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Effect of Preparation Conditions on the Development of Crystallinity in Compatible Polymer Blends: Poly(styrene-*co*-acrylonitrile)/Poly(ϵ-caprolactone)

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ABSTRACT: The development of poly(ϵ-caprolactone) (PCL) crystallinity in poly(ϵ-caprolactone)/poly(styrene-*co*-acrylonitrile) blends of 20% by weight PCL was studied for samples prepared under a variety of conditions. Solution casting was observed to be a method capable of inducing considerable PCL crystallinity, whereas melt blending yielded amorphous samples. The degree of crystallinity of samples prepared from blend solutions was found to be sensitive to a variety of factors. Film thickness, blend preparation temperature, solvent evaporation rate, and the blending solvent were all shown to affect the development of PCL crystallinity. Solvent retention time during film formation was postulated to be responsible for the observed behavior.

Introduction

In recent years much effort has been devoted to studying the crystallization and resulting morphology of binary compatible blend systems in which one or both of the components are crystallizable.[1] In these systems the crystalline regions are essentially phase separated from a miscible amorphous matrix. When two compatible crystallizable polymers are blended, the amorphous matrix is a homogeneous mixture of the two blend components. In this case, the composition of the matrix is dependent on the overall blend composition as well as on the degree to which each of the components crystallizes. If a crystallizable polymer is blended with a compatible amorphous one, the resulting matrix contains all of the amorphous polymer in addition to the amorphous contribution of the crystallizable component.

A frequently used criterion for determining compatibility is the existence of a single glass transition temperature (T_g) located between the T_g's of the pure blend components. Once a system has been classified as "compatible", attention is usually directed toward quantifying the magnitude of the polymer–polymer interactions that yield miscibility. When considering blends with crystallizable components, it might appear that the Nishi–Wang melting point depression approach[2] is the route appropriate for such an investigation. However, a number of authors have recently raised doubt concerning the application of this thermodynamic melting point depression approach without first considering how the crystalline morphology of a polymer would be affected by the addition of a second compatible polymer.[3,4]

From a review of the literature it became apparent that researchers studying compatible blend systems employ a variety of different blend preparation techniques. In fact, some authors believe to have achieved different levels of compatibility by varying their blend preparation mechanisms.[5–7] Methods for both inducing and deterring compatibility have been discussed.

It is well-known that the properties of semicrystalline polymers are largely dependent on the form and extent of crystallinity. It is therefore advantageous to realize the factors that control the development of crystallinity in crystalline/compatible blend systems. Since, in some cases, compatibility has been shown to be sensitive to sample preparation conditions, we felt it would be of interest to determine if blend crystallinity is likewise affected by the mode of sample preparation. It will be shown that significant changes in crystallinity can result from variations in blend preparation conditions.

Experimental Section

The polymers used in this study were a random copolymer of styrene and acrylonitrile (SAN) and poly(ϵ-caprolactone) (PCL). PCL ($T_g \approx 202$ K) is a semicrystalline polyester that melts at approximately 333 K. SAN is an amorphous polymer, and the particular copolymer used in this study was found by elemental nitrogen analysis to be 76% styrene by weight ($T_g \approx 373$ K). The PCL ($M_w \approx 40\,000^8$) was kindly provided by Dr. J. V. Koleske of Union Carbide Corp. Seefried and Koleske[9] utilized a torsion pendulum to monitor the change in the glass transition temperature with composition for blends prepared from these two polymers. They observed intermediate T_g behavior characteristic of a compatible system over the entire compositional spectrum.

In our study, all samples were prepared by either melt or solution blending the polymers in the proportion of 80% SAN:20% PCL by weight. The solution-cast blends were prepared by making individual solutions of the respective polymers followed by stirring for approximately 4 h. The solutions were subsequently blended in the proper proportions and stirred overnight. The resulting blend solutions were then cast into aluminum pans of diameter 57 mm. In all cases, except where otherwise stated, solvent evaporation was performed at room temperature. The resulting films were removed from the pans, placed under vacuum (~6 × 10^{-5} torr) to remove residual solvent, and aged at room temperature. Melt blending was accomplished by melting solution-cast films at 360 K for 4 min followed by rapid cooling to room temperature.

