavior where liquid-liquid and liquid-solid phase separation are pathways are both operative. One area for improvement is in the use of interaction parameters in the regular solution that quantify specific solute-solvent attractive interactions, such as solvent-solute hydrogen bonds that are prevalent in many LMOG systems. These interactions are not accounted for in the basic solubility parameter theory. At the same time, once this deficiency is recognized solubility parameter theory remains a useful tool for an initial assessment of solution behavior.

4.5 Gelation of ionic liquid

An ionic liquid is a salt in the liquid state with a melting point below room temperature; ionic liquids are non-volatile and have good electrical conductivity and excellent chemical stability. They are high-potential liquids in a broad range of applications, for example in chemical reactions as a catalyst, in electronic devices as electrolytes, or as functional and engineering fluids^{23,85}. Gelation of an ionic liquid makes it ion conductive but with the solid-like viscoelasticity, which can be used as stable gel electrolytes in electronic devices such as dye-sensitized solar cells²³.

Here we performed a detailed study on preparation and characterization of an ionic liquid-gel with TREN-EB and the ionic liquid 1-ethyl-3-methylimidazolium thiocyanate (EMINC), which is commercially available. To make the gel, TREN-EB was mixed into 1mL EMINC and co-dissolved in a solvent mixture of CHCl_3 +Methanol (2:1 in volume), followed by rotovapping and vacuum drying at 80 °C to remove the solvent. The minimum gelation concentration was 16.7 mg/mL.

Figure 4.15. The chemical structure of 1-ethyl-3-methylimidazolium thiocyanate (EMINC)

Figure 4.16. A picture of TREN-EB in EMINCS gel, the concentration is 20 mg/mL.

A rotational parallel plate rheometer was used to measure the viscoelastic properties and observe the gel-solution transition temperature T_{gel} of the TREN-EB in EMINCS gel. It was found in Figure 4.18 that at T_{gel} (approximately 90°C), both G' and G'' decrease

sharply due to the loss of solid elasticity. T_{gel} increases with the concentration of gelator as expected, as shown in Figure 4.18.

Figure 4.17. Storage and shear modules of 1 wt% TREN-EB in EMINCS gel as a function of temperature, $\omega=0.1$ rad/s, heating rate = $5^{\circ}\text{C}/\text{min}$.

Figure 4.18. T_{gel} of TREN-EB in EMINCS gels vs. weight percentage of TREN-EB.

Figure 4.19. Storage and shear moduli of 1 wt % TREN-EB in EMINCS gel as a function of frequency at 70 °C.

In the rheological definition of gel, below the gel-solution transition temperature the storage modulus G' and the loss modulus G'' should be frequency independent with a plateau extending over an appreciable range of frequency. Also, because the gel is elastic, G' is higher than G'' ^{11,12}. The frequency dependent rheological measurements data in Figure 4.19 agree with this definition.

The ionic conductivity of the gel can be measured through the electrical impedance (Z) of the gel at different frequencies⁸⁶. Figure 4.20 gives the ohmic resistance R of the gel by the intercept of the impedance curve with the x-axis. The conductivity of the 4%wt Ten-EB + EMIMS gel was then calculated by the following equation,

$$\sigma = L/R \cdot S = 0.046 / (27 \cdot 0.64) = 0.00266 \text{ S/cm} = 2660 \text{ } \mu\text{S/cm}$$

where σ is the specific conductivity, R is the ohmic resistance, L is the thickness of the of the gel, and S is cross sectional area of the gel.

Figure 4.20. Impedance spectrum of a 4%wt Ten-EB + EMIMS gel at room temperature.

The ionic conductivity of pure EMIMS is 2600 $\mu\text{S}/\text{cm}$ at 25 °C (data from BASF), the conductivity of the gel measured by the impedance spectroscopy is very close to that of the pure EMIMS, which proves that the TREN-EB gelator will not negatively affect the ionic conductivity of the ionic liquid.

4.6 Polymeric solvent

Low molecular weight liquid polymers can be used as gel solvents. The use of a polymer as the gelling fluid allows for in-situ characterization of the gel morphology, which is more difficult with gels of volatile organic solvents. Different kinds of low glass transition temperature liquid polyacrylates were synthesized by RAFT polymerization⁸⁷.

DBTC:

Figure 4.21. RAFT polymerization of polyacrylates

Table 4.5. Results of the polymerization

R	Target Mn (kDal)	Mn (kDal)	PDI
methyl	1	1.4	1.13
methyl	1.5	1.7	1.2
methyl	10	11.9	1.2
ethyl	1	1.8	1.18
ethyl	10	10.8	1.16
n-butyl	1	2.1	1.17
n-butyl	10	14.5	1.18

Table 4.5 lists the results of the polymerization products characterized by size exclusion chromatography (SEC), all the polymers with different R groups can be gelled by TREN-EB at 2 wt%. To make the gel, TREN-EB was mixed with the polymer and dissolved in a

solvent mixture of CHCl_3 and methanol(2:1 by volume), and then rotovaped and vacuum dried at 60°C overnight to remove the solvent and obtain the dry gels which would not flow at room temperature. Figure 4.22 shows the picture of 2 wt % TREN-EB in PMA($M_n=1.7\text{KDal}$) gel.

Figure 4.22. PMA(1.7KDal) with 2 wt % TREN-EB gel.

The morphology of TREN-EB-polymer gels were investigated by spin-coated thin films of 2 wt% TREN-EB in 1.7 kDal polymethylacrylate(PMA) by atomic force microscopy (AFM). As shown in Figure 4.23, in the absence of the gelator, the AFM phase image of the pure amorphous polymer is featureless as expected. For the gelator/polymer mixtures, nanostructured morphologies are observed. Since the solid gelator has higher modulus than the PMA matrix, the gelator should be the bright fiber-like structures in the film.

Figure 4.23. AFM phase images of (a) pure PMA and TREN-EB + PMA spun from (b) benzene, (c) toluene, and (d) chloroform.

The gelator concentration changes rapidly during spin-coating from volatile solvent. The morphology differences such as the fiber diameters and the distance between junction points reflect the influence of the solvents. Different solvent volatility is equal to different cooling rate of gelation; and the solubility parameter will control the concentration at which gelation occurs.

