Polystyrene Size Determination in Polystyrene and Poly(vinyl methyl ether) Using Electronic Excitation Transport

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Poly(styrene-*co*-2-vinylnaphthalene) with a 1.25% fraction of naphthyl fluorophores is studied in two polymeric hosts, polystyrene and poly(vinyl methyl ether). In the polystyrene host, measurement of the electronic excitation transport-induced fluorescence polarization anisotropy decay, $r(t)$, in conjunction with a previous quantitative statistical theory of electronic excitation transport on lightly tagged polymer chains, allows a determination of the copolymer radius of gyration. Comparison with light scattering measurements from the literature establishes the θ-condition nature of this solid system. Poly(vinyl methyl ether) forms a compatible polymer blend with polystyrene. Analysis of $r(t)$ data shows that the radius of gyration of a copolymer molecule is expanded in poly(vinyl methyl ether) relative to the θ-condition at room temperature. The synthesis of poly(styrene-*co*-2-vinylnaphthalene) is detailed.

I. Introduction

Many details of polymer structure and dynamics in polymeric melts and glasses remain unresolved despite the variety of experimental and theoretical techniques that have been applied to their study on both macroscopic and microscopic levels. Since individual polymeric molecules can adopt numerous structural configurations in liquid or solid media, it is necessary to describe polymer properties in a statistical manner. The high density of polymer chain segments within a polymeric solid or melt means that both intramolecular and intermolecular segmental interactions are important in determining chain structure.

Polymer blends, in addition to their technological importance, are systems that allow the nature of polymer−polymer intermolecular interactions to be characterized thermodynamically and kinetically. An alternative to the costly development and production of a new polymer is to make mixtures of currently available production polymers to form a blend with the desired properties. However, this process is often thwarted by the presence of small forces between segments of chemically different polymers which leads to macroscopic phase separation. Polymer blending does not result in the large increase in entropy that occurs when two small-molecule liquids are mixed. The connectivity of the polymer segments reduces the number of degrees of freedom within the system and the corresponding favorable increase in the entropy of mixing. Therefore, the components of a potential polymer blend system can have only very minor increases in their enthalpy of mixing if the blend is to be compatible. In some applications, phase separation is beneficial, while in others phase separation is associated with deterioration of desirable material properties. Since the vast majority of potential polymer blend combinations yield incompatible mixtures, it is useful to investigate the minority of blends that show some degree of compatible interactions.

Experimental techniques that sample the relevant distance scale are required to obtain an increased understanding of polymeric interactions. Here, the experimental approach is the measurement of electronic excitation transport (EET) by observation of time-resolved fluorescence polarization anisotropy,

$r(t)$, among naphthalene chromophores attached in low concentration to what are essentially polystyrene chains. This method has been applied to the study of polymer glasses,[1−5] melts,[6−8] and blends.[4,8,9]

To investigate polymer structure with EET-induced fluorescence depolarization, it is necessary to incorporate fluorophores into the polymer chains. This is possible by copolymerizing the probe either into the polymer backbone or pendant to it, as a side chain. While both methods have been explored in the past,[2,10] copolymerization into a side chain is simpler synthetically and provides a smaller perturbation to the flexibility of the main chain of the polymer molecule. Any change in the chemical constitution of a homopolymer will invariably modify its properties somewhat, but the magnitude of change is small for many properties of interest, if the tagging fraction of copolymerization is kept low.

The use of naphthalene as a probe fluorophore has been successful in solutions, solids, and polymer systems.[5,11,12] The photophysics of naphthalene are well understood[11,12] and accessible by standard methods of time-resolved laser spectroscopy. The experiments described in this paper employ naphthalene pendant to a predominantly polystyrene main chain in poly(styrene-*co*-2-vinylnaphthalene). This copolymer (PS2VN) is used as a fluorescence probe-tagged guest polymer in two host systems.

