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Light Scattering of Thermotropic Polyester and Polysulfone Mixtures in Solution

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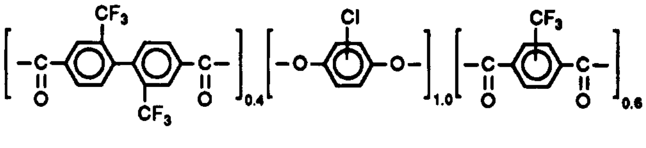
ABSTRACT: A study was made of the static light scattering properties of polymer solutions containing semistiff thermotropic polyester and flexible polysulfone in tetrahydrofuran solvent. These solutions are used as model precursors in the preparation of molecular composites. Light scattering studies of the binary polyester solutions have revealed information on molecular weight, molecular anisotropy, and molecular correlation lengths. The correlation lengths, including orientation and density correlation lengths, were determined by the Stein–Wilson scattering theory for the randomly correlated anisotropic scatterers. Both lengths were found to increase with solution concentration, with the density correlation length being greater than the orientation one. Lyotropic behavior was not observed, even when solution concentration exceeded 50% w/v, which is attributed to the intramolecular repulsive interactions and/or a small aspect ratio due to the unusually large molecular diameter. The addition of flexible polysulfone significantly increases the correlation lengths, indicating that the solubility between polyester and polysulfone is low and that the aggregation of anisotropic molecules may occur.

Introduction

Molecular composites comprising stiff molecules and flexible matrix molecules are of continued interest. The potential advantages of this system over conventional composites can be summarized as follows. First, composite theory suggests that reinforcement by particulate inclusions increases with the axial ratio of the inclusions.[1] Such a principle may be extended to molecular dimensions that can lead to highly efficient reinforcement. Second, failure of composites is often associated with phase separation at the matrix–inclusion boundary where the stress concentration is high. It is thought that such a stress concentration may be significantly reduced as one approaches molecular dispersion. Third, reinforced composites are usually turbid because of the scattering of light by the included particles. As scattering power depends strongly on particle size, a molecular composite could have unusually low turbidity. Finally, manufacturing of the conventional composites often employs costly processes. As one may simplify procedures for processing molecular composites, the cost should be reduced.

Unfortunately, attempts to prepare molecular composites have often been unsuccessful in achieving a level of true molecular dispersion.[2,3] The observed microphase separation can be related to the prediction of theories of Onsager[4] and Flory,[5] which state that rodlike molecules are not soluble in normal solvents or in random coil polymers. Consequently, preparation of molecular composites usually gives rise to molecular aggregates having properties that may not be sufficiently superior to justify the extra effort. Therefore, in this work, a novel approach has been proposed to improve the rod/coil solubility, which may lead to molecular composites having true molecular dispersion.

In our approach, a unique rodlike molecule has been synthesized,[6,7] which has the following chemical structure:



This wholly aromatic polyester contains substituent groups on the biphenyl aromatic rings, which force the rings into a noncoplanar conformation. The lack of crystallinity and the dipolar nature of the substituents has significantly increased the solubility in many common solvents such as tetrahydrofuran (THF). Although the solutions show evidence of the molecular stiffness,[8] no lyotropic behavior (in THF or any other solvents) has been observed, even when solution concentration exceeds 50% w/v. These solutions are not turbid and do not show liquid crystallinity. This phenomenon may be attributed to the intermolecular interactions (both steric and electronic), which oppose the aggregation of these anisotropic molecules, and/or the unusually large molecular diameter (low molecular aspect ratio), which also prevents the formation of an ordered phase.

We feel that this system may offer a suitable compromise, where molecules may be stiff enough to give reinforcement in a blend, while permitting solubility in a flexible coil matrix, thus allowing the formation of a true molecular composite. We have undertaken this study in two parts. First, we have studied the static light scattering of binary solutions (solvent and semistiff molecules) ranging from dilute to high concentrations. Second, we have investigated the molecular aggregation and phase separation of ternary solutions (solvent, semistiff, and flexible molecules). In this paper, we will thoroughly demonstrate the use of light scattering techniques to characterize the state of dispersion of anisotropic molecules in polymer solutions.

Experimental Section

Materials and Sample Preparation. The polyester chosen for this study was synthesized by the Polaroid Corp., Cambridge, MA.[6,7] Its number-average molecular weight (M_n) is approximately 10 400, with a polydispersity of 2.1.[9] Though no lyotro-

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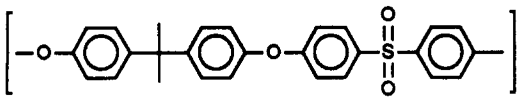
pic behavior has been observed, this material is thermotropic. The addition of bulky substituents hinders crystallization, and the material is completely amorphous below its glass temperature (110 °C). Above T_g it exhibits liquid-crystal character. Its thermotropic behavior under shear has been discussed elsewhere.[10,11]

Solutions of varying concentrations were prepared by dissolving known amounts of the specimen (vacuum-dried at 100 °C for 24 h) in tetrahydrofuran (THF). All solutions were filtered through a 0.2-μm PTFE filter (Millipore, Bedford, MA) to eliminate impurity particles. The maximum solubility of the chosen polyester in THF is approximately 50% w/v. In this work, the highest concentration prepared was 30%, since great difficulty was encountered during the filtration of more concentrated solutions.

