If we take $\eta_0 = 0.335$ cP for diisobutyl adipate at 240 °C, we can compute the hydrodynamic radius R_h for the TEFZEL copolymers with the results also listed in Table I. The ratio of $R_h/R_g \approx 0.58$. As $R_h/R_g = 1.29$, 0.663, and ~ 0.54[8] for a hard sphere, a Gaussian coil, and an expanded coil, respectively, a value of 0.58 for the R_h/R_g ratio again suggests that PETFE copolymer in diisobutyl adipate at 240 °C forms slightly expanded coils, indicating fairly good solubility.

In conclusion, our viscosity data are in good agreement with our previous light scattering characterizations of TEFZEL in diisobutyl adipate and the TEFZEL copolymer forms slightly expanded coils in diisobutyl adipate at 240 °C. We have now established a high-temperature viscosity reference that is experimentally simple to perform for the characterization of TEFZEL.

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Structural Coarsening of Demixed Polymer Solutions[†]

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ABSTRACT: The structural coarsening of demixed polystyrene/cyclohexane solutions was studied by using a quick freeze/freeze-dry technique on solutions allowed to coarsen for various lengths of time. Quenches of near-critical solutions were bicontinuous; however, the coarsening law was found to be consistent with a diffusive coarsening mechanism rather than the expected hydrodynamic flow mechanism. The structural size was found to grow with time with an exponent in the range 0.18–0.32. A quantitative model of the diffusive coarsening process was developed specifically for demixed polymer solutions, and predicted the structural sizes within a factor of 5 of the measured values. The model also predicted a very strong concentration dependence of coarsening, which was experimentally verified. An explanation as to why diffusive coarsening rather than coarsening by hydrodynamic flow occurs is offered.

Introduction

Thermally induced phase separation (TIPS) of polymer solutions is a commonly used technique to prepare microcellular foams or membranes with controlled morphologies. For example, low-density microcellular foams have been prepared with TIPS using many different polymers including atactic polystyrene,[1] isotactic polystyrene,[2] poly(4-methyl-1-pentene),[3] polyacrylonitrile,[4] and many water-soluble polymers such as (carboxymethyl)cellulose,[5] poly(acrylic acid),[6] and dextran.[7] An even larger variety of polymers have been used to prepare higher density foams and membranes.[8] TIPS is effective if the polymer solution exhibits an upper critical solution temperature. It differs from the more traditional approach to induce phase separation, which involves diffusing a nonsolvent into a polymer solution.[9] If the phase separation results in an interconnected polymer-rich phase, then a foam or membrane can be produced with two additional steps. The polymer-rich phase must be immobilized, either by gelation (crystallization) or by freezing of the solution. Finally the solvent must be removed by extraction and supercritical drying of a resultant gel or by sublimation under vacuum of a frozen solution. The type of phase separation and the rate of phase separation determine the ultimate morphology and properties of the membrane or foam. This has been demonstrated with well-characterized polystyrenes.[1,2]

Usually liquid phase separation creates a fine-scaled, "early-stage" structure in the polymer solution, which can be "frozen-in" if the polymer solution gels or if the quench is continued to a low enough temperature so that the solvent freezes. Estimates of the size expected for deep quenches into the spinodal region of polymer solutions have been made[1,10] and typically fall in the range 0.1–1.0 μm. This corresponds to some multiple of the polymers root mean square radius of gyration. The estimates are based upon the Cahn[11] theory for spinodal decomposition as modified by Van Aartsen[10] for polymer solutions. The dynamics of phase separation can also be calculated from Van Aartsen's theory. For polymer solutions the dynamics of early-stage structure development are expected to be very fast, perhaps even experimentally inaccessible for deep quenches. We have previously argued that the structures observed in freeze-dried polystyrene solutions quenched near their critical concentrations almost certainly correspond to coarsened

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structures.[1] Hence, although the early-stage structure development (either nucleated or spinodal) is of tremendous theoretical interest, the late-stage coarsening process is of more technological interest.

Two mechanisms have been described for structural coarsening of solutions. The first is a diffusive process described in the classic paper of Lifshitz and Slyozov.[13] Droplets that are well separated and have well-defined interfaces will coarsen due to the fact that smaller droplets, which have a smaller radius of curvature, have a higher solubility. Hence, smaller droplets preferentially dissolve while larger droplets grow. The Lifshitz–Slyozov theory predicts that the average drop radius will grow with time to the 1/3 power. This model has been previously quantified for small molecules[13] and recently for polymer/polymer systems.[14] If the interfaces are not well separated or are not sharp, then a smaller exponent, 1/4, has been predicted.[15] Numerous other models[16–18] predict a transient behavior where the exponent is initially 1/4 and asymptotically approaches the value of 1/3. In general then, a diffusive coarsening process is characterized by an exponent in the range 1/4–1/3.