EET can provide information on polymer structure because of the well defined distance dependence of the rate of transfer. As described by Förster, for two chromophores, a resonant dipole−dipole interaction leads to a $1/r^6$ distance dependence for transfer of a singlet electronic excited state.[13] The Förster transfer radius, R_0, is the distance at which the probability of transferring the excitation is equal to the probability of fluorescence. Naphthalene has an R_0 of 13 Å. The probability of excitation transfer drops off steeply with increasing distance. Thus, naphthalene has a high sensitivity to the presence of other chromophores within approximately a 30 Å range, a distance which is well suited to the study of problems of polymer segmental interactions. Theoretical treatments of the excitation-

transfer dynamics among chromophores on polymer chains[1,5] make it possible to extract quantitative information regarding the distribution of chain segments. Since the dynamics of excitation transfer are highly sensitive to the chromophore distribution, any change in sample conditions that alters the distribution will be reflected in a change in $r(t)$.

In this paper, the structure of poly(styrene-*co*-2-vinylnaphthalene) dissolved in either polystyrene or poly(vinyl methyl ether) is investigated. Polystyrene is a very common substance. Its uses range from making drinking cups to building materials.[14] In 1996, 11.874 billion pounds of styrene monomer and 6.065 billion pounds of polystyrene were produced in the United States.[15] The technological importance of polystyrene and its ease of preparation in the laboratory make it a good subject for fundamental studies of polymers and polymer blends. Despite the difference between the copolymer synthesized here and polystyrene homopolymer, the magnitude of the chemical perturbation is minor, so that poly(styrene-*co*-2-vinylnaphthalene) is a good model compound for polystyrene.

Poly(vinyl methyl ether), the second polymer host employed in the study, is commercially synthesized by cationic polymerization and has applications as an adhesive and lubricant.[16] The polymer blend system of polystyrene (PS) and poly(vinyl methyl ether) (PVME) is one of the first[17] and most heavily studied to date. Several experimental techniques including NMR,[18] light scattering,[19] and neutron scattering[20] have played roles in the characterization of this system, in both the compatible and phase-separated states. When the host polymer of the blend is changed from PS to PVME, changes in the rate of EET are readily detectable. The changes can be quantitatively modeled using the theory of excitation transfer on polymer chains.[1,4] The results show that while the copolymer in the PS host has a root-mean-squared (rms) radius of gyration consistent with that of PS in a θ-solvent, when the copolymer (essentially PS) is in the PVME host, significant chain expansion occurs at room temperature.

II. Theory

To model excitation transport within an ensemble of side group naphthyl chromophores on a PS2VN molecule, the chromophore distribution function is described by the distribution function of the backbone chain segments, which is modeled as a freely jointed chain. The problem of EET on a lightly tagged freely jointed chain has been treated previously. By employing the cumulant expansion method truncated to first order,[21,22] the self-part of the Green's function solution to the transport master equation, $G^s(t)$, becomes[1]

$$G^s(t) = \frac{1}{\bar{N}} \sum_{i=1}^{\bar{N}} \{\exp[2\pi \int_0^\infty P_i(\mathbf{r})(e^{-2\omega t} - 1)r^2 \, d\mathbf{r}]\} \quad (1)$$

where $\bar{N}$ is the number of statistical segments of the polymer, $\mathbf{r}$ is the separation between chromophores (statistical segments), and ω is defined by eq 2,

$$\omega = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \quad (2)$$

with fluorescence lifetime τ. $P_i(\mathbf{r})$ is a modified segmental distribution function.