The chosen flexible random-coil polymer was a polysulfone resin because of its solubility in THF. This material was purchased from Aldrich Chemical Co. (M_w of 30 000). This polysulfone may be derived from Bisphenol A and 4,4′-dichlorodiphenylsulfone and has the following structure:



The preparation of the ternary solution is similar to that of the binary one. Two rod/coil composition ratios have been prepared for this study; they are 7:1 and 3:1, respectively.

Characterization Techniques. The intrinsic viscosity was determined in a Cannon–Ubbelhode viscometer using 0.1–0.5% w/v solutions at 30 °C. The dn/dC value was determined by using a Cromatix Model KMX16 refractometer with solutions ranging from 0.1 to 0.5% w/v; the transmittance (T) at various solution concentrations was measured with a Perkin-Elmer UV spectrometer at a 633-nm fixed wavelength. GPC analysis was made by using the Waters GPC components equipped with a Viscotek differential viscosity detector. This apparatus was calibrated with polystyrene standards. The cloud-point measurements were done by using a laser light scattering apparatus equipped with an Oriel integrating sphere and a photomultiplier unit.

Light scattering measurements were made on a laser light scattering goniometer, Model B12005M, made by Brookhaven Instrument Corp., Ronkonkoma, NY. This apparatus includes a 20-mw He–Ne laser (633 nm), two polarizers, and an automated photomultiplier/goniometer stage. Intensity measurements were accumulated automatically every 10° between the scattering angle (θ) of 30° and 150° for 10-s periods. The experimental temperature was kept at 25 °C during all of the measurements. Both polarized V_V and depolarized H_V intensities were measured with a vertically polarized incident beam.

Toluene and benzene, whose depolarization ratio and Rayleigh ratio are well characterized,[12] were used for calibration. The absolute Rayleigh ratio of the unknown solution was determined after suitable corrections were made. These corrections compensated for errors from the following sources: detector counting fluctuations, instrumental dark current, scattering volume, reflection, refraction, absorption, and multiple scattering of the solutions. Some of these corrections were atuomatically made by using the Brookhaven light scattering software. These corrections include the use of current counting statistics, subtraction of dark current and elimination of reflection (with a refractive index-matching fluid, decalin). Corrections made additionally were as follows: scattering volume effect requiring a correction factor of sin θ for cylindrical geometry compensation; refraction requiring a factor of $(n_s/n_c)^2$, where n_s is the refractive index of solution and n_c is the refractive index of calibrent; absorption requiring a factor of $1/T$, where T is the internal transmittance of the scattering solution. The refractive indices of the solutions were determined by the dn/dC value, assuming a linear dependence over the concentration range studied. Transmittance (T) was directly measured by a UV spectrometer at a wavelength of 633 nm. The correction for multiple scattering was also estimated and was shown to be insignificant. This is because an insignificant difference in scattered intensity was detected for concentrated solutions held in different size holders.

Theoretical Background

Light Scattering in Dilute Solutions. For anisotropic rodlike molecules, in the absence of molecular aggregation, light scattering measurements as a function of concentration and scattering angle in dilute solution are capable of determining the weight-average molecular weight, M_w, the z-average root-mean-square radius of gyration, $\langle R_g^2\rangle_z^{0.5}$, and the molecular anisotropy, δ. This method has been described in detail by Chu et al.[13-15] In summary, by measuring R_{V_V} and R_{H_V}, which are the vertical and horizontal components of the excess Rayleigh ratio (the difference between the Rayleigh ratio of the solution and the Rayleigh ratio of the solvent), respectively, using vertically polarized incident light, we get

$$\lim_{C\to 0}(KC/R_{V_V}) = (1/M_{app})(1 + (\langle R_g^2\rangle_{app}q^2)/3 + ...) \quad (1)$$

$$\lim_{\theta\to 0, C\to 0}(KC/R_{V_V}) = 1/M_{app} = 1/(M_w(1 + (4/5)\delta^2)) \quad (2)$$

$$\lim_{\theta\to 0, C\to 0}(R_{H_V}/R_{V_V}) = 3\delta^2/(5 + 4\delta^2) \quad (3)$$

$$\langle R_g^2\rangle_z = \langle R_g^2\rangle_{app}(1 + (4/5)\delta^2)/(1 - (4/5)\delta + (4/7)\delta^2) \quad (4)$$

$$K = (4\pi n^2/N_A\lambda^4)(dn/dC)^2 \quad (5)$$

where K is the optical constant, n is the refractive index, N_A is Avogadro's number, λ is the wavelength (633 nm), C is the concentration, M_{app} is the apparent molecular weight, $q = (4\pi n/\lambda)\sin(\theta/2)$ is the magnitude of the scattering vector (or momentum transfer vector), and θ is the angle between the incident and the scattered rays. Equations 1–4 can be summarized into a Zimm plot, which is widely utilized in characterizing anisotropic molecules in dilute solution.

Light Scattering in Concentrated Solutions. It is thought that in dilute polyester solutions, anisotropic molecules are randomly arranged. As concentration increases, the molecules tend to align relatively parallel to each other (not necessary lyotropic), though the system still remains a single phase. Further increase in concentration leads to insolubility, and precipitation occurs before an ordered liquid-crystalline phase forms. In such a case, measurement of the polarizing light scattering can be used in determining the intramolecular correlation of anisotropic molecules in solutions.

If vertically polarized light is scattered by an anisotropic scatterer, its polarizability will be a tensor, so that the induced dipolar moment may be in a direction other than vertical. In this case, there will be a horizontally polarized component of scattered light. The quantity of the depolarization of scattering can be defined as

$$P_V(q) = R_{H_V}(q)/R_{V_V}(q) \quad (6)$$

For isotropic systems, P_V is zero, whereas for an anisotropic system, its value is finite. In dilute solutions, P_V and R_{H_V} depend on the molecular anisotropy, δ, defined as

$$\delta = (\alpha_1 - \alpha_2) \quad (7)$$

where α_1 and α_2 are the polarizabilities along and perpendicular to the axis of the anisotropic molecule. For concentrated systems, they also depend on the degree of the anisotropic molecules.