Figure 4.24. AFM height images of thin films of 2 wt% TREN-EB in a (a) 2kDa PMA and (b) 12 kDa PMA.

The AFM height images of TREN-EB in PMA homopolymer of 2 kDa and 12 kDa molecular weight films are shown in Figure 4.24. Three dimensional supramolecular network of the LMOG is observed in both of them. However, the length scale of the network is an order of magnitude larger in the higher molecular weight polymer. When the molecular weight of the polymer is increased the miscibility of the polymer and gelator will decrease due to the reduction of entropy of mixing³⁰. Therefore, in the higher molecular weight polymer it is more likely that liquid-liquid phase separation would take place between the LMOG and polymer. These results demonstrate that in addition to influencing the ability of a compound to act as a gelator the phase behavior also influences the morphology of the gel. Multiple, competing ordering processes, such as crystallization and liquid-liquid phase separation should produce more complex phase

behavior in gel systems, which could result in a wider range of bulk properties, such as modulus, reversibility, and clarity.

4.7 Summary

In this chapter, the tripodal trisamide compounds were studied as model LMOGs due to the simple one-step reaction and the commercially available chemical reactants. Branched end chain tripodal trisamide compounds form thermoreversible organogels in certain organic solvents, amorphous polymers and ionic liquid. Gelation of organic solvents was investigated as a function of concentration and solvent solubility parameter. SEM and AFM proved the nanofibrillar network morphologies. It has been found that the introduction of branches or cyclic end units have dramatic effects on the gelation ability. The prediction of the liquidus lines using the regular solution model and solubility parameter theory reproduced the shape and scaling of the gel transition temperature vs. composition in different aromatic solvent solutions. These results demonstrate that non-ideal solution behavior is an important factor in the gelation behavior of low molecular mass organic gelators.

CHAPTER V

THE GELATION BEHAVIOR OF 12-HYDROXYSTEARIC ACID

5.1 Introduction

12-hydroxystearic acid (HSA) can serve as a good model LMOG to investigate the thermodynamic phase behaviors of LMOG/liquid system, it is commercially available and has simple chemical structure which can self-aggregate into fibers through intermolecular H-bonding⁶². In this chapter HSA is used to study gelation in a number of systems including organic solvents, vegetable oil, and low glass transition temperature polymers.

5.2 The solution behavior of HSA towards organic solvents

The gelation behavior of 12-hydroxystearic acid (HSA) was tested in a range of selected organic solvents. 20mg HSA was mixed into 1mL of the selected solvent and heated to 150°C, then cooled to 25°C by water bath. The results and the total Hansen solubility parameter for each solvent are listed in Table 5.1.

Table 5.1. Solution Behavior of HSA in different organic solvents.

Solvent	δ (cal ^{1/2} /cm ^{3/2})	Solution Behavior
Squalane	7.3	G(c)
Cyclohexane	8.2	G(c)
s-butylbenzene	8.4	G
o-xylene	8.9	G
Toluene	8.9	G
Benzene	9.2	G
Chlorobenzene	9.5	G
MEK	9.3	S
DMSO	12.0	S
DMF	12.1	S
Methanol	14.5	S

Key: δ - solubility parameter, S - soluble at room temperature, G- gel, (c) cloudy gel.

The formation of an organogel is a result of the gelator-solvent interactions, from Table 5.1 we can see that different solvents act differently towards HSA. Solvent solubility parameters serve as a useful indicator of the solvation power of the solvent toward the gelators and therefore impacts gelation. The gelator-solvent interaction strength can be directly related to the difference of solubility parameters of a gelator and a solvent. Usually, with increasing difference the interactions between gelator and solvent decrease^{44,51,52}. When the distance between the solubility parameters of solvent and the solubility parameters of the gelator $\delta_1 - \delta_2$ is small, the gelator-solvent interaction is very weak such as in some poor solvents with low polarity. Take cyclohexane and squalane for example, gelator-gelator self-interactions are highly preferred, the gelator molecules self-aggregate into fibers large enough to scatter visible light, thus the gels formed are cloudy⁷⁶. When $\delta_1 - \delta_2$ is moderate, the aromatic solvents for example, the gelator-solvent interaction are appropriate to form stable clear gels.

However, when specific solute-solvent attractive interactions exist, such as in solvents with oxygen in their molecules, solvent-solute hydrogen bonds are likely to form, which

will enhance liquid-liquid solubility and form a homogenous solution instead of gelation.⁷⁷ This can explain the solution behaviors from MEK to methanol in Table 5.1.

Figure 5.1. HSA-Xylene gels, from left to right, the concentration of HSA is 0.1, 0.3, 0.5, 0.6, 0.8 g/ml.

Figure 5.1 shows a picture of HSA/xylene gels with increasing gelator concentration, gels get cloudier as the HSA concentration increases, maybe because of denser gelator network and larger aggregation sizes which can scatter visible light eventually.

5.3 Vegetable oil gels

Vegetable oil has a high boiling point which makes it a stable solvent for gelation study under normal condition. Here we prepared gels of HSA of weight percentage at 1, 2, and 4 wt% separately by heating HSA and vegetable oil together at

150°C to form a homogenous solution, followed by cooling at room temperature. Differential Scanning Calorimetry (DSC) was used to determine the melting point of gels of different HSA concentration (Figure 5.2). Heating of a gel resulted in a single endothermic peak which was assigned as the melting point of the gel, T_m . T_m increases with the increase in the gelator concentration due to the thermodynamics of melting point depression. The broad melting peak could indicate a range of crystal sizes in solution.

Figure 5.2. DSC heating curves of HSA-vegetable oil gels of different HSA weight percentage.

5.3.1 Characterization of the rheological behaviors

A parallel plate rheometer was used in oscillatory shear mode to determine the rheological behavior of HSA-vegetable oil gels^{74,88}. The effect of shear strain on the G' and G'' at constant frequency (0.1 rad/s) was evaluated. Below ~1% deformation, it was observed that G' and G'' are independent of the applied strain at each specific strain, i.e. the linear viscoelastic behavior (Figure 5.3). As a result, the frequency and temperature sweep tests were carried out in the linear viscoelastic range. G'' of 1 wt% gel shows large scatter value below 1% deformation, which may be due to the weakness of the gel of extremely low HSA concentration whose modulus is near the limit of the rheometer transducer. There is also a variation in the absolute G' and G'' where it is larger at 2 and 4% strain compared to that measured at 1% strain.