$$p_i(\mathbf{r}) \, d\mathbf{r} = \frac{4\pi}{\bar{N}-1} \sum_{j=1}^{\bar{N}}{}' \left(\frac{3}{2\pi a^2 |i-j|}\right)^{3/2} \exp\left(\frac{-3r^2}{2a^2|i-j|}\right) r^2 \, d\mathbf{r} \quad (3)$$

with the parameter, a, equal to the polymer statistical segment length, and the prime in the summation indicating that $i \neq j$. Equation 3 is the probability of finding a polymer segment a distance r away from the ith segment. It is obtained from the probability of finding the jth segment a distance r away from the ith segment, followed by a sum over all j. Since chromophores are attached to segments, $p_i(\mathbf{r})$ is the probability of finding an unexcited chromophore a distance r away from the initially excited chromophore located on the ith segment. However, it does not include a contribution from the possibility that there is more than one chromophore on the same segment as the initially excited chromophore. An additional term is therefore added, giving

$$P_i(\mathbf{r}) \, d\mathbf{r} = \{np'(\mathbf{r}) + (N - 1 - n)p_i(\mathbf{r})\} \, d\mathbf{r} \quad (4)$$

with n the number of unexcited chromophores on the initially excited segment i, N the total number of chromophores on the polymer, and $p'(\mathbf{r})$ defined by eqs 5,

$$p'(\mathbf{r}) \, d\mathbf{r} = 4\pi r^2 \, dr \qquad 0 \le r \le a/2$$
$$= 0 \qquad a/2 < r \quad (5)$$

The forms of eqs 3−5 have been discussed in detail.[1,4]

$G^s(t)$, obtained from eq 1, is equal to the probability that the chromophore initially excited at $t = 0$ is still excited at a later time, t. $G^s(t)$ is an ensemble-averaged property. It contains contributions from excitations that have not left the initially excited chromophore or have left and returned. It does not contain decay from the fluorescence lifetime. The relation between $G^s(t)$ and the fluorescence polarization anisotropy observable, $r(t)$, is given by eq 6,

$$r(t) = \phi(t) \, G^s(t) \quad (6)$$

where $\phi(t)$ describes fluorescence depolarization caused by processes other than energy transfer, notably orientational relaxation of the chromophore.

With knowledge of R_0 and τ and an independent measurement of $\phi(t)$, the experimentally determined $r(t)$ can be fit using the theory for $G^s(t)$. Knowledge of the copolymer molecular weight (number of monomer units) and chromophore tagging fraction parametrizes $G^s(t)$ in the length of a statistical segment and the number of statistical segments, which are related to the copolymer rms radius of gyration, $\langle R_g^2 \rangle^{1/2}$, by eq 7.

$$\langle R_g^2 \rangle^{1/2} = (\bar{N}a^2/6)^{1/2} \quad (7)$$

Therefore, fits to experimental $r(t)$ data for isolated copolymer molecules (no chain-to-chain EET) are dependent on a single relevant polymer parameter: either the statistical segment length, a, or $\langle R_g^2 \rangle^{1/2}$.

III. Experimental Procedures

A. Data Acquisition. Time-correlated single-photon counting was employed to obtain fluorescence polarization anisotropy decays.[23] Details of the specific apparatus used in the current studies have been previously described.[4,24] Excitation pulses of ~10 ps (full width at half-maximum) duration at 320 nm were provided by the frequency-doubled output of a cavity-dumped dye (DCM) laser that was synchronously pumped by a mode-locked and frequency-doubled Nd:YAG laser. This ultraviolet excitation beam photoselectively excites an ensemble of naphthyl chromophores with their absorption dipoles having

TABLE 1: Properties of Polymers Synthesized or Employed in This Study

polymer	styrene (mL)	2VN (mg)	AIBN (mg)	M_w	M_w/M_n	% 2VN
homopolystyrene	7.0	0	5.5	138 000	2.4	0
rotation PS2VN	7.6	0.8	10.4	115 000	2.1	0.004
1.25% PS2VN	5.6	104.6	4.6	193 000	1.9	1.21
f20 1.25% PS2VN				113 000	1.3	1.25
2.5% PS2VN	7.9	576.4	6.5	94 000	2.8	2.47
poly(vinyl methyl ther)				113 000	2.5	