Thermal analysis of the blends was carried out in a Perkin-Elmer DSC-2 differential scanning calorimeter on a range of 1 (mcal/s)/10 in. and a heating rate of 10 K/min unless otherwise noted. All samples were weighed on a Perkin-Elmer AD-2 autobalance. All sample weights were 5.420 ± 0.05 mg, with the exception of the heating rate study, where weights are noted.

An indium standard was used to correct DSC thermograms for temperature deviations and to calibrate the DSC for heat of fusion calculations. Percent crystallinities were calculated by using a perfect crystal heat of fusion for PCL of 32.4 cal/g.[10] In all cases, whenever the DSC thermograms of different samples are compared, their aging times are identical.

A Gunier camera was utilized to monitor the X-ray diffraction from several samples. The samples were exposed for 24 h to Cu Kα radiation generated at 40 kV and 14 mA. Silicon was used as a reference to correct for film shrinkage.

Results and Discussion

A. Melt vs. Solution Blending. Figure 1 shows the DSC thermogram of a blend (80% SAN:20% PCL) prepared by casting 20 mL of a 3% solution from tetrahydrofuran (THF). This is compared to a thermogram of the same blend that was melted at 360 K, quickly cooled to room temperature, and then held at room temperature

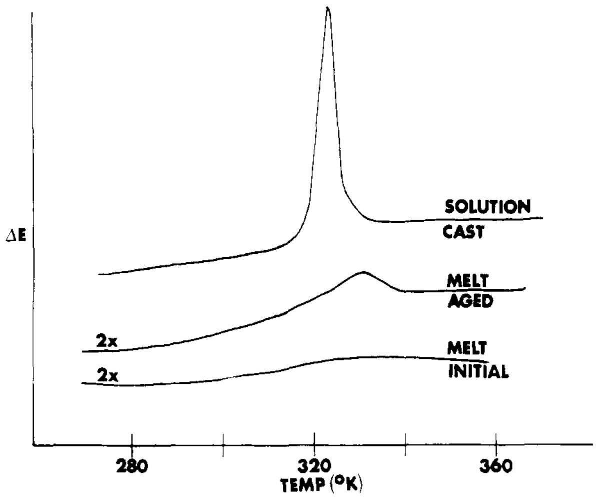

Figure 1. DSC thermograms contrasting melt and solution blending: solution cast, thermogram of a blend prepared by casting 20 mL of a 3% blend solution in THF; melt initial, thermogram of solution-cast blend immediately after melting; melt aged, thermogram of a melt-blended sample after aging for the same time period as the solution-cast sample. Note that the thermogram of the solution-cast sample has been reduced by a factor of 2.

for a time period equivalent to that of the solution-cast sample (11 days). In the case of the solution-cast blend, a large endotherm at ~320 K is observed, whereas in the melt-prepared sample, only a small endotherm whose peak temperature is approximately 6 K higher than that of the solution-cast sample is apparent. X-ray analysis showed diffraction from the 110 and 200 planes ($2\theta \approx 21.4°$ and 23.8°, respectively) of crystalline PCL for the solution-cast blend, supporting the assignment of the large endotherm to PCL melting. However, no such diffraction was observed for samples with endotherms similar to the melt-blended case. To understand the origin of the small endotherm in the melt-blended sample, we must first consider the glass transition temperature of this composition.

Figure 1 also shows the thermogram of a blend immediately after melt blending. Of interest is the base line shift associated with the change in heat capacity characteristic of T_g. The midpoint of this shift occurs at approximately 310 K; hence, a complicating factor of the composition employed is the superposition of PCL melting and the heat capacity change at T_g. Since our samples were stored at room temperature (296 K), they are effectively annealed approximately 10–15 K below T_g. Aging of this type has been shown to cause endothermal responses in glasses at T_g.[11] This phenomenon is believed to be caused by the glass losing free volume as it tends toward an equilibrium state. We believe the small endotherm that appears in the thermogram of the melt-blended sample after aging may be caused by this annealing phenomenon.

