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***Reaction induced phase-separation
controlled by molecular topology.****

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Abstract

Phase-separation can result in the formation of self-assembling structures in networks induced by crosslinking reactions. Vinyl and hydroxyl end-functionalized poly(dimethyl siloxane) (PDMS) chains were employed for the synthesis of these networks using a tetra-functional crosslinking agent. It was found that at a very high molar fraction (approaching 1) of the low molecular weight component, approximately 50% by volume; it was possible to induce composition fluctuations in the system that resulted in phase-separation via spinodal decomposition. Time resolved small angle light scattering (SALS) and optical microscopy were used to determine the character and kinetics of phase-separation and to compare and contrast with the spinodal decomposition of simple blends. A vinyl-terminated system resulted in the formation of interconnected bicontinuous morphology reminiscent of early-stage spinodal decomposition (SD). The morphology obtained by SD was found to be “locked-in”, possibly due to network formation. Late-stage phase ripening was prevented by gelation. Surprisingly, a hydroxyl, end-terminated system was found to display different behavior with simultaneously nucleated close to monodisperse spherical domains. The difference in the mechanisms of phase-separation is believed to arise from the different reaction mechanisms of the two systems with an addition mechanism in the vinyl end-terminated system and a condensation process in the hydroxyl end-terminated system. The reaction mechanism dictates the effective quench depth in the system, which leads to different mechanisms of phase-separation in the two systems. The effect of differences in branch topology, on the phase-separation process has been investigated.

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Chapter 1. Introduction

1. Introduction

Polymer blends are physical mixtures of two or more polymers with little or no chemical interactions between the two species. Blending is carried out to enhance the properties of the resultant material over the constituent polymers. The final properties of the blend are dictated by molecular parameters like the degree of polymerization, statistical segment lengths, Flory-Huggins interaction parameter between the constituent polymers etc. These parameters also dictate the final morphology or structure of the material. So, the morphology of the blend has a significant effect on the end properties obtained. In most cases polymer mixtures are immiscible. Miscibility can only be achieved in case of special interactions between the two different polymer molecules. Phase-separation is therefore expected on mixing two different polymers. Thermodynamic and kinetic aspects govern the mechanism and evolution of structure during phase-separation. It is therefore necessary to have a good understanding of these topics to design and synthesize polymer multi-component systems.

1.1. Flory-Huggins Treatment for Polymer Mixtures

The change in Gibbs free energy on mixing two polymers A and B can be expressed as [1, 2],

$$\frac{\Delta G_{mix}}{RTn_c} = \frac{\varphi_A}{N_A} \ln \varphi_A + \frac{\varphi_B}{N_B} \ln \varphi_B + \chi \varphi_A \varphi_B \quad (1)$$

where χ is the polymer-polymer interaction parameter, known as the Flory-Huggins interaction parameter, φ_A and φ_B are the volume fractions on the two polymers and n_c is the system size. A necessary condition for miscibility of two polymers is that the Gibbs free energy change for mixing in the above equation must be negative. The first

two terms on the right constitute the increase in conformational entropy on mixing. Fig. 1 shows a 2-D lattice model for mixing of two polymers. The lattice on the left represents two polymer molecules on a lattice, with each segment occupying one lattice site. The lattice on the right represents a mixture of two small molecules with each molecule occupying one lattice site. As we can see from this figure, the total number of conformations that a polymer molecule can assume is small as compared to a small molecule due to the chain connectivity. Therefore, the increase in entropy on

Figure 1. 2-D Lattice model for polymer mixtures and a mixture of small molecules.

mixing of polymers is usually not large enough to offset the positive heat of mixing usually seen in polymers. As a result, polymer mixtures generally do not form miscible blends, and compatibility is observed only in case of special interactions between the two polymer molecules like dipole-dipole forces, or hydrogen bonding [1].

1.2. Phase Separation Mechanisms

Fig. 2 shows the change in Gibbs free energy with composition for various values of interaction parameters χ . As the value of the interaction parameter decreases, the

Gibbs free energy decreases [1]. But for values of (χN) , where N stands for the degree of polymerization, greater than a critical value of $(\chi N)_c$, a maxima is observed in place of a minima in the Gibbs free energy. This is shown in Fig. 2 for a symmetric polymer blend, where N_A is equal to N_B . As can be seen in the figure for (χN) values greater than a critical value of 2, it is possible to further reduce the Gibbs free energy by forming a two-phase structure [1], with compositions ϕ_A' and ϕ_A'' for one of the components in the two phases. Hence a miscibility gap is found for all values of χ greater than a critical value of $\chi_c (2 / N)$.

Figure 2. Gibbs free energy of mixing of a symmetric binary polymer mixture as a function of composition.

If phase-separation is observed upon cooling a homogenous mixture, the system is said to have a lower miscibility gap, and the critical point is known as the

upper critical solution temperature. Whereas, if the two-phase region is reached on heating a homogenous mixture, the system is said to have a upper miscibility gap and the corresponding critical point known as lower critical solution temperature. Hence, though a negative value of change in Gibbs free energy of mixing is a necessary condition for homogenous mixing of polymers, it does not always guarantee compatibility. Fig. 3 depicts a hypothetical phase diagram for a two component polymer mixture. The solid curve marks the boundary between the single phase and phase-separated regime, and is known as the binodal, roughly corresponding to the minima in the top curve in Fig. 2, where as the dashed curve is the spinodal or the boundary between the metastable and unstable regions in the phase diagram [1, 2],

Figure 3. Phase diagram for a two component polymer mixture

corresponding to the inflection part in the top curve in Fig. 2. The mechanism of phase-separation depends on the quench depth or the position of the mixture on the temperature composition diagram. If we were to quench the binary mixture from the

stable phase to a temperature T_1 , for compositions between ϕ_a and ϕ_{ac} , or ϕ_{bc} and ϕ_b , nucleation and growth would be the mechanism of phase-separation [1], whereas for compositions between ϕ_{ac} and ϕ_{bc} spinodal decomposition [1] would be observed. The distinction between spinodal decomposition and nucleation and growth could be explained in terms of the Gibbs free energy change. The spinodal point is given by the equation,

$$\frac{\partial^2(\Delta G)}{\partial \phi^2} = 0 \quad (2)$$

In the spinodal regime $\partial^2(\Delta G)/\partial \phi^2$ is negative, whereas in nucleation and growth it is positive. In terms of the phase diagram depicted in Fig. 2, spinodal decomposition is obtained where the free energy curve has a negative curvature. It means that the system is unstable with respect to any infinitesimal fluctuation in composition or density. In nucleation and growth regime $\partial^2(\Delta G)/\partial \phi^2$ is positive, indicating that regions with positive curvature in the free energy versus composition diagram are regions of nucleation and growth. It means that the system is stable with respect to an infinitesimal change in composition. Only a large enough fluctuation in composition or a seed could render such a system unstable and it would then phase-separate by nucleation and growth phenomena. Generally nucleation and growth proceeds from nucleation seeds (impurities) in polymer systems. Impurities act to lower the energy barrier through reduction of surface energy needed for phase-separation. The growth of composition fluctuations, which lead to spinodal decomposition and nucleation and growth phenomena, are shown in Fig. 4. In spinodal decomposition, phase-separation could be induced by an infinitesimal concentration fluctuation (solid curve) of wave number q , where q is defined as [1],

$$\begin{aligned} \mathbf{q} &= 2 \pi / \Lambda \text{ (real space)} \\ \mathbf{q} &= (4 \pi / \lambda) \sin (\theta/2) \text{ (reciprocal space)} \end{aligned} \quad (3)$$

where Λ is the wavelength of the fluctuation, λ is the wavelength of light used in a light scattering experiment and θ is the scattering angle. Once such a fluctuation is induced it would continue to grow in amplitude but at a fixed wavelength (dashed curve in Fig. 4a). Nucleation and growth (Fig. 4b) proceeds by the formation of nuclei