a $\cos^2$ distribution with respect to the polarization of the laser pulse. The fluorescence decay of such an excited state can be described by

$$I_{\parallel}(t) = e^{-t/\tau} \, (1 + 2r(t)) \tag{8}$$

$$I_{\perp}(t) = e^{-t/\tau} \, (1 - r(t)) \tag{9}$$

where τ is the excited-state fluorescence lifetime, $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the time-dependent fluorescence intensities with polarizations parallel and perpendicular to the initial excitation beam, respectively, and

$$r(t) = \frac{I_{\parallel}(t) - I_{\perp}(t)}{I_{\parallel}(t) + 2I_{\perp}(t)} \tag{10}$$

$r(t)$ is the time-dependent fluorescence polarization anisotropy.

Front-face fluorescence from the excited sample passed through a 0.25 m subtractive double monochromator and was detected by a channel-plate detector. A fixed polarizer before the monochromator assured that no polarization bias was inherent in the photon detection system. Fluorescence was detected over a wavelength range of approximately 325−370 nm, with an intensity maximum near 337 nm.

A Pockels cell was used to switch the polarization of the excitation beam relative to the fixed polarizer before the monochromator. The fluorescence intensities polarized parallel and perpendicular to the excitation pulse were collected in alternate 20 s intervals to eliminate the effects of any long-term drifts in laser intensity. These two decays were each stored in a multichannel analyzer array with 76 ps per channel. To construct the fluorescence anisotropy decay at each time point, $r(t)$ was calculated from $I_{\parallel}(t)$ and $I_{\perp}(t)$ using eq 10. The instrument response function, measured by the time-resolved scattering intensity profile at 320 nm from a nonfluorescent scatterer, was a near-Gaussian curve with a full width at half-maximum of approximately 56 ps.

B. Synthesis of Polystyrene and Poly(styrene-*co*-2-vinyl-naphthalene). To synthesize the PS homopolymer[25] and copolymers for this study, a free-radical method was chosen due to its speed and ease of implementation. The PS was synthesized because commercially available PS was found to have fluorescent impurities that could not be removed. Table 1 lists the amounts of reagents used in the four syntheses and the physical properties of the resultant polymer or copolymer.

The styrene monomer from Sigma was supplied with 10 ppm of the common polymerization inhibitor *tert*-butylcatechol. The inhibitor was removed by allowing the monomer to pass slowly down a Scientific Polymer Products DTR-7 inhibitor removal column. For each synthesis, the monomer was separately purified and immediately used. This noninhibited styrene monomer, a small amount of the free-radical thermal initiator azobis(isobutylnitrile) (AIBN), and any (Aldrich) 2-vinylnaph-thalene (2VN) were dissolved in 15 mL of benzene. This

solution was transferred into a round-bottom flask that had been fitted with a spherical ground glass joint. A small additional amount of benzene was used to rinse the sides of the flask.

The reaction flask and its solution were immersed in liquid nitrogen and, once frozen, attached to a vacuum line and subjected to three pump−thaw−refreeze cycles to remove as much dissolved oxygen as possible. With the solution still frozen, the upper neck of the flask was closed with a glass-blowing torch. The vessel was then placed in an oven preset at 60 ± 3 °C and maintained at that temperature for 36 h until the reaction had run to near completion. Upon removal from the oven, the flask was placed into a freezer to quench any remaining reaction. When the contents of the flask had been sufficiently cooled, the flask was opened and the solution added dropwise into a flask of stirring methanol. The resulting fluffy white precipitate was suction-filtered, dried overnight, and further dried in a vacuum desiccator for several days.