The polarized light scattered from the randomly correlated assemblies of anisotropic scatterers has been described by the theory of Stein and Wilson.[16] For the cross-polarized condition, the theory gives

$$R_{\mathrm{H_V}}(q) = 4\pi(N/V_{\mathrm{s}})(1/\lambda)^4(1/15)\langle\delta^2\rangle\int_0^\infty f(r)\times(\sin(qr)/qr)r^2\,\mathrm{d}r \quad (8)$$

where N is the number of the correlated rod molecules per volume, V_{s} is the scattered volume, and λ is the wavelength of the light. The quantity $f(r)$ is an orientation correlation function, defined as

$$f(r) = [3\langle\cos^2\theta_{12}\rangle_{\mathrm{r}} - 1]/2 \quad (9)$$

The angle θ_{12} is that between the optic axes of volume elements 1 and 2. The symbol $\langle\ \rangle_{\mathrm{r}}$ designates the average value over all pairs of volume elements separated by distance r. At $r = 0$, this function is unity, since the optic axis of a volume element must be parallel to itself, so $\theta = 0°$. As r approaches infinity, if there is no long-range order, θ_{12} becomes random and $\langle\cos^2\theta_{12}\rangle_{r\rightarrow\infty} = {}^1/_3$; thus, $f(r)$ is zero.

For many systems, the orientation correlation function can be represented by the empirical exponential equation

$$f(r) = \exp(-r/a_{\mathrm{o}}) \quad (10)$$

where a_{o} is an orientation correlation length, at which $f(r)$ falls to $1/e$. In this case, eq 8 reduces to

$$R_{\mathrm{H_V}}(q) = 8\pi(N/V_{\mathrm{s}})(1/\lambda)^4(1/15)\langle\delta^2\rangle(a_{\mathrm{o}}^3/(1 + a_{\mathrm{o}}^2q^2)^2) \quad (11)$$

where a plot of $R_{\mathrm{H_V}}(q)^{-0.5}$ vs q^2 should be linear with a ratio of slope/intercept equal to a_{o}^2. This is referred to as a Debye–Bueche plot.[17]

For parallel polarization, or $\mathrm{V_V}$ scattering, the theory gives

$$R_{\mathrm{V_V}}(q) = 4\pi(N/V_{\mathrm{s}})(1/\lambda)^4[\langle(\Delta\rho_{\mathrm{i}})^2\rangle\int_0^\infty\gamma(r)\times(\sin(qr)/qr)r^2\,\mathrm{d}r + (4/45)\langle\delta^2\rangle\int_0^\infty f(r)(\sin(qr)/qr)r^2\,\mathrm{d}r] \quad (12)$$

where $\Delta\rho_{\mathrm{i}}$ is the density fluctuation or the fluctuation in the isotropic component of the average polarizability, defined as

$$\Delta\rho_{\mathrm{i}} = \alpha_{\mathrm{i}} - \langle\alpha_{\mathrm{i}}\rangle \quad (13)$$

The correlation function associated with this fluctuation is referred to as a density correlation function and is defined as

$$\gamma(r) = \langle n_1n_2\rangle_{r12}/\langle n^2\rangle \quad (14)$$

Similar to $f(r)$, this function decreases from unity to zero as r increases from zero to infinity. It may also be approximated by an exponential function with a correlation length a_{d}, related to the size of the rod. In this case, $R_{\mathrm{V_V}}$ is given by

$$R_{\mathrm{V_V}}(q) = 8\pi(N/V_{\mathrm{s}})(1/\lambda)^4[\langle(\Delta\rho)^2\rangle(a_{\mathrm{d}}^3/(1 + a_{\mathrm{d}}^2q^2)^2) + (4/45)\langle\delta^2\rangle(a_{\mathrm{o}}^3/(1 + a_{\mathrm{o}}^2q^2)^2) \quad (15)$$

Combining eqs 6, 11, and 15, we get

$$P_{\mathrm{V}}(q) = (1/15)\langle\delta^2\rangle(a_{\mathrm{o}}^3/(1 + a_{\mathrm{o}}^2q^2)^2)/\{\langle(\Delta\rho)^2\rangle(a_{\mathrm{d}}^3/(1 + a_{\mathrm{d}}^2q^2)^2) + (4/45)\langle\delta^2\rangle(a_{\mathrm{o}}^3/(1 + a_{\mathrm{o}}^2q^2)^2)\} \quad (16)$$

For the systems that we studied, it is usually true that $a_{\mathrm{d}} \ll \lambda$, so that $a_{\mathrm{d}}^2q^2 \ll 1$. Thus the term $1 + a_{\mathrm{d}}^2q^2$ in the above equation is close to 1. Furthermore, if we may regard the suspension of rods as a two-phase system with discrete boundaries, then one may use the Debye–Anderson–Brumberger[18] results that

$$\langle(\Delta\rho)^2\rangle = \phi_{\mathrm{r}}(1 - \phi_{\mathrm{r}})(\alpha_{\mathrm{r}} - \alpha_{\mathrm{m}})^2 \quad (17)$$

where α_{r} and α_{m} are the average polarizabilities of the rods and the imbedding medium, and ϕ_{r} is the volume fraction of rods. With these results, P_{V} can be expressed as

$$P_{\mathrm{V}}(q) = (1/15)\mathcal{A}\mathcal{P}(q)/(\phi_{\mathrm{r}}(1 - \phi_{\mathrm{r}}) + (4/45)\mathcal{A}\mathcal{P}(q)) \quad (18)$$