The second mechanism that has been described for structural coarsening of demixed solutions is applicable only when the phases formed are bicontinuous, which may occur for a critical quench. In this case the structure can coarsen by hydrodynamic flow. The first observation of this was by McMaster, who observed a growth law that was linear in time.[19] An analysis of flow-induced coarsening, which predicted a growth law linear with time, was originally given by Tomotike.[20] Voigt-Martin et al.[21] observed this type of coarsening with critical deep quenches of a polystyrene/poly(vinyl methyl ether) system. Siggia (ref 22 and references therein) describes both types of coarsening processes and the expected crossover between them. For small molecule systems there is good qualitative agreement with the predictions.[23,24] The basis of the hydrodynamic flow mechanisms is an interfacial instability. Phases of different size, and therefore different radii of curvature, would have different pressures, which in turn would cause flow.

In this paper we describe our experimental results on the coarsening of demixed polystyrene (PS) and cyclohexane (CH) solutions. When these demixed solutions are fast-frozen and freeze-dried, highly interconnected "foamlike" structures result.[1,2] It is reasonable to assume that such interconnected structures also exist in the precursor liquid. Intuitively, one would expect that the most efficient coarsening mechanism would involve hydrodynamic flow and that the structural size would be proportional to the coarsening time. Surprisingly, however, the coarsening rate will be shown to vary with time, raised to a power in the range 0.18–0.32, which indicates a diffusive coarsening process. This is distinctly different from demixed solvent/solvent or demixed polymer/polymer systems. To our knowledge, no previous work has studied the late-stage coarsening of demixed polymer solutions.

Experimental Section

Atactic PS, synthesized by Pressure Chemical Co. with $M_w = 2.233 \times 10^6$ and $M_n = 1.988 \times 10^6$ (lot no. 50405), was used without further purification. Reagent grade CH (Fisher) was used as received.

Cloud points were determined by first preparing solutions in clear glass vials (diameter = 2 cm), which were sealed with a vacuum stopper. The PS was then dissolved at 45 °C. Days were required for complete dissolution at the lower concentrations and weeks for the highest concentration. Cloud points were then determined by the ability to read a scale through the vial at a given temperature. The quench rate was always less than 1 °C/h, taken in increments of 0.1 °C. Solution homogeneity was assured by the appearance of uniformly clouding solutions. Cloud points determined in this way were reversible and were reproducible within 0.2 °C.

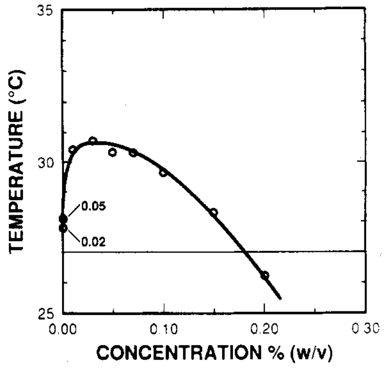

Figure 1. Cloud point curve for polystyrene ($M_n = 1.988 \times 10^6$) in cyclohexane.

Solutions for coarsening studies were made in a solution flask with a reflux condenser. After dissolution, the solution was transferred to 1-cm-diameter test tubes, which were sealed and placed in the quench bath held at 27 ± 0.2 °C for times ranging from 1 to 60 min. The solution temperature approached the quench temperature (27 °C) relatively quickly compared to most quench times. Within the accuracy of the temperature measurements (0.2 °C), the quench temperature was attained within 3 min. This is somewhat of an overstatement of the thermal lag, however, because the solution would be in the one-phase region during some of this time. Once the cloud point was reached, the time for the solution to be within 0.2 °C of the quench temperature was only 2 min in the worst case and decreased as the solution concentration was increased (with a simultaneous decrease in cloud point temperature).

After coarsening, the solutions were fast-frozen by quenching the test tube into liquid nitrogen and the solvent was then removed by sublimation under vacuum. The structure in the resulting dry PS was characterized by scanning electron microscopy (SEM) and BET surface area measurements (Quantachrome Monosorb model). The structural size in the dry PS was quantified by utilizing a previously developed relationship between the BET surface area, the density (approximated as the original solution concentration), and the average spacing between phases.[12] The relationship takes the form

$$d = 4/[\rho S] \tag{1}$$

where ρ is the density, S is the BET surface area per unit mass, and d is the desired average spacing between phases (see Figure 5). In this way, the structural coarsening could be followed qualitatively by the SEM photomicrographs and also quantitatively. The later was necessary in order to differentiate between possible coarsening mechanisms.

The viscosity for one solution (18% (w/v)) was measured by the fall time of a steel ball (nominal diameter = 2.75 mm) within a solution (2-cm-diameter tube). The validity of this measurement was confirmed by the good agreement obtained with viscosity standards (Polyscience poly(dimethylsiloxane) 10 000 cSt (centistokes), lot no. 54838, and 100 000 cSt, lot no. 54839, at 25 °C). The viscosity was measured 1 °C above the measured cloud point (for an 18% solution) in order to ensure that a one-phase solution existed.