Both the styrene homopolymer and the very low tagging fraction PS2VN copolymer (used for orientational relaxation studies) were used as synthesized, after reprecipitation. To provide samples with narrower ranges of molecular weights to simplify data analysis, the two higher-tagging-fraction PS2VN samples were each fractionated by dissolving them in toluene and injecting them into a Waters 590 gel permeation chromato-graph equipped with an automatic fractionator. The resulting copolymer fractions had narrow molecular weight distributions. Polymer molecular weights and polydispersities were quanti-tatively determined with a Waters analytical gel permeation chromatograph using tetrahydrofuran as solvent. Only the 1.25% PS2VN fraction 20 listed in Table 1 was used in the excitation transport chain-size determination studies described in this paper. All subsequent references to PS2VN refer to this specific copolymer fraction. Of the polymers listed in Table 1, only fraction 20 (f20) has a relatively narrow polydispersity. The other polymers are either used as hosts or for comparisons to f20, and therefore, their polydispersity should have little consequence on the results of the chain-size determination. The rotation sample is used to determine the orientational relaxation of the naphthyl chromophore. Orientational relaxation is controlled by local interactions that should be essentially independent of the size of the chain the chromophore is attached to or embedded in.

The copolymer tagging fractions of 2-vinylnaphthalene listed in Table 1 were determined spectroscopically. A small amount of the unfractionated or fractionated copolymer was weighed and transferred into a 2 mL volumetric flask. The copolymer was dissolved in CH_2Cl_2 and the solution diluted quantitatively. Then, the solution of known copolymer weight concentration was transferred to a quartz cuvette with a 1 cm path length. An ultraviolet absorption spectrum was acquired with a Cary 3E spectrophotometer. The absorption of the naphthyl chro-mophore of the copolymer at the peak of the transition (320 nm) was determined. An extinction coefficient of 350 M^{-1} cm^{-1} for 2-ethylnaphthalene in CH_2Cl_2 was used as a standard for the 2-vinylnaphthalene side group. From the application of Beer's law, the molecular weight of the copolymer, and the weight concentration, the mole fraction of monomers with naphthyl groups was calculated. This is converted to an average number of naphthyl chromophores per copolymer molecule for use in the calculations of the energy-transfer dynamics.

C. Sample Preparation. For the measurement of $\phi(t)$, a sample of the low-tagging-fraction copolymer, the rotation PS2VN sample, was prepared. The very small amount of 2-vinylnaphthalene used in the synthesis yielded a copolymer

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with an average of one chromophore for approximately every 20 complete polymer molecules. It was unnecessary to fractionate this copolymer, since the dynamical rotational depolarization of a single pendant side group is invariant to changes in polymer molecular weight. Also, because of the very low concentration of naphthalene in the sample as synthesized, no further dilution with homopolystyrene was required to ensure the absence of EET.

To obtain an accurate measurement of $G^s(t)$ from the guest/host samples, it was necessary to ensure the absence of all energy transport dynamics resulting from interactions between chromophores on neighboring copolymer molecules. This was accomplished by dilution of the tagged PS2VN so that no excitation transport can occur between chromophores on different isolated chains. This synthetic homopolystyrene showed negligible background fluorescence, enabling its use in the blend samples. The commercial homopolymer PVME also showed negligible background fluorescence and was used without further purification.

Both types of polymer samples were prepared by the method of solution casting. The appropriate amount of PS2VN copolymer was weighed on an analytical balance and quantitatively transferred to a dry glass vessel. Usually ∼1 mg of the fractionated, tagged copolymer was required for each sample. Any homopolystyrene was also measured by weighing, but PVME was added by quantitatively transferring from a calibrated solution of polymer in benzene. Additional benzene was added to dissolve the copolymer and homopolymer into a solution of approximately 5 w/w % polymer/solution. At this low concentration, the polymer molecules are fully solvated and spatially isolated from each other with essentially no entanglements, ensuring homogeneous mixing. A cylindrical glass ring was placed in the center of an ultraviolet-transparent, fused silica substrate to form a solution receptacle. The polymer solution was added by glass pipet to the interior of the glass ring cavity and allowed to evaporate in a desiccator saturated with benzene vapor overnight, leaving a polymer blend film of good optical quality. The sample was placed under vacuum for several hours to ensure complete solvent removal. At no time during the solvent removal procedure was the sample heated above ambient temperature, ensuring the absence of phase separation. The resulting sample, about 1 mm thick, was optically clear and free of strain birefringence as observed between crossed polarizers under a microscope. Every sample had an absorbance of less than 0.2 at 320 nm, so that fluorescence reabsorption was minimized.