Figure 4. Growth of composition fluctuations in the early stage of a) Spinodal Decomposition, b) Nucleation and Growth.

or from existing seeds with a composition close to the equilibrium composition ϕ_b or by lowering of the energy barrier by surface growth. A large enough local fluctuation or a seed (which can be a dirt particle) is the starting point in nucleation and growth [1]. This is the nucleation step. Then, nuclei with a size greater than a critical size continue to grow at the expense of smaller nuclei, which is the growth step. The critical size of the nucleus is given by the Gibbs-Thomson equation [3] given as,

$$\Delta G_n = -\phi n + \psi n^{2/3} \quad (4)$$

where ΔG_n is the free energy change for the formation of a nucleus, Φ gives the volume component or the bulk energy and ψ is the surface energy. The critical size of the nucleus, n^* is obtained from the maxima in the free energy change given by the previous equation. This critical size is given as,

$$n^* = \left(\frac{2\psi}{3\phi}\right)^3 \quad (5)$$

Another important aspect in these mechanisms is the direction of diffusion of the components. As indicated by the arrows in Fig. 5, they are opposite in spinodal decomposition and nucleation and growth. In spinodal decomposition, the diffusion of

Figure 5. Direction of diffusion depicted by arrows in spinodal decomposition (top) and nucleation and growth (bottom).

one of the components is from lower concentrations to regions of higher concentration because the change in free energy is lower for all two phase systems. Fig. 6 shows the morphologies obtained by the two mechanisms of phase-separation for a bimodal mixture of end-linked PDMS. Spinodal decomposition results in the formation of an

interconnected bicontinuous morphology of A rich and B rich phases. Nucleation and growth results in the formation of spherical particles dispersed in a matrix. Those particles, having a size greater than the critical nucleus would grow with time, at the expense of the smaller particles due to Ostwald ripening.

Figure 6. a) Nucleation and Growth with spherical particles dispersed in a matrix, b) Spinodal decomposition with an interconnected bicontinuous morphology [1].

1.3. Theory of Spinodal Decomposition

1.3.1. Development of Cahn-Hilliard Theory

Let us consider two hypothetical systems, one with uniform composition c_0 and the other where the composition at any point varies infinitesimally from the average composition c_0 . Cahn and Hilliard [4-6] gave an expression for the change in free energy for going from such a homogenous system with composition c_0 to an inhomogeneous system with composition fluctuations given by,

$$\int (c - c_0) dV = 0 \quad (6)$$

i.e. the composition at any point in the system varies infinitesimally about the average composition c_0 . They used a Ginzburg-Landau free energy functional to give this free energy change. The Ginzburg-Landau free energy functional is given by [4-6],

$$F(c) = \int [f(c) + \kappa(\nabla c)^2] dV \quad (7)$$

where $f(c)$ is the free energy density of a homogeneous system, ∇c is the gradient in composition, and κ can be regarded as a constant for regular mixtures with no compressibility, i.e. c goes to one phase or the other. The Taylor series expansion of $f(c)$ about c_0 is given as [4-6],

$$f(c) = f(c_0) + (c - c_0) \frac{\partial f}{\partial c} + \frac{1}{2} (c - c_0)^2 \frac{\partial^2 f}{\partial c^2} \quad (8)$$

The difference in free energies of a homogenous and an inhomogeneous system could be calculated from the above equations. It would be given as [4-6],

$$\begin{aligned} \Delta F &= \int [f(c_0) - f(c_0)] + (c - c_0) \frac{\partial f}{\partial c} + \frac{1}{2} (c - c_0)^2 \frac{\partial^2 f}{\partial c^2} + \kappa (\nabla c)^2 + \dots \\ &= \int \left[\frac{1}{2} (c - c_0)^2 \frac{\partial^2 f}{\partial c^2} + \kappa (\nabla c)^2 \right] dV \end{aligned} \quad (9)$$

We can see in the above equation that if $(\partial^2 f / \partial c^2)$; the curvature of free energy curve, is negative, i.e. spinodal, the free energy change for the process could be negative. This means that it would lead to a spontaneous change driven by fluctuations. The change would be of the system going from an initial homogeneous state to an inhomogeneous state.

To obtain the kinetics of this process Cahn [7] used a simple constitutive equation given by,

$$-J_A = M \nabla (\mu_A - \mu_B) \quad (10)$$

where J_A is the flux, M is the mobility.

We can get the above relationship (eq. 10) as follows: Consider a mixture of **A** chains and **B** chains with concentrations ϕ_A and ϕ_B respectively. Let us consider that there are no interactions. The flux of the A chains will be given as [7],

$$J_A = -D_A \nabla \varphi_A \quad (11)$$

We can also express the flux in terms of the chemical potential of the A chains, which would be given as [7],

$$\frac{\mu_A}{kT} = \frac{1}{N} \ln \varphi_A + \text{const.} \quad (12)$$

Now if we assume that the A and the B chains interact, the chemical potential of the A chains would change and can be given as [7],

$$\frac{\mu_A}{kT} = \frac{1}{N} \ln \varphi_A + \chi \varphi_B \quad (13)$$

The flux of the A chains would now change and would be given as [7],

$$J_A = -\Lambda_A \nabla [(\mu_A + U) / kT] \quad (14)$$

where Λ_A is the A component of the kinetic Onsager coefficient and U is a certain repulsive potential due to the system reaching an equilibrium being imposed due to the relationship [7],

$$\varphi_A + \varphi_B = 1 \quad (15)$$

From random phase approximation which implies that the total flux in the system must have zero divergence for an incompressible system, we obtain an expression for the repulsive potential U given by [7],

$$U = \frac{(\Lambda_A \mu_A + \Lambda_B \mu_B)}{\Lambda_A + \Lambda_B} \quad (16)$$

Substituting this value of U in eq. 14 we get a modified expression for the flux of the A chains as [7],

$$J_A = -\Lambda \nabla (\mu_A - \mu_B) \quad (17)$$

where the mobility parameter known as the kinetic Onsager coefficient is given by [7],

$$\Lambda = \frac{\Lambda_A \Lambda_B}{\Lambda_A + \Lambda_B} \quad (18)$$

The difference in chemical potential for the eq. 17 was obtained by taking the variational derivative of eq. 7 and discarding terms higher in order and degree, as it would not matter in the earlier stages of phase-separation. An approximation for change in chemical potential can be given as [7],

$$\mu_A - \mu_B \sim \frac{\delta F}{\delta c_A} = \frac{\partial f}{\partial c_A} - 2\kappa(\nabla^2 c_A) \quad (19)$$

The change in composition with time could be expressed in terms of a diffusion equation on the lines of Fick's second law of diffusion given by [4-7],

$$\frac{\partial c}{\partial t} = -\nabla \cdot J_A \quad (20)$$

Substituting the expression for flux from eq. 10 and change in chemical potential from eq. 19, we get [7],

$$\begin{aligned} \frac{\partial c}{\partial t} &= -\nabla \cdot [M \nabla (\frac{\partial f}{\partial c} - 2\kappa \nabla^2 c)] \\ &= M \nabla^2 [-2\kappa \nabla^2 c + \frac{\partial f}{\partial c}] \end{aligned} \quad (21)$$

As we can see, this is a non-linear equation in c . Cahn linearized this equation about average concentration c_0 by replacing c in the above equation by a new parameter $u(r)$ for fluctuation in composition, which is given by,

$$u(r) = c(r) - c_0 \quad (22)$$

Please note that in eq. 21 the term c refers to $c(r)$. Cahn [7] obtained what is now known as the linearized Cahn-Hilliard equation given by,

$$\frac{\partial u(r)}{\partial t} = M \nabla^2 [-2\kappa \nabla^2 + (\frac{\partial^2 f}{\partial c^2})_{c_0}] u(r) \quad (23)$$

This linearization approximation is a very important aspect of the Cahn-Hilliard theory. As the composition fluctuations were supposed to be very small, we could substitute $(\partial^2 f / \partial c^2)_{c_0} u(r)$ for $\partial f / \partial c$, so that the derivative of the free energy did not depend on c itself, but on the region near c_0 .

deGennes [8] and Pincus [9] applied the theory of reptation [10] to treat the relaxation of composition fluctuations. They also gave the concentration dependence of the Onsager coefficient, Λ , which is analogous to the mobility parameter ‘M’ used by Cahn and Hilliard. Binder [11] worked out the theory for asymmetric polymer blends and he also analyzed the relaxation of concentration fluctuations using a Rouse model. He also considered the effect of thermal forces on phase-separation kinetics.