In a subsequent section the effect of varying the solvent used for solution blending will be discussed. However, to show the utility of DSC in distinguishing the origins of the two endotherms, we present a heating rate study of a blend cast from benzene. Figure 2 shows the thermograms of a blend prepared by casting 20 mL of a 1% blend solution from benzene. Notice the existence of two endotherms, the first of which appears similar to the endotherm attributed to PCL melting in Figure 1. As the heating rate is increased, a number of effects are prominent. Notice that with increasing heating rate the ratio of the endothermal area of the second peak (higher temperature) to the first peak increases. After normalizing for sample weight differences and taking into account the change in the instrument calibration with heating rate, we found that the first endotherm was relatively constant in area whereas the area of the second peak increased significantly with increasing heating rate. If the second endotherm is caused by annealing of the glassy amorphous phase, then the faster the heating rate, the more the equilibrium enthalpy vs. temperature curve will overshoot.[12] This would result in larger endotherms at higher heating rates as has been shown to be the situation in Figure 2. Notice that this premise also correctly predicts that the peak maximum will increase in temperature with increasing heating rate.

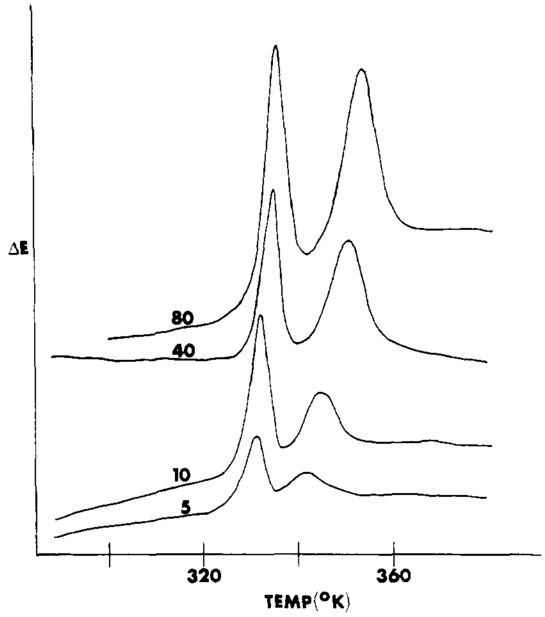

Figure 2. DSC thermograms showing the effect of heating rate on a sample prepared by casting 20 mL of a 1% blend solution in benzene. Weights for the samples were as follows: 5 K/min, 2.314 mg; 10 K/min, 2.242 mg; 40 K/min, 0.7956 mg; 80 K/min, 0.5899 mg.

If the second peak had its origin in the melting of crystallites that have annealed upon heating in the DSC, one would expect that increasing the heating rate would decrease the time available for such crystal annealing processes to occur. This would result in smaller endothermal areas for the second peak with increasing heating rate, contrary to the experimental results. Notice that the peak we associate with PCL melting (lower T_m) also increases in temperature with increasing heating rate. Since polymers typically possess low thermal conductivities, the time necessary to melt a sample can be significant. For a given sample size this can result in higher melting temperatures being recorded for samples analyzed at faster heating rates.[13] In addition to heating rate effects, sample size differences can also complicate melting point determinations, with "large" samples typically yielding higher T_m's.[13] The increase in T_m with increasing heating rate could also be the result of superheating effects that occur when a sample is heated faster than the melt–crystal boundary can progress through the material.[14]

After establishing the existence of two endotherms of different origin, we can now discuss the thermograms in Figure 1 with respect to crystallinity development. The absence of crystallinity in the melt-blended samples is expected since the T_g for this composition is above the crystallization temperature (room temperature). Upon cooling from the melt, PCL molecules are only exposed to an environment suitable for their crystallization at temperatures between the T_m of PCL and the blend T_g. Once the blend T_g is reached, the molecules are frozen in a rigid

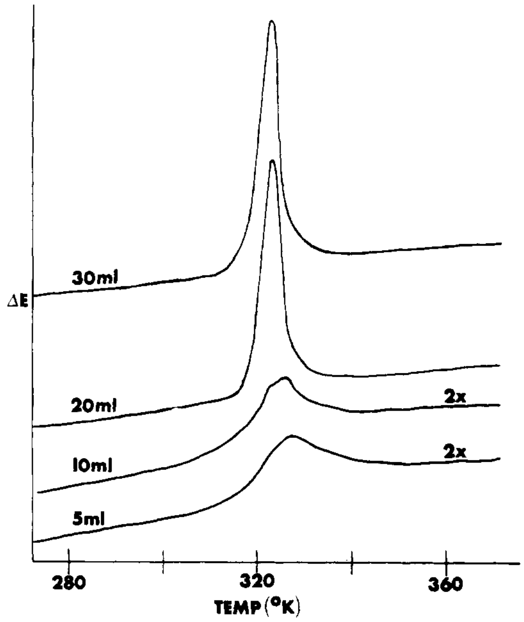

Figure 3. DSC thermograms showing the effect of varying the amount of blend solution cast (film thickness). All runs resulted from samples prepared from a 3% solution in THF. Note that the thermograms for the "5-mL" and "10-mL" samples have been expanded by a factor of 2.