Experimental Results

Figure 1 shows the cloud point curve for PS ($M_n = 1.988 \times 10^6$ and $M_w/M_n = 1.123$) in CH. Coarsening experiments were performed at 27 °C, which would result in the formation of an 18% (w/v) polymer-rich phase. The viscosity of an 18% (w/v) solution at 28 °C (1 °C above the cloud point) was 328 000 cSt. Although the cloud point curve and the binodal must necessarily differ somewhat for this polydisperse sample, we assume that they

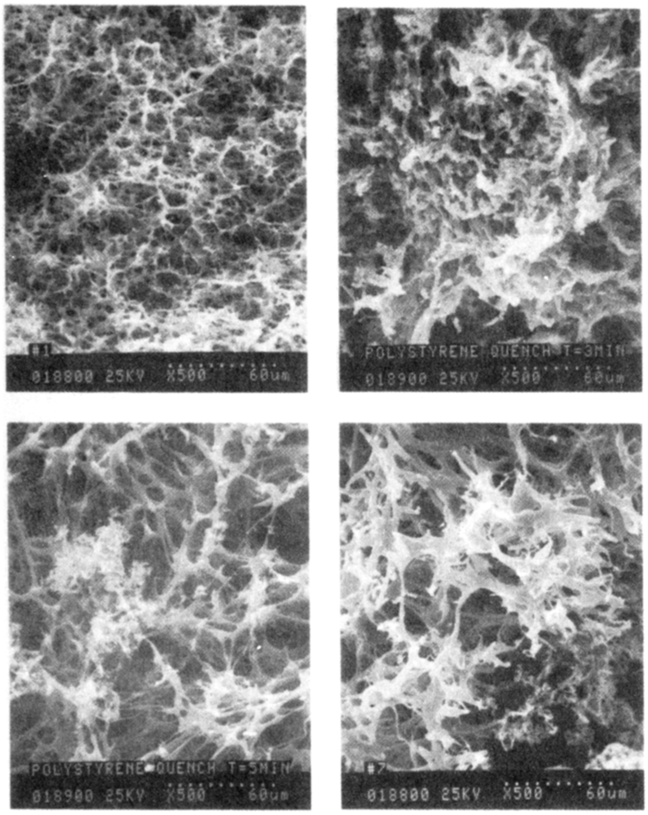

Figure 2. SEM photomicrographs of dried, demixed 3% (w/v) polystyrene/cyclohexane solutions as a function of coarsening time (1, 3, 5, and 7 min). Demixation was done at 27 °C, which is 3.7 °C below the cloud point. The bar in each photomicrograph corresponds to 60 μm.

are identical. Our qualitative conclusions should not be affected by this assumption.

Coarsening experiments were done with PS concentrations of 3, 5, 7, and 10% (w/v), which had cloud points of 30.7, 30.3, 30.3, and 29.6 °C, respectively. The maximum in the cloud point curve occurs at about 3%, which is quite close to the expected critical concentration for PS of this molecular weight.[25] Figure 2 shows SEM photomicrographs of dried, demixed, 3% polystyrene solutions as a function of coarsening time. Coarsening times of 1, 3, 5, and 7 min were observed. After 7 min, the demixed 3% (w/v) solutions showed signs of gravity settling, which was evidenced by a solvent layer growing on the top of the solutions. This was not observed until after 30 min for the 5% (w/v) solution and not until after 60 min for the 7 and 10% (w/v) solutions. Figure 3 shows SEM photomicrographs of dried, demixed PS solutions as a function of coarsening time for 5, 7, and 10% (w/v) solutions and for coarsening times ranging from 1 to 30 min. Two things are immediately apparent from the photomicrographs. First, any measure of the structural size (e.g., the polymeric phase thickness or the average spacing between phases) grows with coarsening time. Second, the structures remain highly interconnected throughout the coarsening experiments. There is no evidence of the breakup of phases into droplets at any time.

Table I lists the BET surface areas measured for each dried, demixed solution as a function of coarsening time. BET surface areas could be reproducibly measured within 6%.[12] Also listed are the average distances between phases for each, which were calculated from the surface areas according to eq 1. Figure 4 is a plot of the calculated cell sizes as a function of coarsening time for dried, demixed solutions at the four concentrations studied. A least-squares fit to the data for each concentration is shown with the indicated slopes. The least-squares slopes range from 0.18 to 0.32.