1.3.2. Modified Cahn-Hilliard Theory

Pincus [9] and deGennes [8] modified the Cahn-Hilliard theory for phase-separation in multi-component polymeric systems. The primary difference in their theories was that they used a Flory-Huggins type of free energy for mixing of polymers instead of using the Ginzburg-Landau free energy functional. This free energy of mixing of two polymers is given as [8, 9],

$$\frac{F}{kT} = \frac{\phi}{N_A} \ln \phi + \frac{(1-\phi)}{N_B} \ln(1-\phi) + \chi \phi(1-\phi) + \frac{a^2}{36\phi(1-\phi)} (\nabla \phi)^2 \quad (24)$$

where a is the statistical segment length, ϕ is the volume fraction of A and χ is the interaction parameter. Cahn and Hilliard had not considered the effect of

concentration on mobility in the basic constitutive equation (eq. 10) used as a starting point for their theory. Pincus and deGennes gave the concentration dependence of the transport parameter called the Onsager coefficient $\Lambda(q)$. The flux given by eq. 11, was modified by them as [8, 9],

$$J(q) = -\frac{\Lambda(q)}{kT} \nabla \mu(q) \quad (25)$$

where $\mu(q)$ is the Fourier transform of the A chemical potential. The kinetic Onsager coefficient is given as [8, 9],

$$\Lambda(q) = D(q) \varphi (1 - \varphi) \quad (26)$$

where $D(q)$ is the wave-vector dependent diffusion constant for a polymer chain. The factor $\varphi(1 - \varphi)$ expresses the incompressibility of the system. deGennes [8] used the reptation model to study the relaxation rate of the composition fluctuations in polymers. He gave an expression for relaxation rate ($1/\tau_q$) for fluctuations at a wave vector q as [8],

$$\tau_q^{-1} = q^2 \Lambda(q) \left[\frac{1}{N\varphi(1-\varphi)} - 2\chi + \frac{(aq)^2}{36\varphi(1-\varphi)} \right] \quad (27)$$

For a specific set of wave vectors q , satisfying the inequality,

$$0 < q < q_c \quad (28)$$

it is seen that the relaxation rate give by the above equation is negative. These fluctuations in composition are amplified instead of decaying. Thus the prediction of exponential growth rate of fluctuations of these wave-vectors is justified.

1.3.3. Kinetic Aspects of Spinodal Decomposition

Spinodal decomposition is divided into three regions or regimes [12] depending on the evolution of elastic scattered intensity $I(q, t)$ in a light or x-ray scattering experiment and $q_m(t)$, the wavenumber of the fluctuations with maximum growth rate. The three stages of evolution of phase-separated structure are classified as early, intermediate and late stage. Fig. 7 shows the time evolution of the fluctuations during the course of spinodal decomposition from early to late stages. In the early stages the composition fluctuations undergo an exponential growth but at a fixed value of q_m , i.e. at a fixed wavelength of composition fluctuations. In the intermediate stages both the amplitude as well as the wavelength of these fluctuations increase with time. The late stage is characterized by the fluctuations reaching the equilibrium amplitude dictated by the value $(\phi_a - \phi_b)$, but the growth of the wavelength of the fluctuations continues.

Figure 7. Schematic of the evolution of composition fluctuations in the early, intermediate and late stages of spinodal decomposition.

The linearized Cahn-Hilliard equation for the evolution of composition fluctuations during spinodal decomposition was given by eq. 23. Taking the Fourier transform of this equation yields [12],

$$\frac{\partial u(q)}{\partial t} = -M\kappa q^2 [q^2 + \kappa^{-1} (\frac{\partial^2 f}{\partial c^2})_{c_0}] u(q) \quad (29)$$

The linearization approximation simplifies obtaining this transform because we don't have to take the Fourier transform of $\partial f / \partial c$, as this can now be treated as a constant.

As we can see from the form of the above equation, $u(q)$ will have an exponential growth with time (as the derivative of the function $u(q)$, is a function of $u(q)$). We

would like to define a new term, called the structure factor $S(q, t)$ which is widely used by experimentalists. It is defined as [12],

$$S(q, t) = [u(q)]^2 \quad (30)$$

The evolution of the structure factor in a scattering experiment is known to follow a behavior given by [12],

$$S(q, t) = S(q, 0) e^{2R(q)t} \quad (31)$$

where $R(q)$ is the rate of growth of the composition fluctuations leading to spinodal decomposition and is given as [12],

$$R(q) = M\kappa q^2 [q^2 + \kappa^{-1} (\frac{\partial^2 f}{\partial c^2})_{c_0}] \quad (32)$$

As shown by the eq. 27 and eq. 28, the relaxation time for fluctuations at a certain wave vector q smaller than a critical wave vector q_c is negative. This means that these fluctuations will be amplified. Thus the prediction of growth of the structure factor is justified.

The major predictions of the linearized theory for the early stages of spinodal decomposition can thus be listed as follows [12]:

- a. The elastic scattered intensity increases exponentially with time. This behavior can be expressed in terms of the following equation,

$$I(q, t) = I(q, 0) \cdot \exp[2R(q)t] \quad (33)$$

- b. The wave number q_m , at which we get maximum growth rate of the composition fluctuations is independent of time. This can be given by the following expression.

$$q_m(t) \approx t^0 \quad (34)$$

- c. As can be seen from eq. 27, $R(q)$ has a crossover from positive to negative values at $q = q_c$, where q_c is given by,

$$q_c^2 = 2q_m^2 \quad (35)$$

This linear theory is applicable only in the early stages of spinodal decomposition where the thermal effects and the non-linear terms in the expression given by eq.19 were neglected; do not have any effect on the kinetics of the phase-separation process. In the latter stages, with the passage of time, these non-linear terms come into play and the linear theory, which was applicable in the early stages, falls apart. The major differences in the latter stages of spinodal decomposition are as follows [12],

- a. The growth rate of the intensity of the elastic scattered light does not follow an exponential behavior. Instead a power law growth rate is seen.

$$I_m(t) \approx t^\beta \quad (36)$$

- b. The wavenumber q_m of the fluctuations with maximum growth rate of fluctuations is no longer independent of time. It is given by,

$$q_m(t) \approx t^{-\alpha} \quad (37)$$

1.4. Chemically Induced Phase Separation

The Flory-Huggins interaction parameter has a temperature dependence of the following form [1],

$$\chi = \frac{1}{T} \quad (38)$$

As stated earlier, phase-separation sets in when the value of (χN) is greater than some critical value of $(\chi N)_c$. In the case of symmetric polymer blends where $N_A = N_B$ and

$a_A = a_B$ (statistical segment length), the critical value of (χN) is found to be given by [1],

$$\begin{aligned} (\chi N)_c &= 2 \\ \chi_c &= \frac{2}{N} \end{aligned} \tag{39}$$

It follows from the above relation that phase-separation could set in due to reaction/polymerization. Consider a case where we have a homogeneous mixture of two different monomers A_m and B_m , where the suffix m indicates that the species A and B are in monomeric form. Now we simultaneously begin to polymerize the two monomers. The individual molecular weights of the two species begin to increase. In light of eq. 39 this means that there is an effective lowering of the apparent critical value of the interaction parameter χ_c . At some point in the reaction when the molecular weights of the A and B chains, N_A and N_B , are sufficiently large, phase-separation will set in. This is known as chemically induced phase-separation. As can be seen from eq. 38 it is analogous to phase-separation induced by temperature jumps from the one-phase to two-phase region of the phase diagram.