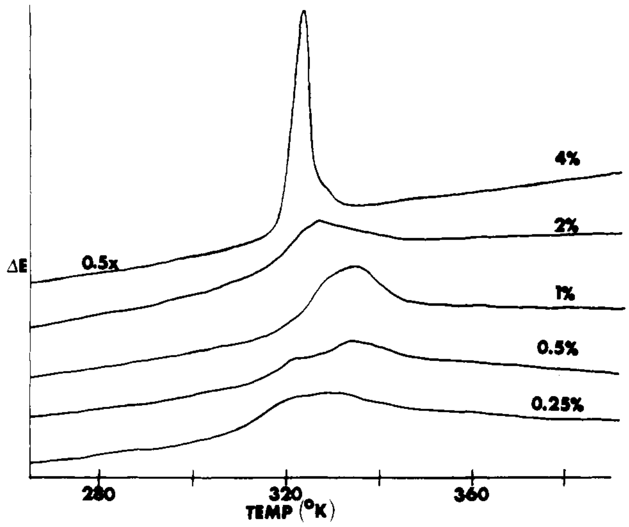

Figure 4. DSC thermograms showing the effect of varying the concentration of the blend solution cast (film thickness). All runs resulted from samples prepared by casting 20 mL of blend solutions in THF. Note that the thermogram of the "4%" sample has been reduced by a factor of 2.

amorphous matrix and are incapable of crystallizing. In our study, the cooling rate was apparently too rapid to allow crystallization within the T_m to T_g interval.

From the thermograms of the solution-cast samples it is apparent that the solvent has induced considerable crystallization. During the film-forming process the solvent apparently lowers the T_g of the system to below room temperature. This T_g depression allows for enhanced mobility of the PCL molecules, allowing crystallization to occur at lower temperatures than would be expected in the absence of solvent.

B. Effect of Film Thickness. The effect of varying film thickness by changing only the amount of the blend solution cast is shown in Figure 3. These thermograms resulted from samples prepared by casting a 3% blend solution (THF) onto pans of constant surface area. Notice that with increasing film thickness the endothermal area associated with the melting of PCL increases. Figure 4 shows the thermograms from a separate series of experiments in which film thickness was varied by changing the concentration of the blend solution cast. In these experiments the quantity of blend solution used is always 20 mL. Approximate values for film thickness range from 0.218 mm for the 4% (20 mL) sample to 0.013 mm for the 0.25% (20 mL) sample. Notice again that with increased film thickness, PCL crystallinity increases.

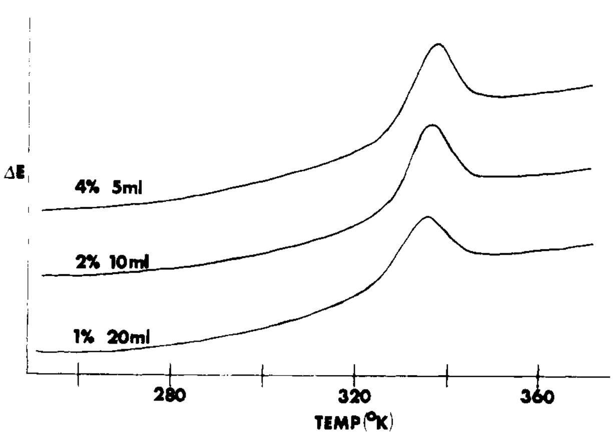

Figure 5. DSC thermograms resulting from samples of constant film thickness prepared from THF.