Discussion of Results

The structural size of demixed PS/CH solutions in the concentration range 3–10% (w/v) grows with time raised to a power in the range 0.18–0.32. Because of scatter in the data and other experimental uncertainties, we make no attempt to differentiate between these exponents. However, we can clearly conclude that the exponent is in a range consistent with a diffusive coarsening process (slope 1/4–1/3) and inconsistent with a hydrodynamic flow mechanism (slope 1). This is a surprising result because the demixed solutions are highly interconnected as expected for near-critical quenches. Intuitively, we expected that a flow process would be faster than diffusive coarsening. This is what is both expected and found experimentally for interconnected, demixed phases of solvent/solvent[22] and polymer/polymer[19,21] systems. With the aid of a simple morphological and diffusive coarsening model, we hope to explain this unexpected observation.

Morphological Model

A model of the diffusive coarsening process requires a morphological model of the demixed solutions. Figure 5 shows a representation of a two-phase bicontinuous structure that is qualitatively similar to the dried, demixed solutions and is our model for the precursor, demixed solutions. We are primarily concerned with the average spacing between phases because this will be the average diffusion distance for coarsening. The average distance between surfaces of the polymer-rich phase (α) is d^α, and the average distance between surfaces of the solvent-rich phase (β) is d^β. These averages are directly related to the interfacial area according to[12]

$$(d^\alpha + d^\beta)/2 = 2/S_V \qquad (2)$$

where S_V is the interfacial area per volume of solution. This is a very general result. Equation 1 differs by a factor of 2 because for the dried, demixed solutions the average spacing between surfaces of the polymer phase is small compared to that between the voids and is ignored.[12]

The cloud point curve corresponds to the typical situation in which the solvent-rich phase contains little polymer. Hence, a polymer mass balance allows us to relate the average spacing between phases, the interfacial area, and the concentration of polymer in the polymer-rich phase:

$$c_p = c_p{}^\alpha S_V d^\alpha/2 \qquad (3)$$

where c_p is the polymer mass fraction in the original solution and $c_p{}^\alpha$ is the polymer mass fraction in the polymer-rich phase (determined by the quench temperature and the cloud point curve). The quantity $S_V d^\alpha/2$ is the volume of the polymer-rich phase per total volume of solution. Equations 2 and 3 allow us to relate the average thicknesses of the two phases.

$$d^\beta = d^\alpha[2(c_p{}^\alpha/c_p) - 1] \qquad (4)$$

Diffusive Coarsening Model. We follow the arguments of de Gennes given previously for polymer/polymer demixation.[14] Associated with the interfacial tension between the demixed phases and the variability of