The effect of crosslinking on phase separation has been well documented [13-16]. If the two components are crosslinked in the one-phase region and then brought into the two-phase region, crosslinking suppresses the growth of phases, i.e. the size is restricted. In this case we would obtain what is known as microphase separation. In the current study, we are interested in the end-linking reaction of PDMS chains. The two systems studied are the vinyl end-linked and the hydroxyl end-linked system. The reaction taking place in the vinyl end-linked system is shown in Fig. 8. It is known as hydrosilation reaction. As we can see from the reaction scheme it is an addition reaction to produce a crosslinked network.

Figure 8. End-linking reaction of vinyl terminated PDMS

The hydroxyl-terminated system is crosslinked by a condensation reaction as shown in Fig. 9. It leads to the formation of a by- product viz. ethanol.

Figure 9. End-linking reaction of hydroxyl terminated PDMS

The kinetics of simple addition and condensation reactions leading to polymerization are well known [17]. The molecular weight increase is faster in an addition reaction as compared to a condensation reaction. Though the rate of increase of molecular weight for a condensation reaction is initially high, it drops off in the latter stages of the reaction, as we can see from the reaction scheme in Fig. 10, that in order to sustain the reaction rate we would have to continuously remove the condensation by-product to push the reaction to the right. Fig. 10 shows a comparative schematic of the rise in molecular weights in the two systems. In case of the hydroxyl system, it would be difficult to push the reaction to completion, as we do not remove the reaction by-product ethanol. Thus the quench in the hydroxyl system due to rise in molecular weight might be shallower when compared to the vinyl-terminated system. Fig. 10 is a generalized schematic of comparison of the rates in an addition reaction and a condensation reaction [17], and it is important to note that it does not reflect silanes in particular.

Figure 10. Rise in molecular weight with time for vinyl and hydroxyl systems

1.5. Phase Separation in Bimodal Networks

Bimodal network's, formed by crosslinking end-functionalized chains of high molecular-weight with low molecular-weight or oligomeric chains have been shown to have a significant effect on the properties of the final material [18, 19]. Generally, mechanical properties, especially toughness and tear resistance, improve with polydispersity of network components [20]. Some works in literature indicate that phase-separation can be obtained in bimodal networks [21]. In this work it is shown that phase-separation occurs only over a narrow range of conditions. We observe the formation of a spinodal-like (as true spinodal is always reversible [22, 23]) structure in a bimodal poly(dimethyl siloxane), PDMS, network formed via the end-linking reaction of vinyl end-functionalized precursors known as hydrosilation [24]. This phenomenon is reminiscent of crosslinking-reaction induced phase-separation

suggested by deGennes a number of years ago [25, 26]. Under some specific conditions a beautiful interpenetrating and correlated phase structure can result which is reminiscent of the product of early stage spinodal decomposition [27]. The morphology, however, is not reversible and late-stage decomposition to polydisperse, non-correlated domains is not seen.

This observation is in agreement with the works of Schulz et al. [28, 29]. It is proposed, following deGennes, that network formation and phase-separation are collaborating events, and that the process represents a balance between thermodynamic and kinetic interests. The effect of crosslinking on the phase-separation behavior has been well documented by various authors over the years [13-16]. We propose that in our system, crosslinking brings about an increase in the molecular weights of the components and this is the primary driving force for the onset of phase-separation, but the final morphology is governed by the “freezing-in” [28, 29] of the spinodal structure due to the crosslinks.

Unique to this system is that phase-separation does not involve a conventional mixture of chemically different species, but involves a pseudo polymer blend where the two phases differ, for the most part, topologically, that is, in terms of branch content or crosslink density. In a similar system using hydroxyl-terminated crosslinking by a hydrolysis/condensation reaction [30] completely different morphologies result. Though the hydroxyl-terminated precursors are similar to the vinyl-terminated precursors, the final morphology obtained is reminiscent of phase-separation via the nucleation and growth mechanism. It is believed that the reaction mechanism involved in the formation of the network from the hydroxyl-terminated precursors brings about a shallower quench as compared to the hydrosilation reaction in the vinyl-terminated system. It will be shown in the next section that the

crosslinking phases are more PDMS-like in the hydroxyl system as compared to the vinyl system.

1.6. Effect of Topology on phase-separation

Phase-separation in blends of polyolefin's, due to difference in branch topology has been widely reported in literature [31-35]. Wignall et al. [31] have shown that blending linear high-density polyethylene (HDPE) with a linear low-density polyethylene (LLDPE) with high branch content, could lead to phase-separation of the highly branched component of the blend, even if the overall branch content is low.

The occurrence of phase separation in such systems was ambiguous, because conflicting views supporting phase-separation [36-38], and complete miscibility [39] had been reported. Small angle neutron scattering (SANS) had been widely used for characterization of these blends. Evidence of phase-separation was neglected and attributed to H/D isotope effects [39]. Alamo et al. [35] established the fact that phase-separation in these blends occurs on a micron-size scale, which might not have been detected by these works.

Alamo et al. [35] quantified the critical amount of branching that would be needed to drive the phase-separation. In blends of linear chain HDPE and highly branched LLDPE, they estimated that phase-separation would result for LLDPE branching greater than 8/100 backbone carbon chains. They characterized the phase-separated blends on the basis of a lack of fit of the SANS data to the homogeneous random phase approximation, which assumes the polymer coils to be Gaussian.

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Chapter 2. Experimental

2. Experimental

2.1. Chemicals

All the chemicals for the vinyl-terminated system were purchased from Gelest Inc. Two different molecular weight pre-polymers were used to form the networks. For the vinyl system, the low molecular weight oligomeric material used was 1, 3- divinyl tetramethyl-disiloxane of molecular weight 186.4 g/mol. The high molecular weight pre-polymer used was vinyl-terminated polydimethylsiloxane (PDMS) (22,000 g/mol). The crosslinker was tetrakis(dimethylsiloxy)silane and a platinum-divinyl tetramethyl disiloxane complex in xylene, also known as Karstedt's catalyst [1], was used to catalyze the end-linking reaction. Molecular weights of the PDMS pre-polymers as used from Gelest Inc. could have a distribution. We did not perform investigations on the molecular weight distributions due to constraints.

In the Silanol terminated system, the pre-polymers used were silanol-terminated PDMS of molecular weights 750 g/mol and 18,000g/mol obtained from Gelest. Tetraethylorthosilicate (TEOS) of 98% purity from Aldrich was used as the crosslinker. Dibutyl tin dilaurate, 25% in cyclic dimethyl siloxane from United Chemicals Technologies Inc. was used as the catalyst. The hydrolysis/condensation reaction results in the formation of 4 ethanol molecules per TEOS in the hydrolysis reaction, consuming 4 water molecules followed by the release of 4 water molecules per molecule of TEOS on condensation. The total hydrolysis/condensation reaction consumes 4 moles of water and produces 4 moles of ethanol and water per mole of TEOS. Ethanol is generally outgassed and or extracted from the final network. For our in situ studies, forced outgassing using a vacuum was not possible leading to an even slower rate of gelation and network formation. The rate of increase in molecular weight was lower in the hydroxyl system as compared to the vinyl system as evident

from a much longer gelation time. For chemically driven phase-separation the extent of reaction parallels the thermal quench depth in traditional thermally controlled phase-separation. In this context, the hydrosilation system represents a deep quench condition, far from the critical point, while the hydrolysis/condensation system represents a shallow quench condition near the phase separation boundary for much of the network forming reactions.