Figure 5.3. Strain dependence of the G' and G'' at a constant angular frequency (0.1 rad/s) for the HSA-vegetable oil gels of different HSA weight percentage.

The plots of G' and G'' vs frequency are given in Figure 5.4-5.6. It can be seen that for each gel with increasing frequency G' and G'' slightly increase, that's because with increasing frequency, i.e. shorter relaxation time, the sample flexibility is reduced and becomes even more rigid. And the storage modulus G' is higher than the loss modulus G'' in the whole frequency range, which proves that the elastic behavior of the gel predominates over its viscous behavior and the gels exhibit mechanical rigidity. In addition, there is a dependence of the storage modulus on the strain amplitude, where in

general G' decreases as the strain increases. This could reflect a perturbation of the gel by the applied strain.

Figure 5.4. Angular frequency dependence of the G' and G'' at constant strains for 1 wt% HSA-vegetable oil gel at 25°C.

Figure 5.5. Angular frequency dependence of the G' and G'' at constant strains for 2 wt% HSA-vegetable oil gel at 25°C.

Figure 5.6. Angular frequency dependence of the G' and G'' at constant strains for 4 wt% HSA-vegetable oil gel at 25°C.

The strain amplitude for all measurements in Figure 5.7-5.9 was well within the linear viscoelastic regime. The temperature was increased slowly from 25 to 75°C at 5°C per minute. It is clearly shown by the decreasing in G' and G'' , that on increasing temperature the HSA molecules go from an ordered structure to a disordered structure. The point at which G' and G'' begin to decrease sharply tells us the gel-solution transition temperature, above which only the liquid phase exists. Again there is some dependence of the modulus on the strain amplitude. It is difficult to get a systematic correlation comparing the frequency and temperature dependent data, which could be due to a convolution of the

perturbation of the sample and the history during the rheological testing. The effects of the testing on the properties of the gel therefore make it more difficult to interpret the rheological data.

Figure 5.7. Temperature dependence of the G' and G'' at constant strains for 1 wt% HSA-vegetable oil gel. Angular frequency = 0.1 rad/s.

Figure 5.8. Temperature dependence of the G' and G'' at constant strains for 2 wt% HSA-vegetable oil gel. Angular frequency = 0.1 rad/s.

Figure 5.9. Temperature dependence of the G' and G'' at constant strains for 4 wt% HSA-vegetable oil gel. Angular frequency = 0.1 rad/s.

5.4 Cavitation rheology measurements

The mechanical properties of HSA-vegetable oil gels were also measured using cavitation rheology over a range of temperature. The cavitation rheology measurements were done by Steve Wood, a high school teacher at Hoover High School in North Canton, OH who was a summer researcher in the laboratory. In the cavitation rheology measurement, the pressure inside an air bubble blown in a gel was monitored

and recorded. When the pressure in the syringe pump reaches the gel's critical pressure, which is related to the local modulus of the material, the bubble suddenly expands and the pressure drops^{89,90}. Cavitation rheology is a simple and easy method to determine the modulus of a gel, it doesnot have the problem of after experiment cleaning and requirement of large amount of sample like in the parallel plate rheometer measurements. Figure 5.10-5.12 shows the results of the temperature sweeps of HSA-vegetableoil gels of different HSA concentrations. The dots are data from cavitation rheology measurements, the vertical line is the T_{gel} measured by the heat and tilt method, which is in the range of the pressure dropping zone and proves the effectiveness of the measurement. For each sample, an almost constant pressure was found at low temperature followed by a sharp drop indicating the onset of the elastic instability due to heating, which causes the gelator network to collapse and melt eventually. In other words, measuring the critical pressure for cavitation can provide a simple, quantitative measurement of gel-solution transition temperature. Compared with the rough decreasing G' & G'' vs. temperature data from rotational rheometry of low HSA concentration gels (1%, 2%), the cavitation rheology gives out more accurate measurement with a pressure plateau and a clear pressure drop afterward. This could be due to the brittle nature of HSA organogels. As seen from the rheology experiments the linear viscoelastic region only existed up to ca. 1% strain. Therefore, there is always the trade-off in the oscillatory shear measurement of applying enough strain to obtain a signal to measure the gel modulus while possibly distorting the gel at higher strain.

Figure 5.10. Temperature dependence of pressure of air cavitation for 1 wt% HSA vegetableoil gel.

Figure 5.11. Temperature dependence of pressure of air cavitation for 2 wt% HSA vegetableoil gel.

Figure 5.12. Temperature dependence of pressure of air cavitation for 4 wt% HSA vegetable oil gel.

Table 5.2. The transition temperatures from different measurements

<div style="display: inline-block; transform: rotate(-45deg);"> T_{gel} °C wt% of HSA </div>	Heat and tilt	Cavitation rheology	Parallel plate rheology
1	53	40	45
2	59	45	50
4	64	51	55

In Table 5.2 the transition temperature for cavitation and parallel plate rheology are listed for the main deviation of the modulus or critical pressure with increasing temperature. These are significantly lower than the transition temperatures measured by the heat and tilt measurement. Therefore, as the gel is heated it appears to go through a broad transition region where its stiffness is slowly reduced until it can no longer support and stress and flows under shear or gravity.

5.5 Phase behaviors of HSA-Naphthalene binary mixture

Naphthalene is used as a crystalline solvent here to study the phase behaviors with HSA. Naphthalene is an aromatic hydrocarbon chemical and should not form any specific interactions with HSA molecules such as H-bonding, and is thus a simple systemsuitable for thermodynamic phase behavior study (Figure 5.13). To obtain a uniform mixture of HSA and Naphthalene, a powder mixture was melt at 120°C followed by cooling at the room temperature. Differentialscanning calorimetry (DSC) analysis was then conductedwhere the temperaturewas increased from room temperature to 100°C at a rateof 5°C per minute (Figure 5.14).

Figure 5.13. Chemical structure of naphthalene.

Figure 5.14. DSC measurements of HSA and naphthalene mixtures, wt% of HSA increases from 0 to 100%.