The majority of solvent-induced crystallization studies to date have consisted of films being exposed to solvents or their vapors, with crystallization believed to be controlled by the rate of diffusion into the films.[15] In our studies, however, we envision crystallization as occurring during and after gelation as the solvent evaporates. One might then expect that increasing the film thickness would cause increased solvent retention in the incipient film (gel). This increased retention time therefore allows a greater time period over which crystallization can occur. The longer the solvent plasticizes the film, the longer the period of time that the system T_g is low enough for crystallization to occur. By constructing an approximate base line under the PCL endotherm, we calculated the degree of crystallinity for the sample cast from a 3% blend solution (30 mL) to be approximately 64% based on the weight fraction of PCL in the blend. This amount is significant when one considers that upon crystallization from solution, PCL alone (i.e., in the absence of a second polymer) typically crystallizes to approximately 70%.[16,17]

If indeed crystallization in these previous experiments is film thickness dependent, one would expect that samples of similar crystallinity could be prepared by varying the amount and concentration of the initial blend solution such that film thickness is constant. This is shown to be the case in Figure 5, where 5, 10, and 20 mL of 4, 2, and 1% blend solutions are cast, respectively.

After considering the effect of film thickness, one can easily recognize that a level casting surface is a prerequisite for the formation of homogeneous films.

C. Effect of Temperature. Figure 6 shows the DSC thermograms of samples prepared by casting 20 mL of 1% blend solutions in THF at various temperatures. After the films were dried, they were brought to room temperature to ensure that all samples were exposed to the same environment during aging. Notice that the lower the temperature at which the film forms, the greater the PCL crystallinity.

Two possible causes of this behavior are the decreased solvent evaporation rate and lower solvent diffusion rate through the swollen films that would be expected at lower

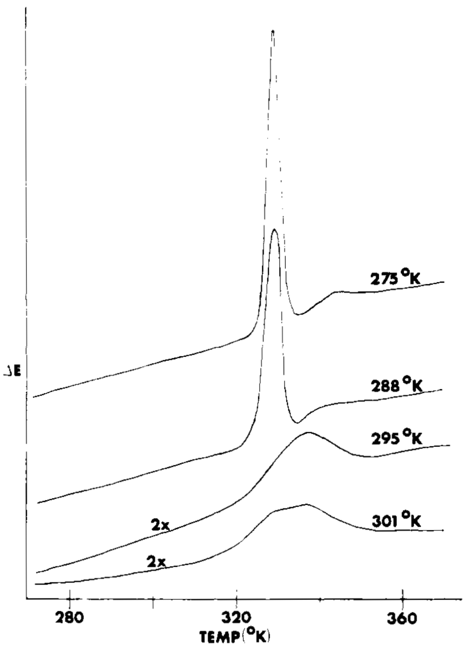

Figure 6. DSC thermograms showing the effect of sample preparation temperature on samples prepared by casting 20 mL of a 1% blend solution (THF). Note that the thermograms of the "295 K" and "301 K" samples have been expanded by a factor of 2.

temperatures. Decreasing both of these factors would increase the time period over which the solvent plasticizes the blend, allowing PCL more time to crystallize. Another factor to be considered is the decreased solubility that occurs at lower temperatures. As solubility decreases, the ratio of solvent to polymer at the gel point increases. This increased solvent/polymer ratio would result in a system T_g lower than that normally obtained in preparing films at room temperature. If the decrease in T_g one obtains by casting at lower temperatures is greater than the decrease in the crystallization temperature (i.e., the casting temperature), then one would expect a greater tendency for crystallization at lower temperatures.

Although the above arguments can rationalize the experimental results, there are factors of a more complicated nature that may be prominent. A troublesome question is how the rate of crystallization of PCL in an SAN/THF mixture varies with temperature. This problem is complicated by the fact that as the solvent evaporates, the composition of the ternary system will continuously change. This compositional variation will affect the temperature range (T_g to T_m) over which crystallization can occur. For example, as solvent evaporates, one would expect the system T_g and the equilibrium T_m (or equilibrium dissolution temperature) to increase. Therefore the rate of crystallization (as well as the degree of supercooling) for a given crystallization temperature may change during solvent evaporation in a complicated fashion. Notice also that the T_m's of the samples prepared at 288 and 275 K are some 5 K greater than those prepared from THF at room temperature (see Figure 3). This aspect will be discussed in section E.