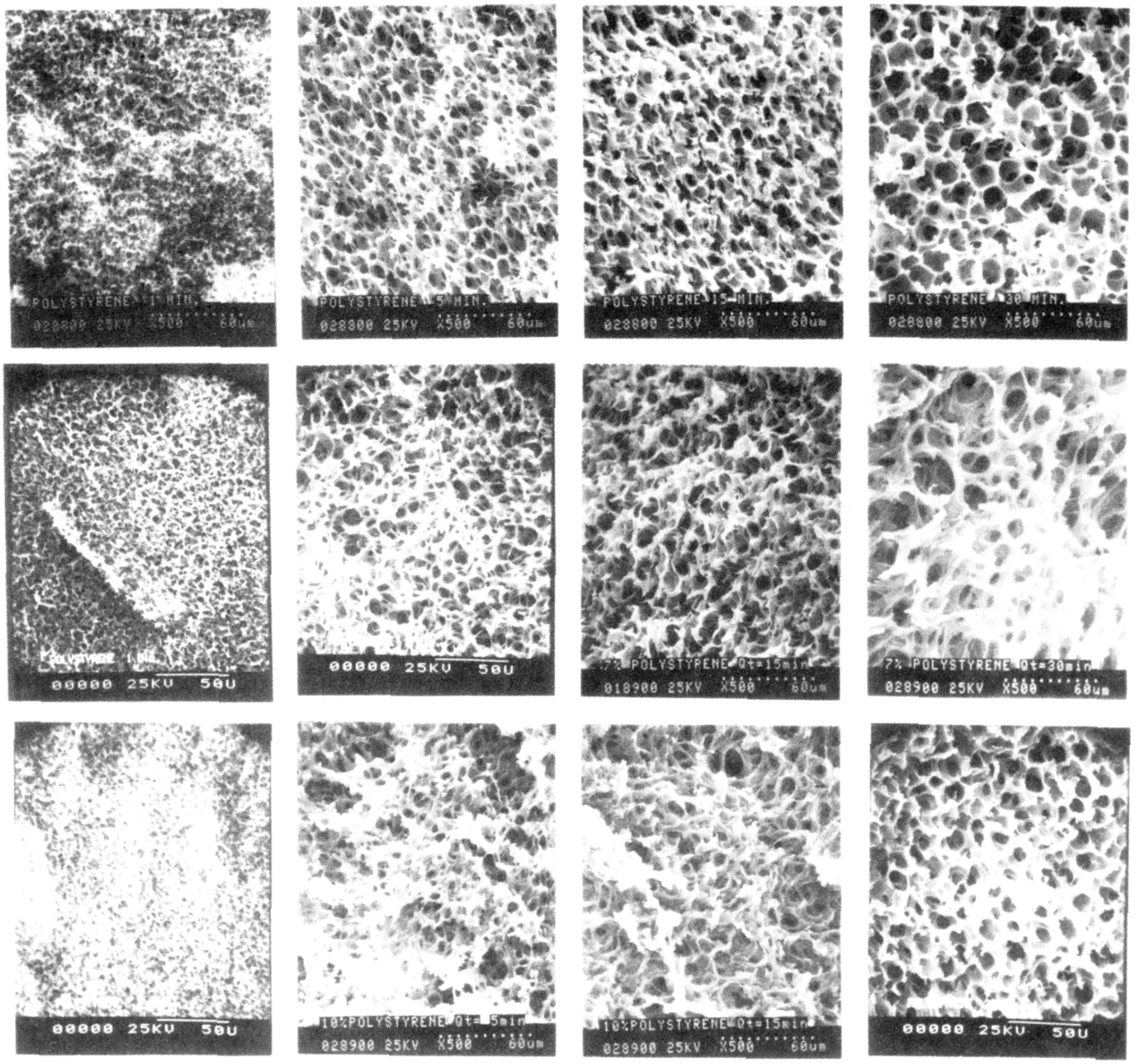

Figure 3. SEM photomicrographs of dried, demixed polystyrene/cyclohexane solutions as a function of coarsening time (1, 5, 15, and 30 min). Demixation was done at 27 °C, which is (top) 3.3 °C below the cloud point (5% (w/v) solution), (middle) 3.3 °C below the cloud point (7% (w/v) solution), and (bottom) 2.6 °C below the cloud point (10% (w/v) solution). The bars in the photomicrographs are either 50 or 60 μm as indicated and correspond to the same magnification.

radii of curvature, there is a shift in polymer and solvent chemical potentials:

$$\Delta\mu_p = 4\sigma V_p[1/d_i^{\alpha} - 1/d^{\alpha}] \quad (5)$$

$$\Delta\mu_s = 4\sigma V_s[1/d_i^{\alpha} - 1/d^{\alpha}]$$

where V_p (V_s) is the volume of a polymer (solvent) molecule and d^{α} is the average thickness of phase α and is taken as representative of twice the average radius of curvature, whereas d_i^{α} is taken to be the same quantity for a particular region of phase α labeled i. The latter may vary from the average, which is the origin of diffusive coarsening. The interfacial tension is σ.

The gradient in chemical potentials gives rise to a diffusive flux of both polymer and solvent, which can be described by

$$J_p = -J_s = -L_{pp}[\Delta(\mu_p - \mu_s)]/d_i^{\beta} \quad (6)$$

L_{pp} is the Onsager phenomenological coefficient and can be related to the ordinary diffusion coefficient by[26]

$$D_{ps}^{\beta} = (L_{pp}^{\beta}/pc_s^{\beta})(\partial\mu_p/\partial c_p)_{T,P}^{\beta} \quad (7)$$

Note that the diffusivity is taken to be that appropriate to the dilute phase, β, because polymer molecules diffuse from phase α to another part of phase α through phase β. The total solution density is p. Since phase β is dilute, the polymer chemical potential can be approximated with the ideal solution result, $(\partial\mu_p/\partial c_p)_{T,P}^{\beta} = kT/c_p^{\beta}$, and the flux of the polymer becomes

$$J_p = \frac{2D_{ps}^{\beta}pc_s^{\beta}c_p^{\beta}\sigma[1/d^{\alpha} - 1/d_i^{\alpha}](V_p - V_s)}{kTd_i^{\beta}} \quad (8)$$

Again following de Gennes,[14] we can relate the flux of the polymer to the rate at which the thickness of phase

Table I
Surface Area (m^2/g) and Average Spacing between Phases (μm)^a

coarsening time, min		concentration 3% (w/v)	5% (w/v)	7% (w/v)	10% (w/v)
0	surf area	28.1	22.2	17.4	27.1
	spacing	4.7	3.6	3.3	1.5
1	surf area	12.0	12.0	10.8	9.5
	spacing	11.1	6.7	5.3	4.2
3	surf area	9.6	8.9	9.2	10.1
	spacing	13.9	9.0	6.2	4.0
5	surf area	7.9	8.4	8.7	8.0
	spacing	16.9	9.5	6.6	5.0
7	surf area	6.1	8.8	7.6	8.3
	spacing	21.9	9.1	7.5	4.8
10	surf area		4.4	7.1	6.5
	spacing		18.2	8.0	6.2
15	surf area		6.2	6.1	6.2
	spacing		12.9	9.4	6.5
20	surf area		6.1	7.2	5.7
	spacing		13.1	7.9	7.0
30	surf area		4.4	6.0	5.2
	spacing		18.2	9.5	7.7
60	surf area			5.0	4.7
	spacing			11.4	8.5

^{a} Calculated from eq 1, as a function of coarsening time for four solution concentrations of polystyrene/cyclohexane.