Figure 5.15 shows T_m vs. mol fraction of HSA in naphthalene. Melting points from DSC scans are marked as red and black points, which shows a typical two-component eutectic phase diagram with a eutectic point at a mole fraction of $x_{\text{HSA}} = 0.4$. Using the ΔH_f° and T_m° values for HSA and naphthalene measured for the pure components, three lines are shown in the Figure. For each line the data to the left or right of the eutectic point was used to fit the naphthalene or HSA melting, respectively. The dotted line is the liquidus line predicted for an ideal solution from Equation 2.9 where the interaction parameter $A = 0$. Here the liquidus line is below the ideal prediction, which would indicate a larger

attractive interaction HSA and naphthalene then with the individual component molecules. From the solubility parameters and interaction parameter of coefficient of zero is predicted as both naphthalene and HSA have a solubility parameter of $20 \text{ MPa}^{1/2}$ where the solubility parameter of naphthalene is the tabulated value and the solubility parameter of HSA is calculated by the group contribution theory⁹¹. The navy line in Figure 5.15 is a fit to Equation 2.9 with A as a free parameter. A negative value of A is found indicating that the χ parameter is negative with a A/T temperature dependence. This negative χ cannot be predicted from the solubility parameter theory as $\chi \geq 0$ is only allowed. The pink line is a fit using $\chi = A/T + B$ where A is fixed at 0 from the solubility parameter prediction and B is a free parameter. Here a negative B parameter is obtained to account from the greater miscibility compared to the ideal solution model. The results of the fitting are listed in Table 5.3. These results are difficult to explain using just the regular solution model. First, there are no obvious specific interactions between HSA and naphthalene, which would indicate negative enthalpies of mixing giving a negative χ parameter. Therefore, further investigation is needed to understand the thermodynamic phase behavior of this system. A recommendation is to try and incorporate effects from solid solubility and crystal order into the fitting of the liquidus lines⁸¹. This includes additional free parameters, which may allow the negative deviation of the system from ideality to be explained.

Figure 5.15. T_m vs. mol fraction of HSA in naphthalene. The fitting lines are described in the text.

Table 5.3. Fitting results of liquidus lines to Equation 2.9 and 4.2.

	A_{fit} (K)	A_{predict} (K)	B
$X_2 < 0.4$	-1462	0	-4.24
$X_2 > 0.4$	-324	0	-0.95

5.6 Phase behaviors of polymer gels

In this section well-defined polybutylacrylates(PBA) and Polydimethylsiloxane (PDMS) polymers were used to study the phase behavior and thermodynamics of the gelator/liquid system by changing the LMOG concentration and degree of polymerization of the polymer. By changing the size of the gelled fluid it is possible to tune the entropy of mixing of the system. This could provide an addition method to systematically vary the thermodynamic phase space and investigate its influence on the gelation behavior.

5.6.1 Polybutylacrylates

Here two molecular weights of PBA were synthesized by RAFT polymerization, the number average molecular weights are 2.5kDal and 3.6kDal separately, and both of them were viscous liquids at room temperature. Different amounts of HSA were mixed with liquid PBA and co-dissolved in methanol, and then rotovaped and vacuum dried at 60°C to remove the solvent and obtain dry gels which did not flow at room temperature. Figure 5.16 shows a picture of HSA/PBA(Mn=2.5K) gels with increasing concentration. The gels get cloudier as the HSA concentration increases because of denser gelator network and larger aggregation sizes which can scatter visible light.

Figure 5.16. Gels of HSA in PBA(Mn=2.5K), from left to right, the concentration of HSA is 10, 30, 40, 60, 70, 100 mg/mL, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 wt%.

T_m from DSC vs. the mole fraction of HSA instead of the volume fraction is plotted in Figure 5.17. Here the data is counter-intuitive as the melting temperature is higher in the lower molecular weight polymer solution at equivalent mole fraction contrary to what would be expected from the Flory diluent theory where the melting point should increase with the increase in the size of the solvent due to reduction in the combinatorial entropy of the system. However this inconsistency is a consequence of plotting the data of a function of mole fraction, which does not accurately reflect the unequal molar volumes of the HSA and the polymer. Therefore in this case where there is a large molar volume asymmetry the data must be plotted as a function of volume fraction rather than mole fraction.

Figure 5.17. T_m measured by DSC vs. mol fraction of HSA in PBA of two molecular weights.

In Figure 5.18 the DSC results are plotted as a function of mole fraction and fit to The

results and fittings to equation 2.10: $\frac{1}{T_m} - \frac{1}{T_m^o} = -\frac{R}{\Delta H^o} \left[(\ln \phi_2 + (1 - \frac{1}{N})\phi_1 + \chi \phi_1^2) \right]$.

The Flory diluent theory in the introduction section predicts that in a polymer of larger degree of polymerization a larger T_m should be observed at the same volume fraction due to the increase in molecular weight until a high molecular weight limit is reached where the influence of molecular weight becomes negligible. In Figure 5.17 the liquidus line of HSA in PBA 3.6K is above that of HSA in PBA 2.5K. However, the difference is only slight,

which is likely due to the small difference in the two molecular weights rather than a reaching a high molecular weight limit where $1/N \approx 0$.

Figure 5.17. T_m measured by DSC vs. volume fraction of HSA in PBA of two molecular weights.

The fitting values of A listed in Table 5.4 of these two polymers are also close, which makes sense because of the similar chemical structures thus similar solubility parameters of the two polymers. A_{predict} can be calculated using Equation 2.12 from the solubility parameter of the two components. The molar volume V is set as the geometric mean of the molar volume of HSA and PBA, the molar volume of HSA ($305 \text{ cm}^3/\text{mol}$) is calculated by the group contribution method, the molar volume of PBA ($119.34 \text{ cm}^3/\text{mol}$) is found in <Polymer Handbook (4th Edition⁹¹)>. The Hansen solubility

parameter of PBA ($20.42(\text{MPa})^{1/2}$) is found in <Polymer Handbook (4th Edition⁹¹) >, and the solubility parameter of HSA ($20(\text{MPa})^{1/2}$) is calculated by the group contribution theory. Similar to results of the tripodal trisamide compounds A_{fit} overpredicts the interaction parameter coefficient compared to A_{predict} . This is likely due to the simplicity of the model, which ignores effects, such as the excess entropy of mixing. The positive values of A observed from the fitting indicate that this system can be treated with the regular solution model and solubility parameter theory in contrast to HSA in naphthalene where negative A values were observed from the fitting. This again indicates that complexities in the HSA/naphthalene system are due to the eutectic phase behavior of the system.