Here, $\mathcal{A}$ is a dimensionless quantity, which is a function of the polarizability difference of anisotropic rod axis, the polarizability difference between rod and matrix, and the ratio of orientation and density correlation distances. $\mathcal{A}$ can be defined as

$$\mathcal{A} = [(\alpha_1 - \alpha_2)/(\alpha_{\mathrm{r}} - \alpha_{\mathrm{m}})]^2(a_{\mathrm{o}}/a_{\mathrm{d}})^3 \quad (19)$$

$\mathcal{P}(q)$ is an interference function, which is defined as

$$\mathcal{P}(q) = (1 + a_{\mathrm{o}}^2q^2)^{-2} \quad (20)$$

It has the property that $\mathcal{P}(q) = 1$ at $q = 0$ and decreases to zero as q becomes large at a rate that is dependent on a_{o}. It is evident that the q dependence of P_{V} is determined by $\mathcal{P}(q)$, but its magnitude depends on $\mathcal{A}$.

For systems in which the anisotropy is small or the orientation correlation lengths are small compared with their size, $\mathcal{A}$ approaches zero so P_{V} becomes small. P_{V} will be the smallest at a volume fraction of 50%, where the density fluctuations are the greatest. In the other limit, when anisotropy and its orientation correlation distance are large, P_{V} is large and approaches a limiting value of ${}^3/_4$. If the orientation correlation distance is small as compared with the wavelength of the light, $\mathcal{P}(q)$ will be close to 1 and P_{V} will not vary much with scattering angle. For large orientation correlation lengths, $\mathcal{P}(q)$ decreases with angle, so P_{V} will decrease with angle. However, the above theory assumes the rods are small as compared with the wavelength, so that intrarod interference need not be considered also its assumes "random orientation correlations" so the theory will not apply as disclination networks develop.[19,20]

Results and Discussion

Measurements of Dilute Solutions. The intrinsic viscosity index (Mark–Houwink coefficient, a) of the anisotropic polyester, in the equation

$$[\eta] = kM^a \quad (21)$$

was determined by a combination of viscometric measurements and GPC analysis, where $[\eta]$ is the intrinsic viscosity and M is the molecular weight. This coefficient was estimated in the range of 1.0–1.1. As a random-coil polymer usually has the coefficient about 0.8 and the theoretical limit for rod molecules is 2,[21,22] it is apparent that this polyester exhibits "marginal" chain stiffness and should be considered as a semistiff system.

Light scattering measurements of binary polyester solutions having five concentrations, ranging from 0.1% to 0.5% w/v, were made. As solution concentration increased, the refractive index also increased, indicating that the scattered intensity due to refraction ought to be corrected. The correction for refraction involved multiplying a factor $(n_{\mathrm{s}}/n_{\mathrm{c}})^2$, as described before. To calculate this factor at various concentrations, the following values were measured (at 25 °C): $\mathrm{d}n/\mathrm{d}C$ was 0.1235 mL/g,

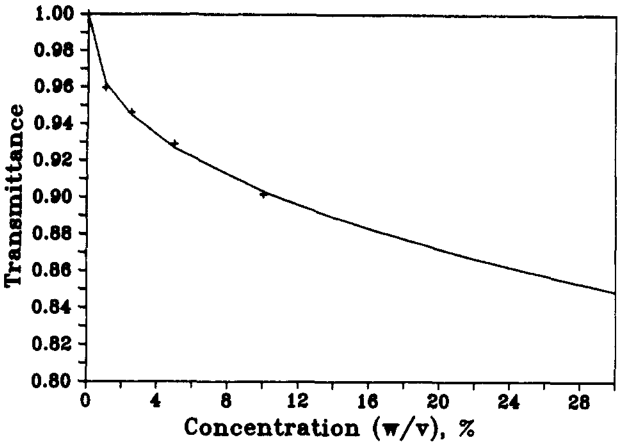


Figure 1. Transmittance vs concentration plot of polyester/THF solutions. The wavelength is 633 nm.

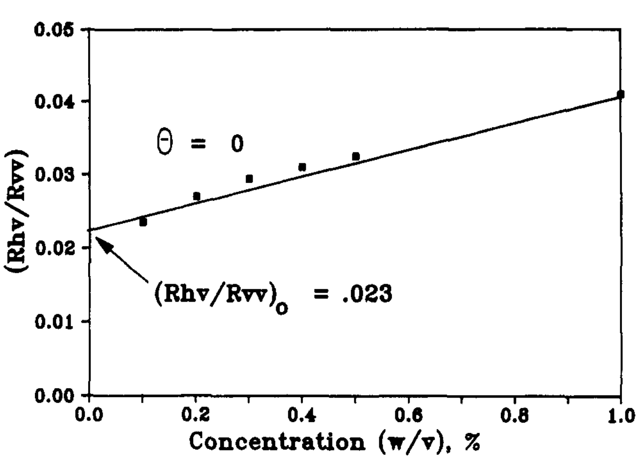


Figure 3. Determined molecular anisotropy at zero angle and zero concentration.