2.2. Network Formation

Vinyl-terminated, bimodal networks were formed using 98 to 99.5 mole percent of short chains and the remainder long chains. This represents roughly a 50% mixture by volume. A stoichiometric amount of crosslinker was employed in all the formulations. Catalyst loading appears to be vital to production of the spinodal-like structure in the vinyl system, presumably due to the influence of the rate of crosslinking on the development of the spinodal-like morphology. It was found that the minimum amount of catalyst for gelation and network formation was optimal and in order to achieve relatively low catalyst concentrations the initial catalyst solution was diluted in toluene to 10 % by volume of the initial solution. Through trial and error it was found that 0.5 mg of this diluted catalyst per gram of base polymer mixture was optimal for production of the spinodal-like structure. Networks produced under these conditions showed phase separation in bulk when synthesized in a glass vial as well as when synthesized between glass cover-slips. It should be noted that thin films prepared by placing a drop of the reaction mixture on a single glass cover slip, open to the atmosphere, did not display phase separation. This may be associated with the sensitivity of the hydrosilation reaction to atmospheric oxygen.

The hydrolysis/condensation system consisted of 98.5 mole percent short chains (about 50% by mass) and also utilized a stoichiometric amount of tetraethylorthosilicate, TEOS, crosslinker. Dibutyl tin dilaurate catalyst loading was varied from 2-5% by weight of the polymer mixture. It was observed that higher catalyst loading (5%) was needed to synthesize networks that displayed phase-separation. Using 0.2% catalyst loading [2] as indicated in literature did not work for our system as at such low catalyst concentrations we were unable to obtain gelation in the samples.

2.3. Light Scattering Measurements

Light scattering was performed on samples prepared between glass cover slips that were 1 mm in thickness. A 20 mW Helium-neon gas laser at 632.8 nm wavelength was used. Using a single pinhole near the sample, the scattering pattern was projected on a screen and imaged with a CCD camera, Princeton instruments Optical Multichannel Analyzizer (OMA) camera [3, 4]. Background scattering from an identical sample except for the absence of crosslinker was subtracted from the light-scattering patterns. The data was corrected for $1/r^2$ decay due to the flat projection of the scattering pattern; and the 2D data was radially averaged. A schematic of the light scattering setup is shown in the figure below.

Figure 11. Light scattering experimental setup to study phase-separation and gelation kinetics.

In order to determine possible differences in the chemical composition of the phase-separated systems IR measurements were performed. Attenuated, total-reflectance IR spectra of the samples were measured using a Nicolet Magna 760 infra-red spectrometer. The spectra were obtained by summing 256 scans on the samples.

Optical micrographs were obtained by placing 1-2 drops of the reaction mixture between two microscope glass cover slips and observing it under a Nikon Optiphot2-pol optical microscope connected to a PC. The digital images were obtained using Image Pro 4.1 software.

2.4 Light Microscopy

Optical micrographs were obtained by placing 1-2 drops of the reaction mixture between two microscope glass cover slips and observing it under a Nikon Optiphot2-pol optical microscope connected to a PC. The digital images were obtained using Image Pro 4.1 software.

2.5 ATR-IR Spectroscopy

In order to determine possible changes in the chemical composition of the phase-separated systems IR measurements were performed. Attenuated Total Reflectance IR Spectra of the samples were conducted using a Nicolet Magna 760 infra- red spectrometer. The spectra were obtained by summing 256 scans on the samples.

2.6 DSC

Differential scanning calorimetry measurements were performed on two samples, monomodal networks synthesized from short chains and a bimodal network, all from vinyl end-terminated precursors. Universal V3.7A 2910 DSC instrument at Equistar research center was used to carry out these measurements. A sampling interval of 1.0 sec/pt was employed. The samples were equilibrated at -50° C and maintained under isothermal conditions for 5 minutes. The samples were heated to 100° C at a rate of 20° C/min.

2.7 Swelling Experiments

Swelling experiments were conducted on bulk gelled samples obtained from vinyl-terminated as well as hydroxyl-terminated systems. The primary goal of carrying out this experiment was to characterize the polymer networks formed, in terms of amount

of soluble fraction present in the final material. This should be a good measure of how complete the network forming reactions were. The samples were swollen in toluene, which is a good solvent. After obtaining equilibrium swelling, the samples were deswollen in a series of mixtures of toluene and methanol, with increasing methanol content. Finally the samples were completely deswollen in pure methanol, and dried. The difference in the weights of the swollen and dry polymer were used to calculate the soluble fractions present in the material by using the following formula [5, 6],

$$v_2 = \left[1 + \frac{\rho_{poly}}{\rho_{solv}} \left(\frac{w_{swoll}}{w_{dry}} - 1 \right) \right]^{-1} \quad (40)$$

where, v_2 is the volume fraction of the rubber in the swollen state, ρ_{poly} is the density of PDMS (0.98 g/cm³) and ρ_{solv} is the density of the solvent, toluene (0.867 g/cm³).

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Chapter 3. Results and Discussion

3. Results and Discussion

3.1.1. Vinyl Terminated System

Samples were prepared on microscope cover-slips, both open to atmosphere and sandwiched, as described above. The samples usually gelled in about 20 minutes for the hydrosilation system. The onset of spinodal-like decomposition took place approximately at the gel point. The cloud point for the samples, where turbidity was visually noticed, was close to 45 minutes after mixing. As noted above, spinodal-like decomposition is absent from samples produced as open slides. This indicates that atmospheric oxygen, water, or transport of evaporating components might interfere with the crosslinking reaction. These samples showed no turbidity in spite of undergoing gelation. The correlation-ring pattern in light scattering, Fig. 2 inset, is a hallmark of spinodal decomposition. The ring is observed immediately on gelation, which usually occurred in about 20 minutes after sample preparation. The ring indicates the formation of a correlated structure with no preferred orientation. The structure formed has co-continuous morphology as seen in optical micrographs, Fig. 12.

Figure 12. Phase-separated, co-continuous structure on the onset of spinodal-like decomposition in the hydrosilation system. The spinodal-like, correlation distance is approximately 2 microns both in the micrograph and in the SALS pattern as discussed below. The cloud point time is 45 minutes after preparation of the reaction mixture.

Fig. 13 shows radially averaged, azimuthal, time-resolved light-scattering plots of intensity versus the scattering vector $q = 4\pi \sin(\theta/2)/\lambda$, following the progress of the spinodal-like decomposition, where λ is the wavelength and θ in the scattering angle. As in conventional spinodal decomposition, we see an increase in the intensity of the peak with time. The peak obtained in these plots is due to correlation between phases, with the ring angle, q^* , corresponding to the correlation distance $\xi = 2\pi/q^* \sim 2.2 \mu\text{m}$.

Normally, for linear polymer mixtures at deep thermal quenches, a spinodal-peak is seen to decay (move) to lower- q and to broaden as Ostwald ripening occurs at later stages of phase separation. This ripening is driven by the reduction in free energy of the system through reduction in the surface area of phases [1]. Surprisingly, in the crosslinked system, phases are not observed to ripen whatsoever (Fig. 13). We attribute this to the presence of a gel structure, which limits transport. However, an additional factor contributing to the lack of ripening could be a limited surface-energy difference between phases of similar chemical composition differing mainly in crosslink density. That is, ripening might not be expected if the surfaces of the two phases are chemically similar. The end effect is that the early-stage spinodal-like

structure is "locked-in" [2] by the network formation and a permanent early-stage spinodal-like structure results.