Table 5.4. The fitting values of A .

Mn of PBA (kDa)	$A_{\text{fit}}(\text{K})$	$A_{\text{predict}}(\text{K})$
2.5	647	3.86
3.6	669	3.86

5.6.2 Polydimethylsiloxane

PDMS is a commercially available polymer with a wide choice of molecular weights. It is a clear, colorless, viscous liquid at low molecular weight, which is good to be used as a non-evaporative solvent for gelation study. Here trimethylsilyloxy terminated PDMS was used to eliminate the end group interaction with HSA molecules. To make the gel, HSA was mixed with PDMS and heated above 180 °C to form a

homogenous solution, followed by cooling at room temperature. For PDMS of various molecular weights, from 200 to 20000, the mixture heated above 100°C but below 180°C formed solution with liquid droplets inside, which is likely phase separated, liquid HSA. Only by heating to a very high temperature could homogenous solutions be formed.

Figure 5.18 shows the picture of gels of HSA in PDMS ($M_n=237$ Dal), the gels are very opaque and have white lines inside, which may be due to the liquid-liquid phase separation upon cooling from a homogenous solution where the network can be by the HSA-rich phase and stabilized by its solidification. Therefore, these highly incompatible systems should allow for investigation of more complex phase behavior in gelator/solvent systems, such as liquid-liquid phase separation.

Figure 5.18. Gels of HSA in PDMS ($M_n=237$), from left to right, the concentration of HSA is 20,50,30,80,60, 100mg/ml.

5.7 Summary

The solution behavior of 12-hydroxystearic acid in organic solution and polymeric fluids were presented to study the solvent effects on gelation and phase behaviors, solvent solubility parameters and specific interactions are two important factors. The experimental melting temperature of HSA-Naphthalene binary mixtures gives out a typical two solid phase diagram. Cavitation rheology measurements and parallel plate geometry were used to characterize the transition temperature of the HSA-vegetable oil gels. Amorphous polyacrylates and PDMS were used as model liquids for the LMOG/liquid system. By changing degree of polymerization N of PBA we can finely tune the phase behavior and the Flory diluent theory gives an effective prediction of the thermodynamics and phase behaviors of the polymer-gelator system. HSA-PDMS system showed liquid-liquid phase separation behaviors, which should be useful in future investigations for studying the effects of competing liquid-liquid and liquid-solid phase separation on gelation.

CHAPTER VI

CONCLUSION AND RECOMMENDATIONS FOR FUTURE WORK

LMOGs are important due to potential applications in many fields. In spite of extensive research, until now the thermodynamics phase behaviors of the gel system and the nature of the interaction between the solvent and the gelator have not been fully understood.

This research describes the discovery of new tripodal trisamide gelators, which can serve as a good model system to investigate the thermodynamics of LMOG/solvent systems by varying the interaction energy through the choice of solvent, and the entropy of mixing through the relative molar volume of the gelator and solvent. It can be concluded that solvent-gelator interactions play a key role in mediating organogel formation and ultimately determine the properties of the gel. Gelation requires that the gelator-solvent interaction be neither too strong nor too weak, otherwise solution or precipitate are formed. The gelator-solvent interaction strength can be directly related to the difference of solubility parameters of a gelator and a solvent. It has been found that small variations in the structure, such as the introduction of branches or cyclic units can have dramatic effects on the gelation behavior. Compounds made with linear alkyl chains were poor gelators compared with one with branched alkyl end chain or cyclic end units, which might be caused by the different inherent ability of a molecule to form three-dimensional fibrillar structures.

Experimentally measured liquidus lines were fit with the regular solution model to determine LMOG-solvent interactions parameters and the solubility parameter of the LMOG was calculated using solubility parameter theory. Good agreement with the solubility parameter calculated independently from group contribution methods proved that the solution behavior and gelation ability of tripodal trisamide compounds can be interpreted using the regular solution model and solubility parameter theory.

The solution behavior of 12-hydroxystearic in organic solution and polymeric fluids are also presented to study the solvent effects on gelation and phase behaviors. The experimental melting temperature of HSA-Naphthalene binary mixtures display a eutectic phase diagram. However an accurate description of the phase behavior could not be obtained with the regular solution model and solubility parameter theory the fitting results with the regular solution model indicated a negative χ parameter, which is cannot be predicted by the solubility parameter theory. More investigation of these systems with more complex solution models are needed to fully understand the thermodynamic phase behavior in this system.

Amorphous polyacrylates and PDMS could be used as model liquids for the LMOG/liquid system. By changing degree of polymerization N and interaction parameter χ , we can finely tune the phase behavior. Prediction of the thermodynamics and phase behaviors of the gel system by the regular solution model will provide effective ways to design new efficient LMOGs in the future.

In order to study the thermodynamic phase behaviors of the gel systems using the regular solution model and solubility parameter theory, there should be no specific interactions between the gelator and the solvent molecules. Thus solvents and gelator molecules with

no or least amount of functional groups are good choices in order to avoid the specific interactions such as H-bonding. In the future research, long chain alkanes are possible simple gelators aggregating through Van der Waals interactions; Polybutene and polyisobutylene are simple liquid polymers which can be used as solvent.

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APPENDIX

DERIVATIONS AND RAW DATA

1. Derivation of equations

For solid/liquid equilibrium in binary solutions, the chemical potential in solution is

$$\mu_j^c = \mu_j^o + RT \ln x_j^l + RT \ln r_j^l$$

r_j^l is the rational activity coefficient of substance j in the liquid mixture at mole fraction x_j and temperature T . For an ideal solution $r = 1$,

$$\frac{\mu_j^c - \mu_j^o}{RT} = \ln x_j = -\frac{\Delta G_m}{RT} = -\frac{\Delta H_m}{RT} + \frac{\Delta S_m}{R}$$

$$\frac{\Delta \mu_j}{RT} = -\frac{\Delta G_m}{RT} = -\frac{\Delta H_m}{RT} + \frac{\Delta S_m}{RT}$$

$$\Delta \mu_j = 0 \text{ at } T_m^o,$$

$$\text{So } \frac{\Delta H_m^o}{RT_m^o} = \frac{\Delta S_m}{R}$$

$$\frac{\Delta \mu_j}{RT} = -\frac{\Delta H_m}{RT} + \frac{\Delta H_m^o}{RT_m^o}$$

Suppose heat of fusion is invariant with temperature,

$$\Delta H_m = \Delta H_m^o$$

For solid/liquid equilibrium in binary solutions with pure perfect crystals, we have

$$-\frac{\Delta\mu_j}{T_{m,j}} = \Delta H_j^o \left(\frac{1}{T_{m,j}} - \frac{1}{T_{m,j}^o} \right) \quad (3)$$

$T_{m,j}$ and $T_{m,j}^o$ are the equilibrium melting temperatures of component j in the mixture and in the pure state. ΔH_j^o is the latent heat of fusion per mole of repeat units of pure component j.