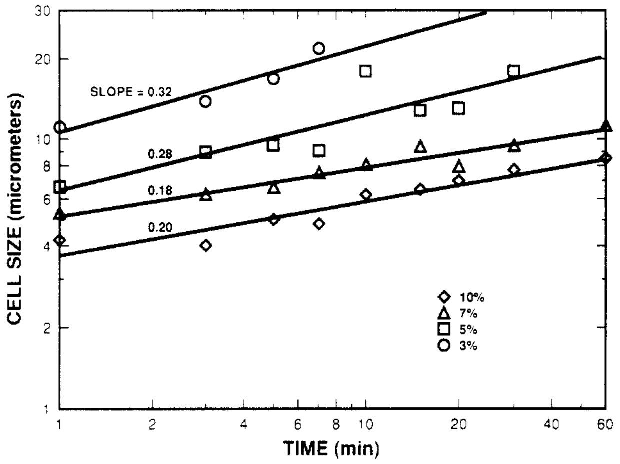

Figure 4. Cell sizes calculated on the basis of the measured surface areas for dried, demixed PS/CH solutions of four concentrations. The line through each data set is a least-squares fit with the indicated slope.

α_i is decreasing:

$$J_p = \frac{c_p{}^{\alpha} p \, \mathrm{d}(d_i{}^{\alpha})/\mathrm{d}t}{2} \tag{9}$$

If we equate these two expressions for the polymer flux and replace $d_i{}^{\alpha}$ with $d_i{}^{\beta}$ by using eq 4, then the flux becomes

$$\frac{\mathrm{d}(d_i{}^{\beta})}{\mathrm{d}t} = \frac{8D^{\beta}_{ps}c_s{}^{\beta}c_p{}^{\beta}\sigma[1/d^{\beta} - 1/d_i{}^{\beta}](V_p - V_s)[2(c_p{}^{\alpha}/c_p) - 1]^2}{kTd_i{}^{\beta}c_p} \tag{10}$$

Comparing this result to the classic result of Lifshitz and Slyozov[13] allows us to write the rate of growth of the average phase size, d^{β}, as

$$(d^{\beta})^3 = \frac{32D^{\beta}_{ps}c_s{}^{\beta}c_p{}^{\beta}\sigma(V_p - V_s)[2(c_p{}^{\alpha}/c) - 1]^2}{9kTc_p{}^{\alpha}}t \tag{11}$$

This equation can be evaluated by using independently measured values of the solution properties to give the rate of growth of the average thickness of phase β. This equation differs in an important way from prior results for either solvent/solvent or polymer/polymer systems. There is a very strong concentration effect predicted. This is absolutely necessary to describe the experimental results. We now compare calculated growth rates to those experimentally observed in the dried, demixed solutions.

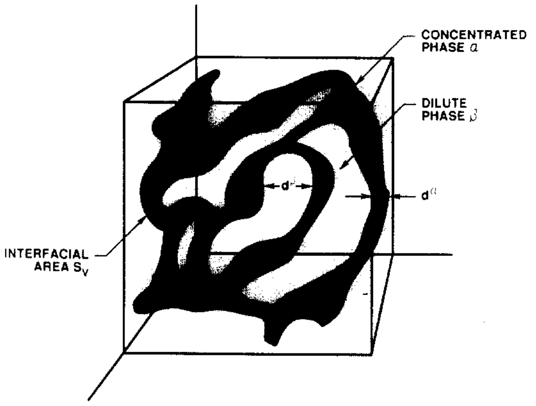

Figure 5. Schematic of the morphological model showing bicontinuous phases of average thicknesses d^{α} and d^{β}. The interfaces are assumed to be quite sharp with an interfacial area per volume of S_V.

Model Predictions. The infinite dilution diffusivity of PS in CH was estimated by using a correlation given in the Polymer Handbook.[27] The estimated diffusivity is 9.37×10^{-8} cm^2/s. The following polymer and solvent molecular volumes were based upon the number-average molecular weights and the bulk densities:[27] $V_p = 3.16 \times 10^{-18}$ cm^3 and $V_s = 1.79 \times 10^{-22}$ cm^3. The equilibrium polymer concentration of the polymer-rich phase was estimated from the cloud point curve to be 18% (w/v) or 18.8% by weight. The predictions of eq 11 are very sensitive to the polymer concentration in the polymer-poor phase. For this value we equilibrated solutions at 27 °C, decanted off the top phase, and measured the polymer content directly after evaporation of the solvent. For 5% (w/v) solutions a value of 0.2% was obtained. The result differed substantially from the observed cloud points in this low-concentration region. We also measured the polymer content of the polymer-rich phase in the same way after equilibration at 27 °C. In this case a concentration of 18.3% by weight was obtained, which is very close to the observed cloud point curve. No attempt was made to measure the interfacial tension of the demixed phases. Since no published data could be found, we estimated the value to be 10^{-2} dyn/cm. This is the order of magnitude obtained with demixed polystyrene/methylcyclohexane solutions with approximately the same undercooling.[28]