ATR spectra of two samples, a bimodal sample having undergone spinodal-like decomposition and the second of a normal mono-modal PDMS network formed from vinyl end-linked precursors is shown in Fig. 14. Comparison of the two spectra indicates that the phase-separated sample is chemically similar to the normal mono-modal PDMS network and that the phase separated domains may not arise due to differences in chemical composition, as detectable by ATR)).

Figure 13. Time-resolved, light-scattering plot. Log-scattered intensity versus log- q . The peak position indicates correlated domains at 2.2 micron spacing in agreement with figure 2. Ripening of the phase-structure at late stage is not observed, i.e. the peak position remains constant at late stages of decomposition.

Wignall et al. [3] have demonstrated the occurrence of phase-separation in blends of linear and branched polyethylene's arising from a disparity in branch content amongst the separated phases. Their work, in addition to previous literature [4-6], indicates that blends whose constituents are of similar chemical species but are topologically different can undergo phase-separation. The work of Alamo et al. [7] quantified the critical amount of branching in a blend of linear and branched polyethylene which would lead to phase-separation.

Figure 14. ATR Spectra, Top: Bimodal PDMS network showing spinodal- like phase separation, Bottom: Monomodal PDMS network formed from vinyl end linked chains.

They found this critical value of branch content to be ≥ 8 branches/ 100 backbone carbon atoms of the branched constituent. In order to derive an analogue for our system it is assumed that the high-molecular-weight precursor forms a phase dominated by linear chains. The low molecular weight PDMS chains are found to have ~ 28 branches/100 backbone atoms for the vinyl terminated system, and ~ 10 branches/100 backbone atoms in the hydroxyl terminated system. So it is possible for

the observed phase separation in our system to arise from topological differences in the phases if Alamo's results can be generalized to other polymer systems.

A schematic of the difference in the kinetic nature of the reactions taking place in the vinyl and hydroxyl-terminated systems is shown in Fig. 15 [8]. The vinyl-terminated system undergoes crosslinking by an addition mechanism. It is proposed that due to the fast nature of this reaction [8], the system is rapidly quenched into the two phase region demarcated by the critical branch content in Fig. 15. Moreover,

Figure 15. Schematic of proposed reaction mechanism kinetics in the vinyl (addition) and hydroxyl (condensation) terminated systems. t_s^* is the time for onset of spinodal-like phase separation in the vinyl system. $t_{N\&G}^*$ is the time for onset of nucleation and growth in the hydroxyl system. The value of 8/100 is from reference [7].

since it is possible for the addition reaction to go to completion [8], the quench obtained is not only fast but deep as well, i.e. far from the phase-separation boundary; lower dashed line in Fig. 15, proposed by Alamo [7].

On the contrary, in the hydroxyl-terminated system a condensation reaction is responsible for crosslinking. The reaction rate of such a condensation [8] reaction can be maintained only if the condensation product; ethanol in our case, is continuously removed from the system. As this is not possible for the in-situ measurements, the quench obtained in the hydroxyl-terminated system is much shallower as compared to the vinyl-terminated system. This may lead to a different mechanism of phase-separation in the hydroxyl-terminated system as will be discussed later.

Figure 16. Schematic of the proposed reaction mechanism leading to phase-separation.

Fig. 16 shows a schematic a mechanism that explains a possible progression for the crosslinking reaction and the subsequent formation of separated phases. The different stages can be explained as follows; a) Mixture of short and long chains before initiation of reaction, b) On addition of a tetra-functional crosslinker, short chains react more rapidly due to their superior mobility which allows diffusion towards reaction sites, c) The short chains react further from their terminal reactive sites; reaction of both end groups of the short chains leads to chain extension, the onset of phase separation and gelation are believed to be near this schematic stage. The arrows in Fig. 16 c indicate transport due to topological immiscibility, d) Chain extension decreases the difference in size of the precursor short and long chains, the long and short chains now have similar probabilities of diffusing to the reaction sites, e) Formation of two phases rich in highly branched short chains and close to linear long chains.

The contrast between the phases for light scattering experiments could possibly arise due the difference in density of the separated phases associated solely to the crosslink density difference. One of the phases is rich in crosslinked, short precursor chains (Fig. 16e), whereas the other phase comprises mostly long linear chains reacted only at the ends. The density difference can be estimated by the method of group substitution suggested by Bondi [9, 10]. Using this method $\Delta\rho$ was calculated to be 0.06 g/cm^3 for the vinyl terminated system and 0.02 g/cm^3 for the hydroxyl terminated system. The higher density difference in the vinyl terminated system is due to the presence of $(-\text{CH}_2-\text{CH}_2-)$ groups in the short chains which remain embedded in the system due to the addition reaction mechanism. These groups could also further drive the deep quench.

The Lorenz- Lorentz [11] equation, gives the relationship between the density and refractive index for spherical molecules as,

$$\frac{n^2 - 1}{n^2 + 2} = C\rho \quad (41)$$

where n is the refractive index, ρ is the density and C is a constant known as the specific refraction and is given by the ratio of molecular refraction to the molecular mass. Eq. 41 can be used as an approximation for the crosslinked phases to gain an idea of the feasibility for contrast in the light scattering measurement. The difference in the refractive indices of the two phases when calculated from eq. 41 is found to be nearly 0.09 for the vinyl-terminated system and 0.02 for the hydroxyl-terminated system, which is a sufficient contrast for scattering of light [12]. Then it is feasible that phase-separation driven by a large difference in crosslink density between short and long chains could give rise to the observed SALS patterns.

3.1.2. Spinodal Analysis

The kinetics of the early stage spinodal decomposition can be explained on the basis of the linearized Cahn-Hilliard theory [13-16]. According to their theory, concentration fluctuations associated with spinodal decomposition, in the early stages, display a linear rate law, $\delta\phi \sim (R\phi)dt$, where R is the linear growth rate, ϕ is the concentration and t is the time [17, 18]. This corresponds to an exponential increase in the scattered intensity of light on integration, and is given by eq. 42 as,

$$I(q, t) = I(q, t = 0) \exp[2R(q)t] \quad (42)$$

where $I(q, t = 0)$ is the scattered intensity at zero time associated with native composition fluctuations, and $R(q)$ is the rate of phase separation. From Fig. 13, the

maxima in scattered intensity occurs at a wave vector q_m of $2.8 \mu\text{m}^{-1}$. This value of maximum scattering vector does not change with time.

The time-evolution of scattered intensity shown in Fig. 13 has an interesting characteristic. The peak obtained in the intensity at wave-vector $2.8 \mu\text{m}^{-1}$ is because of the spinodal correlation length between the phases, as can be seen in the micrograph (Fig. 12). But, in addition to the growth of this peak, a flat background intensity increases in time and seems to “wash-out” the spinodal peak at latter stages. This increasing background intensity may be associated with the growth of sub-micron scale clusters of branched chains.

The total scattering obtained in Fig. 13, is then a sum of two contributions, scattering due to the evolution of the spinodal morphology, and scattering arising from growing network clusters. The spinodal scattering at high- q reflects a random 3-D web structure on a micron scale. Scattering from such an interpenetrating fractal structure can be approximated by $I \sim Bq^{-d_f}$. For a random walk structure with intersection of paths, (Brownian walk), $d_f \sim 2$. The total scattered intensity at high- q , above the spinodal peak, could then be given as,

$$I(q) \sim B(t)q^{-2} + C(t) \quad (43)$$

The first term on the right-hand side of eq. 43 represents the contribution from the random spinodal structure at sizes smaller than the correlation length, i.e. high- q , above the peak position in q . The second term is the contribution from the growing nano-scale clusters, and is a time dependent term, as molecular cluster growth progresses with time. Fits for the high- q scattering data using eq. 43 are shown in Fig. 17.

Figure 17. Log-log plot of intensity versus q , at high- q , showing fits to eq. 43 used to estimate $C(t)$.