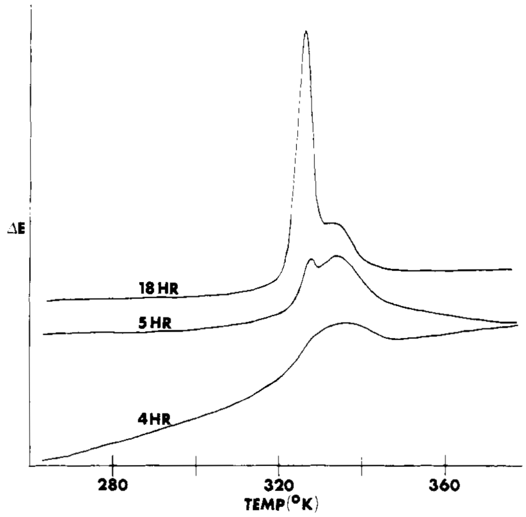

Figure 7. DSC thermograms showing the effect of evaporation rate on samples prepared by casting 20 mL of a 1% blend solution (THF). The notation on each thermogram refers to the time period necessary for the last visible trace of solvent to disappear.

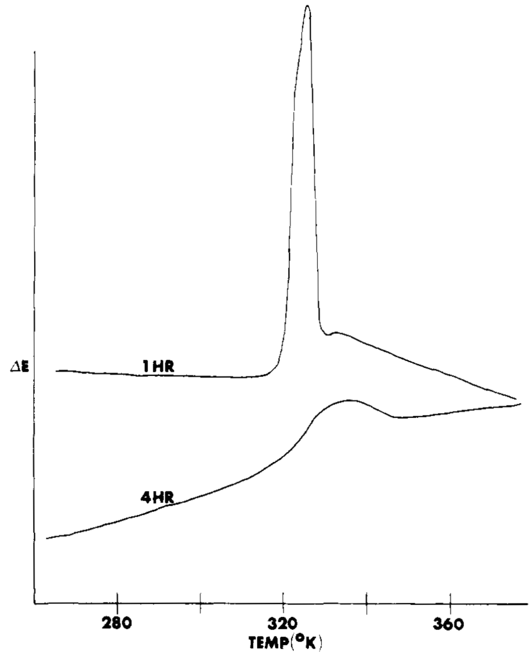

Figure 8. DSC thermograms showing the effect of evaporation rate on samples prepared by casting 20 mL of a 1% blend solution (THF).

D. Effect of Evaporation Rate. After noting that solvent evaporation rate or retention time may be a factor controlling the crystallinity in our system, we proceeded to investigate the effect of varying the evaporation rate of the blend solutions. This was accomplished by placing a pressure-regulating device (cartesian diver) in the line between a vacuum pump and a desiccator in which the blend solution was cast. The function of the diver was to regulate the vapor pressure of the blend solution and hence control the evaporation rate.

Figure 7 shows the effect of varying the evaporation rate on samples prepared by casting 20 mL of a 1% blend solution. The times noted in Figure 7 correspond to the period of time taken for all visible traces of solvent to evaporate. The thermograms resulted from samples cast in the desiccator, with the exception of the "4-h" sample, which was cast in the open atmosphere. Notice that deterring the evaporation of the THF to a rate slower than that observed in the open atmosphere allows for the development of PCL crystallinity. The "5-h" sample shows a slight PCL melting endotherm whereas the "16-h" sample shows a rather large endotherm. These results are consistent with the previous discussions relating the development of crystallinity to the solvent retention time. As the evaporation rate is decreased, the PCL molecules are exposed to an environment suitable for their crystallization for an extended period of time. Notice, however, the

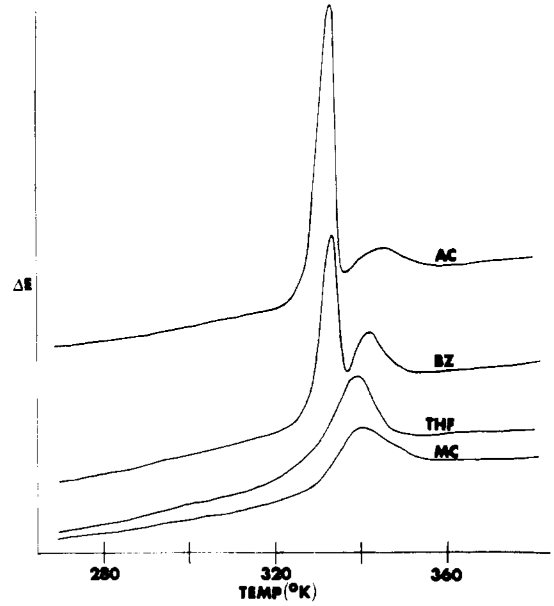

Figure 9. DSC thermograms of samples prepared by casting 20 mL of 1% blend solutions (AC = acetone, BZ = benzene, THF = tetrahydrofuran, and MC = methylene chloride).