Figure 6 shows the predictions of eq 11 for the average size of the dilute phase as a function of coarsening time. Note the strong effect of solution concentration, c_p. The predicted coarsening rates for each starting concentration are the same order of magnitude as those determined from BET surface area measurements on the dried, demixed solutions (Table I). In general, the values are low by about a factor of 5. As noted previously, the coarsening model predicts an exponent of 1/3 while a lower exponent, 0.18–0.32, was measured. This agreement seems reasonable, however, in light of the experimental uncertainties in the polymer solution properties, the relatively simple morphological model, and the expected differences between the true binodal curve and the measured cloud point curve.

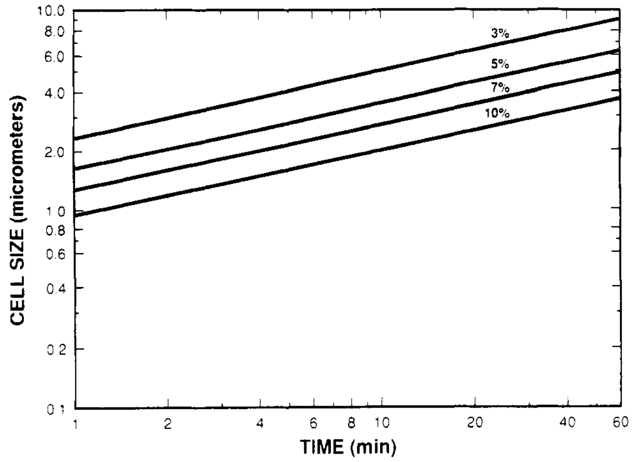

Figure 6. Predictions of eq 11 for the average size of the dilute phase (cell size) as a function of coarsening time for PS/CH solutions of the indicated concentrations. Note the strong effect of solution concentration.

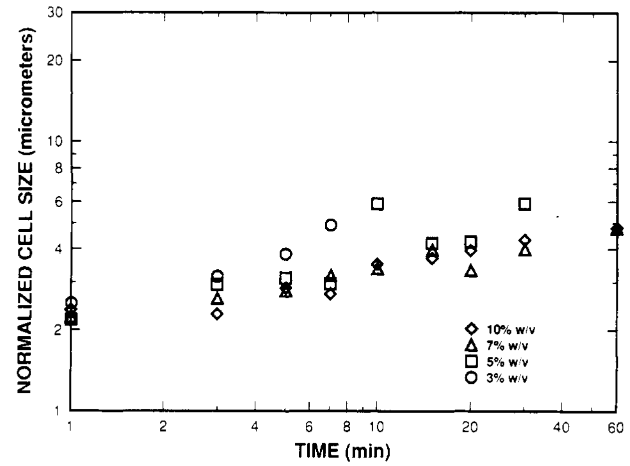

Figure 7. Average size of the dilute phase (cell size) divided by the concentration term appearing in eq 12 as a function of coarsening time for the four solution concentrations experimentally observed.

A direct result of the morphological model is a prediction of the effect of solution concentration. Equation 11 can be rewritten as

$$\frac{d^\beta}{\left[2\frac{c_\mathrm{p}{}^\alpha}{c_\mathrm{p}}-1\right]^{2/3}} = A^{1/3}t^{1/3} \qquad (12)$$

The prefactor A contains all of the polymer solution properties. The only place where the solution concentration appears is in the denominator of the term on the left side of the equation. Figure 7 is a plot showing the experimentally determined cell size for each solution concentration divided by the concentration term appearing in eq 12, i.e., $d^\beta/[2(c_\mathrm{p}{}^\alpha/c_\mathrm{p}) - 1]^{2/3}$. This should reduce all of the data to a single curve regardless of solution concentration. As Figure 7 shows, this does indeed occur. This plot should be compared to Figure 4, which shows the calculated cell sizes prior to this normalization. This strong effect of solution concentration is absolutely necessary to explain the experimental data.

The molecular weight dependence of coarsening has not been experimentally studied in any detail. Qualitatively, molecular weight has a relatively small effect.[1] This is consistent with the predictions of eq 12, since the factor A has a small molecular weight dependence and this is raised to the 1/3 power. Experimentally, the largest effect of molecular weight is that it defines the critical concentration. Bicontinuous phases are obtained only at concentrations above this.[1] On the other hand, a very strong molecular weight dependence is predicted for coarsening by hydrodynamic flow. For this mechanism, the coarsening rate is predicted to be proportional to the inverse of viscosity,[22] and for a semidilute solution the viscosity varies as molecular weight to the 3.4 power. This is inconsistent with our qualitative observations and is further evidence that the coarsening mechanism is a diffusive one.