Since $C(t)$ represents the low- q Rayleigh limit for nano-scale cluster scattering, it can be expressed as,

$$C(t) \sim N_{cluster} [d_{cluster}(t)]^6 \quad (44)$$

where, $N_{cluster}$ is the number density of growing molecular clusters, and is assumed to be a constant, and $d_{cluster}$ is the size of the branched nanoscale molecular clusters. The molecular clusters are fractal objects with $d_{cluster} \sim z^{1/d_f}$, where z is the weight average molar mass (number of molecular units) of a cluster and d_f reflects the average mass-fractal dimension of a cluster. We assume $d_f = 2$, as an approximation. Using this approximation, since d_f cannot be measured in the available q -range, we get,

$$C(t) \sim z^3(t)$$

$$\therefore C(t)^{1/3} \sim z(t) \quad (45)$$

In Fig. 18 $\log C(t)^{1/3}$ is plotted against $\log t$ to approximate the growth of z in time for the molecular clusters. A power-law relationship is observed, approximately $z \sim t^{1/2}$ (dash-dot line) which reflects a slow growth in molar mass compared with conventional models, diffusion limited growth would indicate $z \sim t$ for instance [19]. Fig. 18 indicates that the plateau for addition polymerization, Fig. 15, is correct, here with a weak $t^{1/2}$ slope, and that the initial, rapid conversion occurs prior to 20 minutes reaction time in Fig. 18 (solid line).

Figure 18. Log-log plot of the cube root of scattered intensity ($C(t)^{1/3}$) arising from network formation versus time, where $z \sim [C(t)]^{1/3}$. Dot-dashed line follows $z \sim t^{1/2}$ as discussed in text.

The intensity data, from Fig. 13, were corrected for this contributions arising from network formation, $C(t)$ in eq. 43, and plotted against time, as shown in Fig. 19, (following eq. 42) which shows a plot of intensity arising from spinodal

decomposition at various q -values versus time. The rate of phase-separation, $R(q)$, [19] is calculated from the slopes of Fig. 19 and the projected initial spinodal intensity, $I_{t=0}(q)$, is obtained from the intercept. $I_{t=0}(q)$ reflects a hypothetical initial intensity under constant quench conditions for the reacting system. In the hydrosilation system, the reaction is rapid enough for the approximation of a constant quench depth, Fig. 15 as supported by Fig. 18 and Fig. 19. This approximation is better in the latter stages.

Figure 19. Log-linear plot of corrected intensity arising from spinodal decomposition, versus time for the vinyl-terminated system.

Fig. 20 shows the variation in the rate of phase-separation $R(q)$, and the hypothetical extrapolated intensity at zero time $I_{t=0}$, as a function of q . As we can see from the wave-vectors at which a maxima in the values of $R(q)$ and $I_{t=0}$ are observed, the manifestation of the maximum growth rate in a scattering experiment ($I_{t=0}$) occurs at a

length scale smaller than the maximum growth rate itself. Normally, phase ripening is observed in spinodal decomposition driven by a reduction in surface area [20-22] leading to an increase in size for q^* . The data shows the opposite of this behavior as $q^* < q_{I=0}$. This indicates that the phases observed do not have the thermodynamic potential or drive, to ripen at latter stages. The explanation for this could be that the phases, being of similar chemical compositions, with limited surface energy difference, do not need to further reduce their interfacial area. Additionally, the progressive network formation, taking place due to the reaction, could “squeeze-in” these phases following deGennes [15, 16], thus preventing an increase in size.

Figure 20. a) Rate of phase-separation versus q ; a maxima in growth rate occurs at wave-vector $2.31 \mu\text{m}^{-1}$. b) $I_{t=0}$ versus q , $I_{t=0}$ obtained from the intercepts in Fig. 19; maxima in $I_{t=0}$ occurs at $2.87 \mu\text{m}^{-1}$.

According to the linear Cahn-Hilliard approximation, it is expected that $R(q)/q^2$ linearly decreases with q^2 [19].

$$R(q) \sim Dq^2 \left[\frac{\partial^2 f}{\partial c^2} - \kappa q^2 \right] \quad (46)$$

Fig. 21 shows that this approximation is partially met for the hydrosilation system, dashed line. The x-intercept of the dashed line in this plot gives the value q_c , which is the extrapolated critical wave-vector at which there is a crossover [17] from positive

to negative values of growth rate $R(q)$, i.e. the stability limit in size, $1/q_c$, for spinodal domains; domains smaller than $\sim 1/q_c$ are not stable. Cahn-Hilliard theory, predicts that $q_c^2 = 2q^{*2}$, or that the phase size for maximum growth, q^* , and the critical phase size are related by $\sqrt{2}$. The data for the hydrosilation system agrees with the classical prediction,

$$2q^{*2} = q_c^2 \quad (47)$$

The value of q_c^2 obtained from Fig. 21 is 10.74, which is in close agreement with the value of $2q^{*2}$ of 10.67, from Fig. 20a.

The theory of early stage spinodal decomposition, which is based on the linearization approximation, matches the result of Fig. 21. However, the late stage of spinodal decomposition, which is usually characterized by a deviation from linear theory and coarsening of the phases is not observed possibly because of low surface energy difference between phases and ‘locking-in’ of the structure due to gelation.

Figure 21. Plot of $R(q)/q^2$ versus q^2 where the rate of phase-separation has been calculated from the slopes of Fig. 19. Dotted line follows eq. 46. The x-intercept of the dotted line gives the value q^* .

3.2.1. Hydroxyl Terminated System

Samples were prepared on microscope cover slips, both open to atmosphere and sandwiched, as described above. The reaction in the hydroxyl-terminated system was much slower as compared to the vinyl-terminated system (Fig. 15). Usually, these samples took over 4-5 hours to gel. The samples were exposed to ambient H₂O (air humidity). Initially, a ring pattern observed in the hydroxyl-terminated system was believed to be due to spinodal decomposition. But after inspection of the optical micrographs (Fig. 22) it was found that low dispersion spherical domains formed, resulting in the ring pattern. The light scattering pattern in Fig. 22 (inset) displayed multiple concentric rings similar to the sphere function given by eq. 48 [23].

$$I(q) = \rho_0^2 v^2 \frac{9(\sin qR - qR \cos qR)^2}{(qR)^6} \quad (48)$$

where R is the sphere radius, q is previously defined, ρ^2 is the contrast (Δn^2 for light scattering), and v is the volume of the spheres, assuming small difference in the refractive indices. The optical micrograph in Fig. 22 shows the morphology of the phases formed which are reminiscent of nucleation and growth. Fig. 23 is a log-log plot of scattered intensity versus wave-vector q for a sample with morphology as shown in Fig. 22. The data of Fig. 23 was fit using the maximum entropy method [24-32] that has been demonstrated to yield a good approximation of the particle size distribution for spherical particles [23, 26, 27]. The code for the program is available on the web [25].

Figure 22. Nucleation and growth mechanism of phase separation observed in the hydroxyl-terminated system, inset shows the concentric ring pattern observed in light scattering from the specimen.

The maximum entropy method is widely accepted as a reasonable approach to obtaining the most-likely distribution function and it has been demonstrated to be effective at recreating a wide range of particle-size distributions from model systems. By fitting the scattered intensity using the maximum entropy method, the line in Fig. 11, the size distribution of the spherical domains was obtained as shown in Fig. 24. Fig. 24 shows that the spherical domains display a bimodal distribution, consistent with the micrograph in Fig. 22. The distribution for the two modes are extremely narrow, $\sigma \sim 2 \mu\text{m}$ indicating a fairly narrow time-span for nucleation. The narrowly distributed domains are consistent with Fig. 15. A probable mechanism for this to occur could be as follows; initially the condensation reaction proceeds at a rapid rate to a low conversion. This could lead to the nucleation on the heterogeneous nucleation sites in the system. The micrograph in Fig. 22 and its volume distribution obtained in Fig. 24 support this, i. e. large domains made of $9 \pm 1 \mu\text{m}$.