We can finally get Schröder-van Laar equation,

$$\ln x = \frac{\Delta H_m^o}{R} \left(\frac{1}{T_m^o} - \frac{1}{T_m} \right)$$

For strictly binary mixtures, Flory-Huggins free energy of mixing:

$$\frac{\Delta G}{RT} = \left(\frac{\phi_1}{N_1} \right) \ln \phi_1 + \left(\frac{\phi_2}{N_2} \right) \ln \phi_2 + \chi \phi_1 \phi_2 \quad (1)$$

ϕ_i represents the volume fraction of i th component. Differentiation of free energy of mixing leads to

$$\frac{(\Delta\mu_1 / RT)}{N_1} = \frac{\ln \phi_1}{N_1} + \frac{1}{N_1} - \frac{\phi_1}{N_1} - \frac{\phi_2}{N_2} + \left(\chi - \phi_1 \frac{\partial \chi}{\partial \phi_2} \right) \phi_2^2 \quad (2)$$

We can use equation (2) to evaluate the left hand of equation (3), for a concentration independent χ we find

$$\frac{1}{T_m} - \frac{1}{T_m^o} = -\frac{R}{\Delta H^o} \left[\left(\ln \phi_2 + \left(1 - \frac{1}{N} \right) \phi_1 + \chi \phi_1^2 \right) \right] \quad (4)$$

Here the LMOG is component 2, polymer is component 1 with degree of polymerization N . T_m is the melting temperature of LMOG at volume fraction Φ_2 .

By substituting $\chi = A/T$ and $\phi_1 = 1 - \phi_2$ in equation (4) and rearranging the liquidus line

T_m vs. volume fraction of gelator, ϕ_2 is given. For an organic solvent, $N=1$ giving,

$$T_m = \frac{\Delta H^o/R + A(1-\phi_2)^2}{\Delta H^o/R \left(\frac{1}{T_m^o} \right) - \ln \phi_2}$$

Here the volume fraction can be replaced by the mole fraction of the component.

When $(\frac{\partial^2 \Delta G_m}{\partial \phi^2})_{T,P} = 0$, the spinodal line for the liquid-liquid miscibility gap is given by,

$$\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} - 2\chi + 2(1-2\phi_2) \frac{\partial \chi}{\partial \phi_2} + \phi_2(1-\phi_2) \frac{\partial^2 \chi}{\partial \phi_2^2} = 0 \quad (5)$$

Here we suppose interaction parameter χ is concentration independent, thus $\frac{\partial \chi}{\partial \phi} = 0$,

And with $\chi = A/T$,

$$\frac{1}{N_1 \phi_1} + \frac{1}{N_2 \phi_2} - 2\chi = 0 \quad (6)$$

For binary system with LMOG as component 2, organic solvent as component 1,

$N_1=N_2=1$, the spinodal line comes from equation (6) as,

$$T_s = \frac{2A}{\frac{1}{\phi_1} + \frac{1}{\phi_2}}$$

If the solvent is polymer with degree of polymerization N ,

Then the spinodal line becomes,

$$\frac{1}{N \phi_1} + \frac{1}{\phi_2} - 2\chi = 0$$

$$T_s = \frac{2A}{\frac{1}{N \phi_1} + \frac{1}{\phi_2}}$$

The increase of the surface energy and the increase of the entropy due to the dispersion of crystals should be considered; here we neglect these effects of the dispersion, assuming that it is small.

2. ^1H NMR, ^{13}C -NMR, ESI/HRMS characterization results of the tripodal trisamide compounds:

TREN-EB: Yield 38%. ^1H -NMR (CDCl_3 , 300 MHz) δ (ppm) 0.88 (t, 6H), 1.5 (m, 4H), 1.96 (m, 1H), 2.58 (t, 2H), 3.3 (q, 2H), 6.43 (t, 1H). ^{13}C -NMR(CDCl_3 , 300 MHz) δ (ppm) 12.08(-CH₃), 25.57(CH₂), 37.54(NCH₂CH₂N), 50.82(NCH₂CH₂NC=O), 54.72(CH), 176.44(C=O). ESI/HRMS: m/z 441.4 ($[\text{M}+\text{H}]^+$).

TREN-C5: Yield 15% ^1H -NMR (CDCl_3 , 300 MHz) δ (ppm) 0.92 (t, 3H), 1.36 (m, 2H), 1.62 (m, 2H), 2.22 (t, 2H), 2.56 (t, 2H), 3.29 (q, 2H), 6.62 (t, 1H). ^{13}C -NMR (CDCl_3 , 300 MHz) δ (ppm) 13.77(-CH₃), 22.48(CH₂CH₂CH₂CH₃), 27.89(CH₂CH₂CH₂CH₃), 37.61(CH₂CH₂CH₂CH₃), 36.25(NCH₂CH₂NC=O), 54.51(NCH₂CH₂NC=O), 173.96(C=O). ESI/HRMS: m/z 421.3 ($[\text{M}+\text{Na}]^+$).