anomalous behavior of the sample prepared by evaporation of THF in 1 h (Figure 8). One would expect this sample to possess no crystallinity whatsoever; however, a large endotherm is apparent. A viable explanation for this phenomenon was found by monitoring the temperature of the blend solution during the evaporation process. It was observed that under the conditions of this fast evaporation, the temperature of the blend solution quickly decreased to a minimum of 279 K. After the film began to form, the solvent evaporation rate decreased, implying that the evaporation was controlled by the diffusion of solvent through the forming film. We believe that the decrease in temperature caused the blend solution to gel at a lower concentration than it would by evaporating at room temperature. This would result in a greater ratio of solvent to polymer at the gel point than would otherwise be expected and may be an important factor controlling PCL crystallinity. We also speculate that even though the total time of evaporation was less for the sample prepared by "rapid evaporation", perhaps the time the solvent plasticized the gel was significant since the solution gelled early in the evaporation process. Regardless of the mechanism it is significant that the observation of crystallinity in the sample prepared by fast evaporation is consistent with the results of part C, where crystallinity was observed to increase with decreasing casting temperature. Also notice the discrepancy between the T_m's of the endotherms in Figures 7 and 8 (1 h, $T_m \approx 326$ K; 18 h, $T_m \approx 327$ K) and those of the crystalline samples prepared from THF in the open atmosphere (Figure 3, $T_m \approx 323$ K). This will be discussed in section E.

E. Effect of Varying Solvents. Figure 9 shows the thermograms of blends prepared from 1% solutions with a variety of solvents. Blends cast from acetone and benzene appear much more crystalline than blends cast from THF or methylene chloride. Although analysis of these effects is as yet incomplete, a number of factors appear to be significant. The relative rates of evaporation for these different solvents should be important: one would expect volatile solvents to yield amorphous films and nonvolatile solvents to yield crystalline films. This analysis appears to be applicable to blends cast from benzene (bp 80 °C), THF (bp 66 °C), and methylene chloride (bp 40 °C). However, this argument predicts that blends prepared from acetone (bp 56 °C) should be amorphous, contrary to the experimental evidence. We believe that another variable of importance is the solubility of the blend components in the various solvents. Preliminary results indicate that acetone is a poorer solvent for PCL than the others. If this is correct, then the blend solution prepared with acetone may gel early in the evaporation process. This would allow acetone sufficient time to plasticize the forming film, thereby inducing crystallization. The underlying assumption of this argument is that acetone can still act as a good plasticizer even though it is a "poor" solvent. Since the blend polymers are soluble in acetone at room temperature, this might be expected to be the case. Future work is being directed toward studying the solubilities of the blend components in these and various other solvents so that more conclusive explanations can be drawn.

Another aspect of interest is the melting points of blends prepared from acetone ($T_m \approx 330$ K) or benzene ($T_m \approx 332$ K) compared to the T_m of blends cast from THF ($T_m \approx 323$ K; see Figure 1). Since the film cast from THF is some 3 times thicker than those cast from the other solvents, one might argue that this would cause increased retention of residual solvent in the "thick THF films", thereby depressing the melting points for these blends. The high melting points of the samples in the evaporation rate and temperature studies relative to those of the thicker films can be explained by the same argument. Although the previous discussion is consistent with the experimental data, there are factors of a more complex nature that may be prominent. One argument that was previously utilized to explain crystallinity development was that the ratio of solvent to polymer will be different for samples prepared by different techniques. This ratio would also be expected to affect the supercooling at which the resulting samples were crystallized, thereby affecting their T_m's. However, since the supercooling at which a given sample crystallizes and the rate of crystallization are continuously changing, complete analysis is not feasible at this time.

Conclusions

The development of crystallinity in an 80/20 blend of SAN/PCL has been shown to be strongly dependent on a number of sample preparation variables. The unifying premise of these effects is the retention time of the solvent during film formation. The general conclusion reached is that the longer the solvent is retained in the sample, the longer is the time which PCL is exposed to an environment suitable for its crystallization. In the case of melt-blended samples, the environment is never such as to allow for PCL crystallization since the T_g of the composition selected is greater than room temperature. In the solution-blended samples, the solvent retention time was varied by controlling a number of experimental factors. It was found that by (1) increasing the film thickness, (2) decreasing the casting temperature, and (3) decreasing the evaporation rate, solvent retention time could be increased, thereby resulting in increased crystallization of PCL. Preliminary results on samples cast from a variety of solvents also indicate that the time that a given solvent plasticizes a blend is a controlling factor with regard to the development of PCL crystallinity.