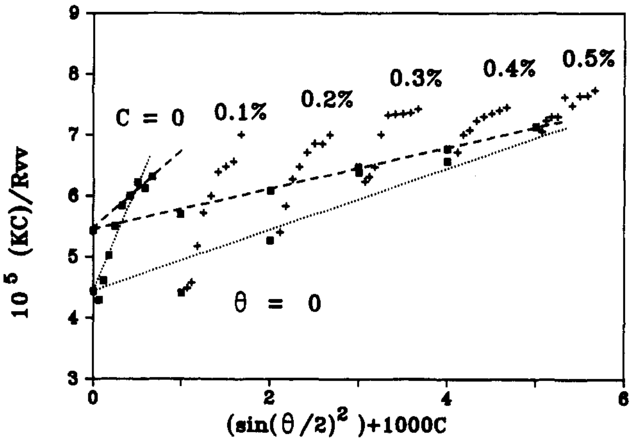


Figure 2. Zimm plot of dilute polyester solutions. Dotted lines represent the extrapolation of the entire data set; dashed lines represent that of the data in the higher angle linear range.

refractive index of solvent (THF) was 1.405, and refractive index of calibrent (toluene) was 1.493.

Another correction made was the compensation of transmittance T, which was also a function of concentration C. The concentration dependence on transmittance T is shown in Figure 1, which is determined by a UV spectrometer at a fixed wavelength of 633 nm. This relationship can be expressed by a numerical equation

$$\log (1/T) = 0.0066883C^{0.5} + 0.010262C^{0.25} \tag{22}$$

where C is in g/100 mL.

Our light scattering measurements of dilute solutions are summarized in a Zimm plot, as shown in Figure 2. The plus symbol represents the experimental data, and the square symbol stands for the extrapolated value at the zero angle or zero concentration. It is found that this Zimm plot exhibits nonlinear behavior, which has also been observed in other rigid macromolecule systems.[14,15] Several pieces of molecular information are determined by using the Zimm plot approach on the entire data set: the apparent molecular weight M_{app} is 22 500, and the slope at $C = 0$ is 3.26×10^{-5}, giving the apparent root-mean-square radius of gyration, $\langle R_g^2\rangle^{0.5}{}_{\mathrm{app}}$, of about 53 nm. The value of $\langle R_g^2\rangle^{0.5}{}_{\mathrm{app}}$ is large and does not satisfy the Guinier criterion, $q < 1/R_g$. A more appropriate way to determine values of M_{app} and $\langle R_g^2\rangle^{0.5}{}_{\mathrm{app}}$ is to only use the data (Figure 2) in the higher angle linear range. This gives a M_{app} of about 18 700 and a $\langle R_g^2\rangle^{0.5}{}_{\mathrm{app}}$ of about 32 nm, which are more correct. The molecular anisotropy δ_0 is determined by plotting the depolarization ratio at $\theta = 0$ vs concentration, as shown in Figure 3. Using eq 3, the molecular anisotropy δ_0 is approximated to be 0.2. This value is small compared with the reported values for rodlike molecules ($\delta_0^2 = 0.12$–0.9).[23] This again indicates that the molecules are not stiff, which is consistent with the intrinsic viscosity results. The above information allows us to calculate the weight-average molecular weight, M_w, to be 18 100 and the z-average root-mean-square radius of gyration, $\langle R_g^2\rangle^{0.5}$, to be 35 nm. The value of $\langle R_g^2\rangle^{0.5}$ is slightly high, considering M_w is only 18 100. A possible explanation is that the molecules may have gathered in the shape of a dimer. We noted that the Zimm plot curve is highly nonlinear, which indicates that a good degree of inaccuracy is involved in these measurements. It is also possible to determine the persistence length by using the solutions of different molecular weights. However, in this work, only one molecular weight sample was studied, such that no persistence length could be estimated.

One important note in the above measurements is the time restriction for data acquisition. This is because the polymer solutions employed unstabilized THF solvent, which would be oxidized after long periods of exposure to air. The oxidation process inevitably changed the refraction and transmission of the solutions. Therefore, all our sample preparations and storages were done under a nitrogen environment, and all of the scattering data are gathered within 1 h after the solutions have been prepared. No addition of the THF stabilizer (antioxidizer) was used, since it might affect the determination of molecular weight by light scattering.

Light Scattering in Concentrated Solutions. Binary Solutions. As solution concentration increased, the light scattering measurements of polarized Rayleigh ratio, R_{Vv}, and depolarized Rayleigh ratio, R_{Hv}, revealed additional information such as intramolecular interactions, molecular orientation correlations, and density correlations. Useful information was obtained by plotting R_{Hv}/C (at $\theta = 90°$) vs concentration, as shown in Figure 4. The division of R_{Hv} by concentration eliminates the effect of volume accumulation of solute on the orientation fluctuations. If R_{Hv} is unrelated to molecular weight, the concentration dependence on R_{Hv}/C will be insignificant, which is only true in the low concentration range where R_{Hv}/C is unchanged. At high concentrations (>12% w/v), R_{Hv}/C becomes dependent on concentration. The increase in R_{Hv}/C at high concentrations indicates that the orientation fluctuations per unit volume of solute have increased.