We were initially surprised that coarsening did not appear to occur by a flow mechanism as has been observed in both bicontinuous, demixed polymer/polymer and solvent/solvent solutions. The explanation for this became clear with our morphological model development. For coarsening by flow to occur, the flow must occur in the polymer-rich phase, which has a very high viscosity. We measured the viscosity of an 18% (w/v) solution to be approximately 328 000 cSt. This high viscosity would make coarsening by flow a very slow process. On the other hand, diffusive coarsening occurs by polymer diffusion through the solvent-rich phase. The polymer concentration was measured to be only 0.2% in this phase. Hence, the diffusion occurs in a dilute phase where the polymer diffusivity is relatively high.

Conclusions

When polystyrene solutions in cyclohexane at concentrations near critical are deeply quenched into the two-phase region, bicontinuous phases are often formed. The largest structural scale of the demixed solutions can be preserved and imaged by a quick-freeze and freeze-dry technique. With the use of scanning electron microscopy and BET surface area measurements, we have characterized how this structural size (cell size) coarsens with time. We find that the growth law varies as a power law of time with an exponent in the range 0.18–0.32. These growth laws are consistent with a diffusive coarsening mechanism.

A quantitative model of the diffusive coarsening process was developed specifically for demixed polymer solutions. The model relied heavily upon a simple morphological model. The quantitative predictions of the model are within a factor of 5 of the measured cell sizes. In addition to this fairly good quantitative agreement, the model predicts a very strong concentration dependence of coarsening. This prediction agrees very well with the experimentally determined concentration dependence. The molecular weight dependence of coarsening has not yet been investigated. Qualitatively, the model predicts a weak molecular weight dependence, which is in agreement with qualitative experimental observations. A flow mechanism of coarsening is expected to have a much stronger molecular weight dependence. Future work will involve this molecular weight effect.

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Preparation and Chiroptical Properties of Tritylated Cellulose Derivatives

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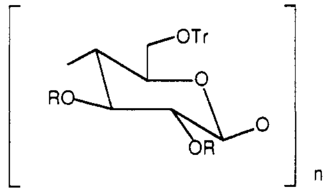
ABSTRACT: Two specifically substituted cellulose derivatives, 6-*O*-trityl-2,3-di-*O*-benzylcellulose (TBzC) and 6-*O*-trityl-2,3-di-*O*-ethylcellulose (TEtC) were found to form lyotropic mesophases in concentrated solution with several organic solvents. The TBzC mesophase in bromoform exhibited cholesteric reflection colors. The cholesteric pitch, measured from the wavelength of apparent circular dichroism of the reflection band, increased with temperature and decreased with increasing polymer concentration. Measurements of the circular dichroism of dilute solutions of TBzC and TEtC showed peaks characteristic of the aromatic substituents, but the sign and magnitude of these peaks changed markedly upon mesophase formation.

Introduction

Cellulose-based liquid crystals have been observed to form both left- and right-handed macroscopic helicoidal structures.[1] In a few rare cases cholesteric inversion or change in the twist sense has been observed to occur as the result of a solvent change,[2,3] chemical modification of the cellulose derivative,[4-6] and change of temperature.[7]

In light of these observations we have begun to study the effects of site-specific cellulose modifications on the optical properties of cellulose mesophases, using (triphenylmethyl)cellulose (tritylcellulose) as a starting material. The heterogeneous preparation of tritylcellulose has been known for many years,[8] and extensive research has shown that the trityl protecting group shows high selectivity for the primary hydroxyl group on the 6-position of the repeating anhydroglucose units composing the cellulose backbone.[9] Following tritylation, selective homogeneous modification of the secondary hydroxyl groups on carbons 2 and 3 of the anhydroglucose units can be achieved. In this work, two selectively modified cellulose ethers have been prepared: 6-*O*-trityl-2,3-di-*O*-ethylcellulose and 6-*O*-trityl-2,3-di-*O*-benzylcellulose,[10] both of which form lyotropic liquid crystals. The incorporation of the trityl groups also provides a useful chromophore for circular dichroism (CD) studies in dilute solution and in the ordered mesophase.



Tr = Triphenyl methyl
R = Benzyl or Ethyl

Circular dichroism has been widely used as a tool in the study of the conformations of biological macromolecules in dilute solution.[11] The CD spectra of polysaccharides is often uninformative because in many cases there are no chromophores with absorption bands above 200 nm, and measurements below 200 nm are more difficult because of restrictions on solvents and instrumentation. Most of the CD work to date has been conducted on polysaccharide derivatives in which chromophore-containing groups have been attached to the carbohydrate backbone. Cellulose for example has been studied

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