IV. Results and Discussion

A. Measurement of $\phi(t)$. The $r(t)$ data acquired from the rotation PS2VN sample at room temperature are displayed in Figure 1. After excitation of an absorbing chromophore, the theoretical maximum initial value of the fluorescence anisotropy is 0.4. However, this maximum will be measured only if the absorption and emission transitions are completely polarized and the emission transition dipole moment is parallel to the absorption transition dipole moment. In the present experiments, $r(t)$ is observed to have a maximum value of ∼0.25. This value has also been observed in all other studies using naphthalene as a fluorescence anisotropy probe,[4,5,24,26] including those experiments in which the naphthyl was attached to a polymer backbone in a solid polymeric sample at low temperature. Thus, it is unlikely that the observed maximum value of $r(t)$ deviates from the theoretical maximum due to a very fast unresolved motion of the chromophore. The probable explanation is the
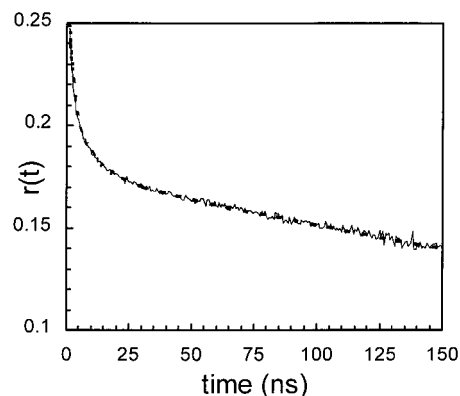
Figure 1. Fluorescence anisotropy decay, $r(t)$, of the rotation-only PS2VN sample. The dashed line is a triexponential fit to the fluorescence depolarization, $\phi(t)$, in the low-concentration sample in which electronic excitation transport does not occur.

detection of very broad-band fluorescence. This fluorescence includes emission to more than one vibrational level, resulting in a reduction of the polarization of the transition.

The fluorescence depolarization data shown in Figure 1 result from reorientational relaxation of the pendant naphthalene fluorophores. The dashed line through the data is an empirical triexponential fit with the six fitting parameters given in eq 11.

$$r(t) = 0.068e^{-t/1.6 \text{ ns}} + 0.039e^{-t/8.85 \text{ ns}} + 0.177e^{-t/636 \text{ ns}} \quad (11)$$

Because there is no excitation transport in this experiment, $G^s(t) = 1$, so that from eq 6, $r(t) = \phi(t)$. The triexponential fitting parameters define $\phi(t)$, which is employed in the subsequent comparisons to fluorescence polarization anisotropy decays. The use of eq 11 is not intended to suggest that the orientational relaxation of the naphthyl side group is actually triexponential. For the purposes of this paper, the exact nature of the functional form of $\phi(t)$ is unimportant. It is only necessary to be able to reproduce the decay for the subsequent data analysis.

The rotational dynamics of the chromophore-bearing copolymer were recorded in a PS host. The $\phi(t)$ for PS2VN in PS was observed to be almost identical to that acquired from a previous sample prepared in a similar manner, but with the important difference that its naphthyl chromophores were pendant to a poly(methyl methacrylate-*co*-2-vinylnaphthalene) copolymer which was dissolved in the homopolymer poly(methyl methacrylate) (PMMA).[2] The similarity of the two decays suggests that, on the time scale observed, the reorientation dynamics of naphthalene pendant to a carbon-backbone polymer are independent of the specific nature of the organic polymer host.