For measurement of R_{Vv}/C, the case is quite different. R_{Vv} is affected by both density and orientation fluctuations. The plot of R_{Vv}/C (at $\theta = 90°$) vs concentration is shown

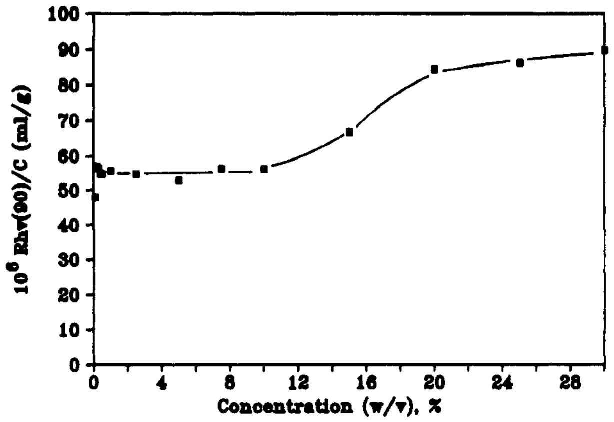


Figure 4. R_{H_V}/C vs concentration plot for polyester/THF solutions.

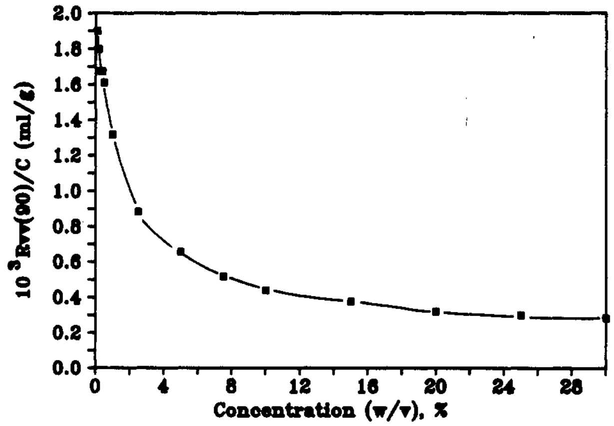


Figure 5. R_{V_V}/C vs concentration plot for polyester/THF solutions.

in Figure 5. It is apparent that R_{V_V}/C decreases sharply at low concentrations and levels off at higher concentrations. This behavior may be due to the highly dipolar substituent groups on the molecular backbone, which give rise to significant intermolecular repulsions. In the dilute concentration regime, such repulsive interactions between solute molecules increase with concentration, resulting in a drastic decrease of density fluctuations per unit volume of solute. At high concentrations, these interactions may achieve a finite value so that R_{V_V}/C is constant. In the case of noninteracting rodlike polymer, R_{V_V}/C should be independent of concentration.[24]

Depolarization ratio, P_V, was measured as a function of q at several concentrations, as illustrated in Figure 6. It is noted that, at low concentrations, P_V varies little with q, whereas at high concentration, this variation increases slightly. This finding indicates that orientation correlation lengths are small as compared with the wavelength of the light λ, as discussed before. If aggregation of the rodlike molecules occurs at high concentrations, density fluctuations should increase substantially, which will eventually lead to a decrease in P_V. Our measurements show that P_V increases with increasing concentration, which provides evidence that aggregation does not occur in the binary solutions, at least at the scale of light scattering resolution.

Orientation correlation length a_o was determined from the Debye–Bueche plot of the depolarized Rayleigh ratio, $R_{H_V}{}^{-1/2}$ vs q^2 (Figure 7). This correlation length is equal to the square root of the slope/intercept. Similarly, density correlation length a_d was calculated by plotting $(R_{V_V} - (4/3)R_{H_V})^{-1/2}$ vs q^2. It is noted that these slopes are very small, so that the precision of measurement is low.

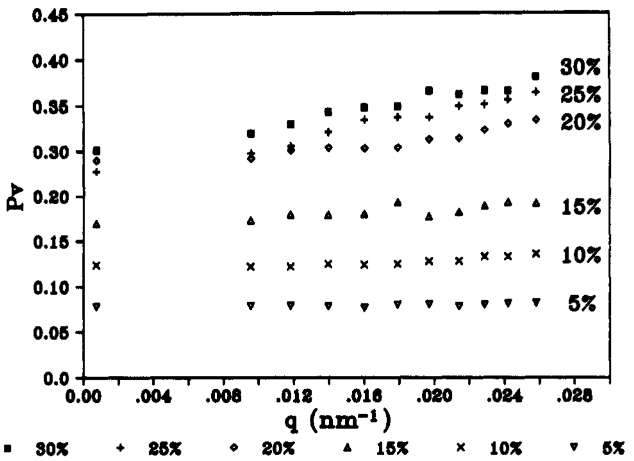


Figure 6. Depolarization ratio vs q plot at different concentrations.

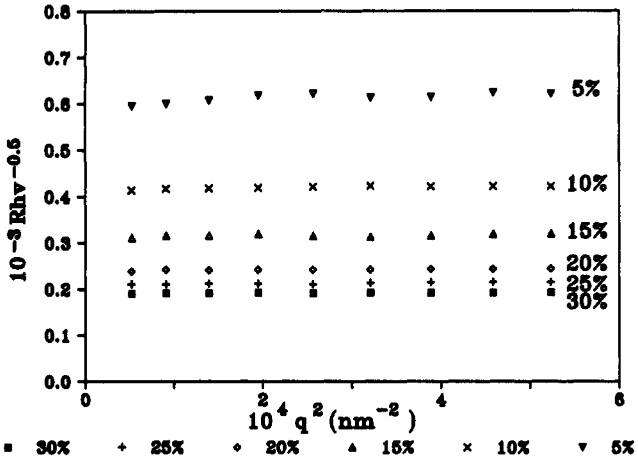


Figure 7. Debye–Beuche plot of depolarized intensity.