Figure 23. Light scattering plot of log-scattered intensity versus log- q ; line indicates a fit to the data using the maximum entropy method of Jemain and Ilavsky [21] for polydisperse spheres.

The nucleation depletion is associated with the reduction in conversion rate, (see Fig. 15.). The nucleation depletion, formation of domains and the absence of remaining unused heterogeneous nuclei could lead to the observed large scale size with narrow size dispersion. Later, when crosslinking has prevented the coalescence of these domains, the slow production of highly branched species in the predominantly long-chain phase could lead to a second nucleation event in the gel network, with nucleation on regions of high crosslink density formed in the reaction. These late stage domains might be expected to be smaller since they nucleate later and since their growth occurs in a gel network. A broader distribution is also expected, $4 \pm 2 \mu\text{m}$ as observed in Fig. 24. This discussion must remain speculative since the details of composition variations in such a reaction system are difficult to observe.

Figure 24. Particle volume distribution function $f(D)$, plotted against particle size.

3.2.2 Gelation in Hydroxyl-terminated PDMS

According to Carothers equation [8], for gelation to occur, the critical extent of reaction, p_c , has to be attained. For the hydroxyl terminated system, crosslinking occurs by the reaction of 4 moles of the di-functional precursor PDMS and one mole of the tetra-functional crosslinking agent. The average functionality of the system can then be given by,

$$f_{avg} = \frac{(1 \times 4) + (4 \times 2)}{1 + 4} = 2.4$$

From which we can calculate the critical extent of reaction as,

$$p_c = \frac{2}{f_{avg}} = 0.83$$

So as will be discussed later the hydroxyl-terminated system can undergo gelation even with around 15-20% solubles.

3.3. DSC measurements

DSC runs were performed on two samples. These runs were conducted to see if we could observe any change in the thermal behavior of the phase separated bimodal PDMS sample as compared to a normal monomodal network formed from similar

Figure 25. DSC run of a monomodal sample, synthesized from short-chain vinyl-terminated precursors.

precursor chains. Vinyl end-terminated chains were employed to synthesize these networks. The samples tested were monomodal networks synthesized from short chains and a phase separated bimodal PDMS network. Fig. 25 shows the DSC run for a sample of end-linked short vinyl-terminated chains, with a glass transition temperature of -4.18°C , which is close to the glass transition temperature of -5.88°C obtained for a phase-separated bimodal PDMS network formed from vinyl-terminated

chains (Fig. 26). Thus it is not possible to distinguish and characterize the occurrence of phase-separation on the basis of DSC for this system.

Figure 26. DSC run of a bimodal phase-separated PDMS network, formed from a mixture of short and long vinyl-terminated precursor chains.

3.4. Swelling Experiments

The swelling experiments were conducted to check the completion of the network forming reactions. Toluene was used to attain equilibrium swelling and these swollen samples were deswollen in methanol. The amount of soluble fraction in the networks formed from the vinyl-terminated system was in the range of 2-5%. In case of the hydroxyl-terminated system, the soluble fraction was considerably higher, around 15-20%. This corroborates our understanding of the two reaction mechanisms. The hydroxyl-terminated system, which follows a hydrolysis/condensation mechanism,

does not proceed to completion whereas, in the vinyl-terminated system the reaction proceeds to near-completion. This is in agreement of our understanding of the reaction mechanisms as depicted in Fig. 15.

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Chapter 4. Conclusions

4. Conclusions

It has been shown in this work that it is possible to control the final morphology in a multi-component polymeric system through the rate of crosslinking reaction. Phase separation can be induced by reaction in a bimodal network of short and long chains over a narrow set of conditions, including molecular weight of the precursors and their stoichiometry. Control of the reaction rate is the critical aspect for controlling phase-separation as not only thermodynamic, but kinetic parameters as well, control the phase-separation mechanism.

Increase in the molecular weights of the components due to crosslinking drives the phase-separation. But, due to network formation, the phase-separated structure gets “locked-in,” and late-stage ripening is not observed for the vinyl-system. The kinetics of the early stages of spinodal decomposition as described by the Cahn-Hilliard theory is applicable to the rapid-reaction vinyl-terminated system.

The reaction rate controls the effective “quench-depth” of the system. In the vinyl-terminated system, where crosslinking takes place by an addition mechanism, phase-separation occurs by spinodal decomposition. The hydroxyl-terminated system follows nucleation and growth mechanism of phase-separation. The reaction mechanism in the hydroxyl-terminated system is hydrolysis/condensation, which is slower as compared to the addition mechanism, and hence the quench that it brings about is expected to be shallower.

Phase separation in the hydroxyl-terminated system results in the formation of simultaneously nucleated, close-to-monodisperse spherical domains. The conversion rate associated with the condensation mechanism leads to two nucleation events with two characteristic sizes of domains associated with these nucleation events.

The role of branch topology in phase-separation of blends, as reported by Alamo et al., has been generalized and applied to our system. Both, vinyl as well as the hydroxyl-terminated systems, meet the critical requirement for initiation of phase-separation in terms of disparity in branch content of the two resulting phases. A lack of chemical difference between the phases by IR spectra, and from the reaction chemical makeup, supports topology as the source of immiscibility. It is shown that the crosslink density difference is sufficient to give rise to light scattering.

Chapter 5. Future Work

Future Work

Although optical microscopic evidence and small angle light scattering runs have been presented on the mechanism of phase separation (nucleation and growth) in the hydroxyl-terminated system, a more through study involving the kinetics of nucleation and growth process would be highly advantageous. A more through understanding of the reaction mechanism taking place in the hydroxyl system will help us to dictate the quench depth by means of reaction and allow for better control of the phase separation mechanism. Research for end-use applications for the vinyl-terminated system of which we have a better understanding and control is expected. This thesis has proposed that,

1. Topology can induce phase-separation.
2. Reaction rate can determine phase-separation morphology.
3. Novel morphologies can be produced.
 - Fixed spinodal.
 - Monodisperse nucleation and growth.
4. Generalization of quench depth for phase-separation induced by reaction.

Based on these results, the following could be studied further in future work.

Wignall (1996) and Alamo (1997) have shown that branch topology can induce phase-separation in blends of polyolefin's. We have shown that it is possible to generalize their results concerning parameters controlling phase-separation, i.e. the number of branches per 100 backbone-chain atoms in the branched component. In case of the systems studied here, viz. polysiloxane's, a much better control over the amount of branching is possible, because of the end-linked precursor chains. Hence it is possible to further develop this generalization and find a specific result for polysiloxane's in terms of critical amount of branching needed for phase-separation.

. It would also be interesting to see if the generalization from the polyolefin's is applicable to systems other than the polysiloxane's.

In systems where phase-separation is chemically driven, we can manipulate the quench depth to obtain desired morphology by controlling the mechanism of phase-separation. This can be done by controlling the rate of the reaction responsible for phase-separation. Other reactions with variable rates should be applied and the ensuing quench depths should be noted.

An application for the fixed spinodal morphology resulting from the vinyl-terminated system could be in the acoustic damping of noise and vibration (Sperling 1980). It is known that the damping characteristics of an incompatible blend are superior to those of a compatible blend. Sperling (1980) describes these blends as blends with "controlled compatibility". The DSC plots for vinyl-terminated system (Figs. 22 & 23), show that the phase-separated structure does not have multiple glass-transitions. It would be interesting to see what effect this would have on the damping properties, because of its the inherent dependence on the glass-transition temperature.

Though it is known that bimodal networks have superior mechanical properties over mono-modal networks, some works in literature (Galiatsatos, 2001) indicate that phase-separation in such bimodal networks, leads to a deterioration of in the mechanical properties of these networks. It would be worthwhile, to check the mechanical properties of our phase-separated networks.