An attempt was made to measure the rotational depolarization of the naphthyl side group in a PVME host. The necessity of further diluting the rotation PS2VN so that no styrenic chains were overlapping caused the fluorescence signal to be attenuated to such a low level that sufficiently high-quality data could not be obtained. However, because of the aforementioned correspondence between the rotational depolarization measured in both PS and PMMA, eq 11 is employed in the data analysis for samples with PVME hosts. This point will be discussed further below.

B. Measurement of $G^s(t)$ and Copolymer $\langle R_g^2 \rangle^{1/2}$ in Polystyrene. Before using a measurement of $G^s(t)$ to determine $\langle R_g^2 \rangle^{1/2}$ for fraction 20 of PS2VN dissolved in the two homopolymers, it is necessary to confirm the absence of interchain excitation transport between copolymer molecules. Several copolymer/homopolymer blend samples were prepared as described previously, with care taken to control accurately the
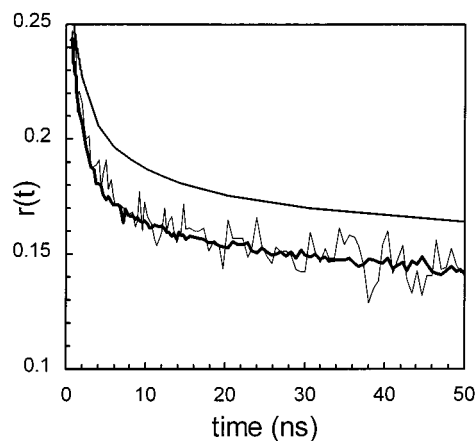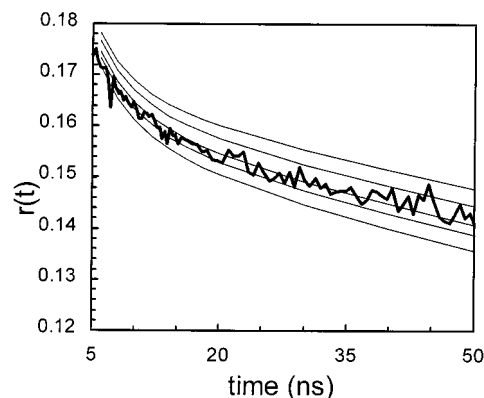
Figure 2. Fluorescence anisotropy data, $r(t)$, for two samples of PS2VN, 0.05% and 0.5% (thicker line), dissolved in homopolystyrene. In both samples, 1.25% of the monomers have the naphthyl side group. The noise level is much higher in the sample with the lower concentration of chains, but the decays are the same. This demonstrates that there is no copolymer aggregation. Also displayed is the fit (upper curve) to the low-concentration sample in which electronic excitation transport does not occur. The difference in the decays is caused by EET.

Figure 3. Fluorescence anisotropy data, $r(t)$, for 0.5% PS2VN dissolved in PS (thick line). Calculated curves (thin lines) are, from top to bottom, for rms radius of gyration: 119, 109, 101, 97, and 92 Å.

amount of copolymer added to the blend. Samples containing copolymer weight fractions of 0.05%, 0.1%, and 0.5% in PS were prepared for study.

Fluorescence polarization decay data, $r(t)$, are displayed in Figure 2 for the two samples of concentrations 0.05% (thinner line) and 0.5% (thicker line). Also included in Figure 2 is the fit to $\phi(t)$ (smooth line) which is given by eq 11. The difference in the decays of the 1.25% tagging fraction copolymer and the rotation-only copolymer arises from excitation transport. It is clear from the figure that the two EET decay curves are identical, within the noise. Thus, both samples are in the dilute limit of chain concentration. The copolymer chains are isolated from each other. Had there been EET between chains in the 0.5% sample, dilution of the copolymer by a factor of 10 to 0.05% would have been detectable as a difference between decays, corresponding to a slowing of $G^s(t)$ as the copolymer chains became more widely separated. The absence of a change in $r(t)$ between the two concentrations indicates that intermolecular energy transfer in the 0.5% sample is negligible, so that further dilution has no measurable effect on $r(t)$. Data from the 0.5% sample were used for the analysis.