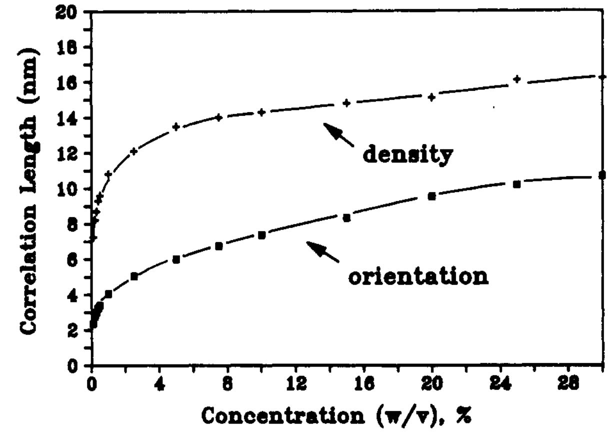


Figure 8. Correlation length vs concentration plot for polyester/THF solutions.

However, such slopes can be assumed constant, and only the intercept varies with concentration. Results of orientation correlation length a_o and density correlation length a_d vs concentration are illustrated in Figure 8. It is seen that a_o increases from approximately 2 to 11 nm and a_d increases from 7 to 16 nm as concentration increases from 0.1% to 30% g/mL. Apparently, density correlation length is greater than orientation correlation length.

One may try to estimate the physical meaning of these calculated orientation correlation lengths. Considering the variation of a_o may be expressed by a random-walk one-dimensional theory of the exponential correlation

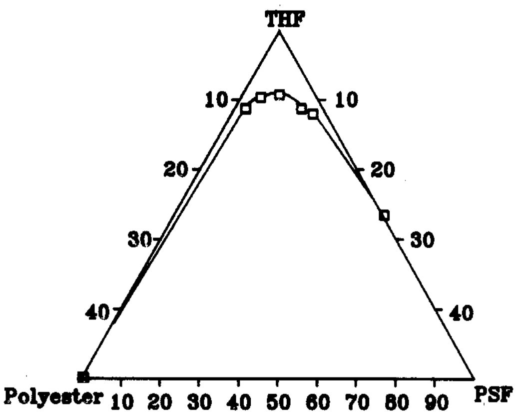


Figure 9. Phase diagram of polyester/polysulfone/THF.

function, as proposed by Stein and Stidham,[25] we get

$$a_0 = b(d/\epsilon^2) \qquad (23)$$

where b is a numerical factor, approximately of the order of unity, d is the distance between rod molecules, and ϵ is the error in angle between adjacent rods. It has been shown that

$$\epsilon = d/L \qquad (24)$$

where L is the length of the rod. As the volume fraction of rods ϕ_r increases, d will decrease proportional to $\phi_r^{-1/3}$. So if L is constant, a_0 is proportional to $\phi_r^{1/3}$. If we consider a concentration increase from 1% w/v to 30% w/v, our model predicts that a_0 should increase by a factor of $(30)^{1/3}$, or about 3. This prediction agrees reasonably well with our experimental results, since a_0 is 3 nm at 1% w/v and is 11 nm at 30% w/v, which is approximately a 3-fold increase. However, this model oversimplifies a very complex system, and perhaps a three-dimensional distribution of rodlike molecules should also be considered.

Ternary Solutions. Ternary solutions containing semistiff polyester and flexible polysulfone in THF were prepared in various compositions. A phase diagram of this three-component system is shown in Figure 9, which was determined by the cloud-point measurement. It is seen that above the solid line a miscible single-phase system is observed, whereas below the boundary line the immiscible, multiphase systems occur. Phase separation is expected since, for mixtures of rod and coil molecules, the entropy of mixing is unfavorable. Miscibility may only occur when the enthalpy of mixing is favorable. In this system, though strong repulsive intramolecular interactions were presented between the rods, no evidence of favorable enthalpic mixing between the rods and coils was observed.

In the miscible single-phase region, the depolarized Rayleigh ratio, R_{H_V}, was measured as a function of polyester concentration. Results are summarized in Figure 10 where R_{H_V}/C at $\theta = 90°$ vs polyester concentration is illustrated. It is seen that R_{H_V}/C remains constant over the concentration range, implying that the presence of coil molecules does not affect the R_{H_V}/C values. However, plotting of the depolarization ratio P_V (at $\theta = 90°$) vs polyester concentration presents a different prospective (Figure 11). It is noted that P_V decreases with increasing coil concentration, suggesting that the denominator of eq 18 (density fluctuations) increases faster than the numerator (orientation fluctuations). This is true since, in the density fluctuations, the $\phi_r(1 - \phi_r)$ term increases sharply with concentration (0–50%), which subsequently reduces P_V. In Figure 11, the dotted line represents the boundary between the single-phase and multiphase regions. It is seen as phase separation occurs, the multiple scattering becomes significant (or solution turbidity appears), and the value of P_V increases. The increase in P_V may be attributed to the increase of local orientation fluctuations of rigid molecules within the confined domains resulting in higher R_{H_V} values.

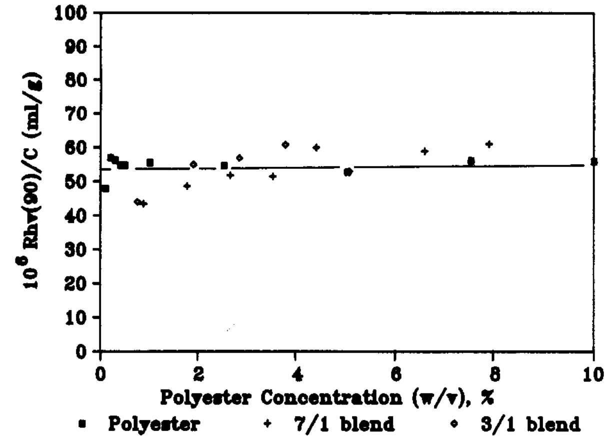


Figure 10. R_{H_V}/C vs polyester concentration plot for polyester/polysulfone/THF solutions.