TREN-C6: Yield 49.8% ^1H -NMR (CDCl_3 , 300 MHz) δ (ppm) 0.89 (t, 3H), 1.30 (m, 4H), 1.62 (m, 2H), 2.19 (t, 2H), 2.53 (t, 2H), 3.26 (q, 2H), 6.53 (t, 1H). ^{13}C -NMR (CDCl_3 , 300 MHz) δ (ppm) 13.90(-CH₃), 22.40(-CH₂CH₂CH₂CH₂CH₃), 25.48(-CH₂CH₂CH₂CH₂CH₃), 31.56(-CH₂CH₂CH₂CH₂CH₃), 36.51(-CH₂CH₂CH₂CH₂CH₃), 37.59(NCH₂CH₂NC=O),

54.51(NCH₂CH₂NC=O), 173.92(C=O). ESI/HRMS: m/z 441.4 ([M+H]⁺), m/z 463.4 ([M+Na]⁺).

TREN-C7: Yield 37.5%. ¹H -NMR (CDCl₃, 300 MHz) δ (ppm) 0.88 (t, 3H), 1.30 (m, 6H), 1.63 (m, 2H), 2.21 (t, 2H), 2.53 (t, 2H), 3.29 (q, 2H), 6.55(t, 1H). ¹³C-NMR(CDCl₃, 300 MHz) δ (ppm) 14(-CH₃), 22.53(-CH₂CH₂CH₂CH₂CH₂CH₃), 25.81(-CH₂CH₂CH₂CH₂CH₂CH₃), 29.13(-CH₂CH₂CH₂CH₂CH₂CH₃), 31.60(-CH₂CH₂CH₂CH₂CH₂CH₃), 36.59(NCH₂CH₂NC=O), 37.59(-CH₂CH₂CH₂CH₂CH₂CH₃), 54.47(NCH₂CH₂NC=O), 173.97(C=O). ESI/HRMS: m/z 483.5([M+H]⁺), 505.5 ([M+Na]⁺).

TREN-C8: Yield 56%. ¹H -NMR (CDCl₃, 300 MHz) δ (ppm) 0.87 (t, 3H), 1.28 (m, 8H), 1.62 (m, 2H), 2.19 (t, 2H), 2.53 (t, 2H), 3.28 (q, 2H), 6.49(t, 1H). ¹³C-NMR(CDCl₃, 300 MHz) δ (ppm) 14.02(-CH₃), 22.59(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 29.07(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 29.42(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 31.73(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 36.58(NCH₂CH₂NC=O), 25.01(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 36.58(-CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 54.84(NCH₂CH₂NC=O), 173.92(C=O). ESI/HRMS: m/z 525.6 ([M+H]⁺), 547.6([M+Na]⁺).

TREN-C9: Yield 10%. ¹H -NMR (CDCl₃, 300 MHz) δ (ppm) 0.88 (t, 3H), 1.27 (m, 10H), 1.6 (m, 2H), 2.21 (t, 2H), 2.54 (t, 2H), 3.27 (q, 2H), 6.56(t, 1H). ¹³C-NMR (CDCl₃, 300 MHz) δ (ppm) 14.07(-CH₃), 22.65(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 25.87(-

CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 29.42(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 31.84(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 36.55(NCH₂CH₂NC=O), 37.53(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 54.35(NCH₂CH₂NC=O), 174.02(C=O). ESI/HRMS: m/z 567.6 ([M+H]⁺), 589.6 ([M+Na]⁺).

TREN-C10: Yield 10%. ¹H -NMR (CDCl₃, 300 MHz) δ (ppm) 0.87 (t, 3H), 1.25 (m, 12H), 1.61 (m, 2H), 2.16 (t, 2H), 2.53 (t, 2H), 3.26 (q, 2H), 6.49(t, 1H). ¹³C-NMR (CDCl₃, 300 MHz) δ (ppm) 14.02(-CH₃), 22.59(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 25.87(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 29.07(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 29.42(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 31.73(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 36.58(NCH₂CH₂NC=O), 36.58(-CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 54.48(NCH₂CH₂NC=O), 173.92(C=O). ESI/HRMS: m/z 609.8 ([M+H]⁺), 631.8 ([M+Na]⁺).

TREN-CH: Yield 48%. ¹H -NMR (CDCl₃, 300 MHz) δ (ppm) 0.88 (t, 6H), 1.5 (m, 4H), 1.96 (m, 1H), 2.58 (t, 2H), 3.3 (q, 2H), 6.43 (t, 1H). ¹³C-NMR(CDCl₃, 300 MHz) δ (ppm) 25.76(-CH₂-), 29.74(-CH₂-), 37.54(NCH₂CH₂N), 63.88(NCH₂CH₂NC=O), 45.23(-CH-), 176.81(C=O). ESI/HRMS: m/z 477.3 ([M+H]⁺), 499.3([M+Na]⁺).

Figure A. 1. ^1H NMR of TREN-EB in CDCl_3 .

Figure A. 2. ^1H NMR of TREN-C₅ in CDCl_3 .

Figure A. 3. ¹H NMR of TREN-C₇ in CDCl₃.

Figure A.4.1-¹H NMR of TREN-C₉ in CDCl₃.

Figure A.5. ^1H NMR of TREN- C_{10} in CDCl_3 .

Figure A.6. ^1H NMR of TREN- C_8 in CDCl_3 .

Figure A.7. ^1H NMR of TREN- C_6 in CDCl_3 .

Figure A.8. ¹H NMR of TREN-CH in CDCl₃.

3. Calculation of the solubility parameters

The solubility parameter is derived from the cohesive energy density of the compound and directly reflects the total forces that hold the molecules together. The solubility parameter, δ , is calculated from the cohesive energy density using group contribution theory:

$$\delta = \sqrt{\frac{\sum E_{coh}}{\sum V}}$$

Table A. 1. The values of the derivation of the solubility parameters

	E	V	number of group	sum of E	Sum V	δ (MPa) ^{1/2}
TREN-EB						
CH3	4710	33.5	6	28260	201	
CH2	4940	16.1	12	59280	193.2	
CH	3430	-1	3	10290	-3	
CONH	33490	9.5	3	100470	28.5	
tertiary amine (-N--)	4190	-9	1	4190	-9	
				202490	410.7	22.2
TREN-CH						
ring	1050	16	3	3150	48	
CH2	4940	16.1	21	103740	338.1	
CH	3430	-1	3	10290	-3	
CONH	33490	9.5	3	100470	28.5	
tertiary amine (-N--)	4190	-9	1	4190	-9	
				221840	402.6	23.5
TREN-Cn						
CH3	4710	33.5	3	14130	100.5	
CH2	4940	16.1	15	74100	241.5	$\# = 3n$
CONH	33490	9.5	3	100470	28.5	
tertiary amine (-N--)	4190	-9	1	4190	-9	
				192890	361.5	23.0

4. DSC 2nd-heating traces of TREN compounds.

Figure A.9. DSC traces of TREN-EB/DOP organogels at (a) low concentration and (b) high concentration.