It is important to note that such dramatic effects would not be expected for blend compositions with low T_g's, since they readily crystallize without the aid of solvents. However, from these results it is clear that researchers attempting to relate the degree of interaction between an amorphous polymer and a crystalline one on the basis of

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the degree of crystallinity should be highly cognizant of the possible effects of sample preparation in their systems.

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Restricted Flexing of Once-Broken Rods

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ABSTRACT: A theory for the dynamic light scattering intensity time correlation functions of dilute solutions of once-broken rods is developed. The rods are assumed to be small enough so that intramolecular interference can be neglected and the amount of bending at the joint is restricted to some maximum angle. Both polarized and depolarized correlation functions are calculated. The theory is then applied to the myosin rod, yielding a maximum angle of 128° (within the range 121–132°), a bending constant (D_r) of 24 ± 6 krad/s, and an overall rotational diffusion coefficient of 4.8 ± 0.8 krad/s. The values obtained are in good agreement with the known structure and size of the rod.

Introduction

Numerous authors have dealt with the motions of a once-broken rod and the effect of these motions on the dynamic light scattering correlation functions, primarily on a theoretical basis.[1-8] However, those papers assumed that the break point was a universal joint, allowing all possible angles between the two segments. Furthermore, the dynamic light scattering theories deal only with the isotropic scattering and intramolecular scattered light interference effects. In this work, an approximate theory is presented for the scattered light intensity time correlation functions from a dilute solution of once-broken rods. Both the isotropic and anisotropic components are found, assuming negligible intramolecular interference, and the angle between segments is restricted to some maximum value.

An example of a once-broken rod with a restricted intersegmental angle may be the myosin rod. The myosin molecule (Figure 1) is composed of three basic functional units.[9-12] The light meromyosin fragment (LMM) is believed to be rather stiff and rodlike. Subfragment 2 (S-2) is more flexible and connects the LMM with the head group. The head group consists of two subfragment 1 (S-1) moieties. The myosin rod is the myosin molecule with the head group removed. Both electric birefringence[9] and electron microscopy[11,12] experiments on the myosin rod and the myosin molecule indicate a considerable amount of flexibility at the joint between the LMM and S-2 fragments, with a possible maximum intersegmental angle of 145° (ref 12, where an angle of 0° means a stiff rod with no bend). Here, the results from dynamic light scattering experiments[13] are compared with our theory of the once-broken rod in an attempt to extract the translational and rotational diffusion coefficients and the maximum intersegmental angle.

Theory of the Dynamic Light Scattering Correlation Functions for a Once-Broken Rod

In the model used here, the motion between the two segments of a once-broken rod is restricted so that the largest angle the rod can bend at the joint is θ^0 (see Figure 2). For small θ^0, a good approximation would be to assume that the bending motion is uncorrelated with the overall translation and rotation. In other words, the broken rod has about the same rotational and translational diffusion coefficients as the unbroken rod but with an additional time dependence of the total polarizability due to the bending motion. For large θ^0, one would expect coupling between all three motions; however, if the bending motion is fast relative to the overall motions (which would be expected for long, thin rods), the assumption of uncorrelated motions should at least yield results that are semiquantitatively correct. Higher order corrections to these approximations would probably be small relative to the experimental errors in the dynamic light scattering results (see Appendix).

The spectral density of the scattered light is determined by the autocorrelation function of the polarizability fluctuations. For dilute solutions of identical molecules, for which only self-correlations need to be considered, the polarizability time autocorrelation function is given by the equation[14]

$$I_{\mathrm{if}}^{\alpha}(q,t) = \langle N\rangle\langle \alpha_{\mathrm{if}}^{*}(0)\alpha_{\mathrm{if}}(t)\exp(i\vec{q}\cdot(\vec{r}(t)-\vec{r}(0)))\rangle \quad (1)$$

The brackets indicate ensemble averages. N is the number of molecules in the scattering volume, $\vec{q}$ is the scattering

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