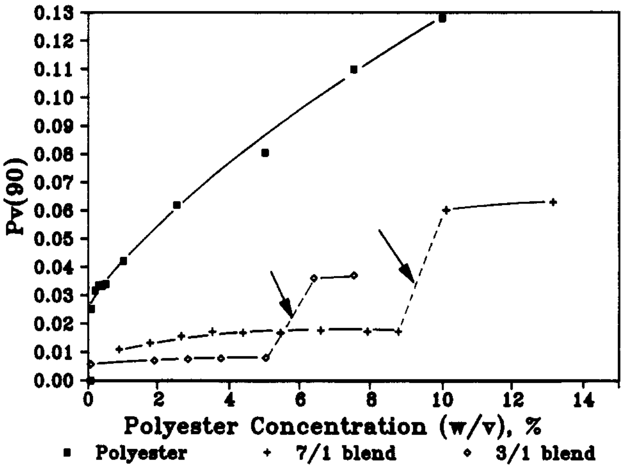


Figure 11. Depolarization ratio vs polyester concentration plot in ternary solutions.

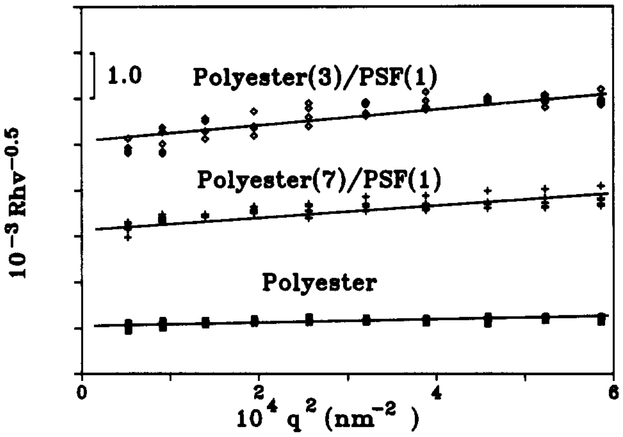


Figure 12. Debye–Beuche plot of depolarized intensity in ternary solutions.

The Debye–Bueche plot of R_{H_V} for ternary solutions in a single-phase region is illustrated in Figure 12. In this figure, all of the intensities measured for various concentrations at a specific rod/coil composition ratio are superimposed on a single curve; a straight line is used to least-squared fit this data. It is seen that the slope of this line increases as the coil molecule content (PSF) increases.

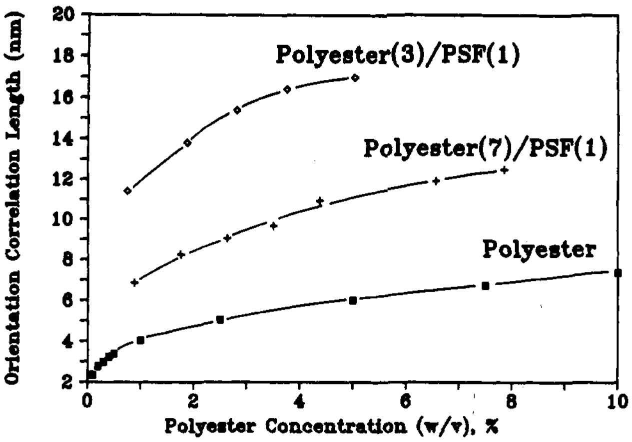


Figure 13. Orientation correlation length vs polyester concentration in ternary solutions.

Since the intercepts of these curves are approximately the same, an increase in slope represents the increase in orientation correlation length. This can be seen in Figure 13, where orientation correlation length vs polyester concentration at three different rod/coil ratios is plotted. In this figure, it is clear that addition of the coil molecules increases the orientation correlation length. In other words, if there are no specific interactions between the rod and coil molecules, addition of coils will favor the aggregation of the rod molecules.

Conclusion

Light scattering techniques were used to characterize molecular information of a polyester in dilute binary solutions and to investigate the state of dispersion of the anisotropic molecules in concentrated binary and ternary solutions. The chosen polyester showed marginal chain stiffness, moderate molecular weight, and good solubility and is considered a semistiff polymer. In a binary system, at high concentrations, the density correlation length (7–17 nm) is larger than the orientation correlation length (2–11 nm). These correlation lengths were determined by the Stein–Wilson theory for depolarized light scattering. The increase in correlation length with concentration indicates that molecular aggregation is favorable in these solutions. Though modification of polyester with strong dipolar substituent groups provides minor solubility in mixtures with polysulfone molecules, the effect of unfavorable entropy of mixing is much greater than the effect of favorable enthalpy of mixing. As a result, addition of polysulfone molecules to polyester solutions always induces a demixing. Such behavior was also verified by the light scattering studies, which showed that orientation correlation lengths increased with the addition of coil molecules.

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Registry No. (Bisphenol A)(4,4′-dichlorodiphenylsulfone) (copolymer), 25154-01-2; (bisphenol A)(4,4′-dichlorodiphenylsulfone) (SRU), 25135-51-7; (2-chloro-4-hydroxyphenol)(2,2′-bis(trifluoromethyl)-[1,1′-biphenyl]-4,4′-dicarboxylic acid)(2-trifluoromethyl-1,4-dicarboxybenzene) (copolymer), 109977-34-6.