5. Calculation of solute mole fraction

The equations for calculating mole fraction from concentration for both pure solvent (equation 1) and mixed solvent (equation 2)

$$x_2 = \frac{a / Mw_2}{a / Mw_2 + \rho_s * 1000 / Mw_s}$$

$$x_2 = \frac{a / Mw_2}{a / Mw_2 + 0.5 * \rho_{s1} * 1000 / Mw_{s1} + 0.5 * \rho_{s2} * 1000 / Mw_{s2}}$$

x- mol fraction of gelator

a-concentration of gelator in mg/mL,

ρ_s -density of solvent in g/mL

M_w -molecular weight in g/mol,

All the solvent data is collected from *SI Chemical Data Book* (4th ed.), Gordon Aylward and Tristan Findlay, Jacaranda Wiley

6. The equations for calculating $T_{gel}(\text{corrected})$ based on the heating block baseline.

$$Y = A + B_1 * X + B_2 * X^2 + B_3 * X^3$$

Y- $T_{gel}(\text{corrected})$

X- $T_{gel}(\text{raw data})$

$$A = -103.4244$$

$$B_1 = 1.91355$$

$$B_2 = -0.0026$$

$$B_3 = 2.33034E-6$$

7. Raw data of gelation

Table A. 2. Gelation of TREN-EB in DOP.

x	Dsc peak, T _m (°C)	T _{gel} read (°C)	T _{gel} read (°C) 2 nd measure	T _{gel} average (°C)	T _{gel} fixed (K)
0.01	120	125	112	118.5	385
0.02	134	135	127	131	397
0.03	143	149	144	146.5	412
0.05	148	159	148	153.5	418
0.07	150	164	150	157	422
0.07	148	155	153	154	419
0.13	160.57	165	165	165	429
0.2	161	167	168	167.5	432
0.29	164	170	170	170	434
0.39	168	176	172	174	438
0.49	169	178	173	175.5	439
0.57	172	183	176	179.5	443
0.67	174.4	180	180	180	444
0.78	176	184	180	182	446
0.89	181	186	186	186	450

Table A. 3. Gelation of TREN-EB in solvents

	Concentration mg/mL	Mol fraction	T _{gel raw} (K)	T _{gel fixed} (K)
xylene	15	0.0028	381	375
	20	0.0041	385	379
	25	0.0055	390	384
	30	0.0069	392	385
	46	0.0082	395	388
	56	0.01	398	391
	66	0.0126	401	394
chlorobenzene				
	15	0.0023	349	345
	20	0.0035	363	359
	25	0.0058	373	368
	35	0.0081	378	372
	45	0.0103	381	375
	58	0.0134	384	378
	71	0.0162	387	381
	84	0.019	389	383
	97	0.0219	395	388

toluene				
	10	0.0024	369	364
	15	0.0036	376	371
	20	0.0048	378	372
	25	0.006	379	374
	30	0.0072	388	382
	36	0.0087	391	385
	46	0.011	394	387
2bubz				
	10	0.0035	394	387
	20	0.007	405	398
	30	0.0105	412	404
	40	0.014	414	406
	60	0.0208	418	410
	80	0.0276	426	417
xy+2bubz(1:1)				
	15	0.0046	394	387
	20	0.0061	398	391
	25	0.0076	399	392
	30	0.0092	401	394
	40	0.0122	410	402
	60	0.0182	413	405

xy+chbz (1:1)				
	15	0.0037	374	368
	20	0.005	376	370
	25	0.0062	379	374
	30	0.0074	382	376
	40	0.0099	388	382
	50	0.0123	391	385
	70	0.0172	397	390

Figure A. 10. T_{gel} vs. x_2 for TREN-EB in different aromatic solvents: chlorobenzene (red circles), chlorobenzene + *o*-xylene (black squares), toluene (olive upward triangles), *o*-xylene (blue downward triangles), *o*-xylene + *sec*-butyl benzene (green left triangles), *sec*-butyl benzene (light blue diamonds). The dotted line is the predicted line for an ideal solution ($\chi = 0$).

Figure A. 11. T_{gel} vs. x_2 fit with Equation 2.9 for (a) TREN-EB in DOP and (b) TREN-EB in different aromatic solvents: chlorobenzene (circles), chlorobenzene + *o*-xylene (squares), toluene (upward triangles), *o*-xylene (downward triangles), *o*-xylene + *sec*-butyl benzene (left triangles), *sec*-butyl benzene (blue diamonds).

Table A. 4. DSC measurement of HSA-naphthalene.

%wt HSA	x_{HSA}	$T_{m1}(\text{K})$	$T_{m2}(\text{K})$
0	0	355	355
10	0.04525	337	353
20	0.096362	337	352
30	0.154554	338	351
40	0.221406	338	349
50	0.299009	338	341
60	0.390179	338	338
70	0.498819	339	339
80	0.630479	345	338
90	0.793344	349	
100	1	355	

Table A. 5. DSC measurement of HSA-PBA2.5K.

volume fractionHSA	$T_m(\text{K})$
0.01	320.75
0.03	326.5
0.04	332.2
0.05	336.1
0.06	335.2
0.07	335.9
0.1	338.5
0.2	346.2
0.3	348.4
0.4	349.3
0.5	350.5
0.6	348.9
0.7	351.7
0.8	351.3
0.9	352.3
1	355

Table A. 6. DSC measurement of HSA-PBA3.6K.

volume fraction HSA	T _m K
0.01	317
0.03	329.7
0.04	330.2
0.05	332.7
0.07	336
0.1	338.5
0.2	346.2
0.3	348.2
0.4	349.1
0.5	349
0.6	351.1
0.7	351.3
0.8	351.3
0.9	352.5
1	355

Figure A. 12. T_m vs. x_2 fit with Equation 2.9 for HSA in Naphthalene

Figure A. 13. T_m vs. x_2 fit with Equation 4.2 for HSA in Naphthalene