The data acquired from the 0.5% PS2VN/PS sample are replotted in Figure 3. Along with the experimental $r(t)$ data are several curves calculated using eq 6 with eq 1 for $G^s(t)$ and eq 11 for $\phi(t)$. Each theoretical curve differs only in the value of $\langle R_g^2 \rangle^{1/2}$ used in the calculation. The calculated $\langle R_g^2 \rangle^{1/2}$ value of 101 Å provides the closest agreement with the data. The data are bounded by calculations for radii of gyration of 97 and 109 Å, but the deviation toward the 109 Å curve is substantially smaller. Based on these results, $\langle R_g^2 \rangle^{1/2} = 102$ Å. The error in this number is estimated at ±3 Å. In Table 2, the chain size determined by EET is compared to measurements from the literature made with light scattering on PS dissolved in θ-solvents.[27−30] The value obtained here with EET is in good agreement with the light scattering results and falls within the respective error bars.

The results of EET size determination demonstrate that PS is acting as a θ-solvent for PS2VN within experimental error. The very light tagging of PS2VN (1.25%) with a naphthyl replacing a benzyl side group should have little effect on chain

structure. Essentially, the experiment is examining PS in PS and demonstrates that a pure polymer material closely approximates a polymer in a θ-solvent. In a previous study of this type, naphthyl-tagged PMMA in PMMA was investigated using EET.[2] The results showed that, within experimental error, PMMA also behaved as a θ-solvent for itself. This type of measurement is not possible with light-scattering techniques due to the lack of scattering contrast between guest and host. Neutron-scattering measurements of $\langle R_g^2 \rangle^{1/2}$ are possible if one component is deuterated. It has been shown that deuterium labeling can effect the phase diagram.[31] Deuterium labeling, like chromophore labeling, may influence the determination of $\langle R_g^2 \rangle^{1/2}$. Fluorescence EET experiments provides an alternative to neutron scattering for investigating polymer blends, and it is useful even at very low concentrations. However, care must be taken to assess the influence that chromophore tagging has on the chain structure. If necessary, a series of copolymers with different tag concentrations may be examined, and the results can be extrapolated to zero tagging concentration.

C. Measurement of $G^s(t)$ and Copolymer $\langle R_g^2 \rangle^{1/2}$ in Poly-(vinyl methyl ether). Figure 4 displays the fluorescence anisotropy for a 2% PS2VN/PVME sample (upper curve) and the 0.5% PS2VN/PS sample (lower curve). Measurements were made at 295 K. The lower curve is the same data that are displayed in Figures 2 and 3. The decay for PS2VN dissolved in PVME is significantly slower at short times than that for PS2VN dissolved in PS. At a volume fraction of 2%, there is still no contribution to $r(t)$ from off-chain excitation transport for randomly distributed chains. The chains are taken to be randomly distributed because a blend with 2% PS in PVME at room temperature is well below the region of the phase diagram in which phase separation occurs. Assuming that the naphthyl orientational relaxation (Figure 2) is not changed significantly in going from a PS to a PVME host, the difference between the decay curves in Figure 4 is due to differences in $G^s(t)$ of the same tagged copolymer guest in the two host homopolymers. (The question of orientational relaxation will be discussed further below.)

The decrease in the rate of excitation transport on the PS2VN in the PVME host indicates that the chain structure of PS2VN is different in PVME then it is in PS. To observe a decrease in the rate of excitation transport, the chromophores must be farther apart. Thus, the ensemble of PS2VN chains in PVME has a larger $\langle R_g^2 \rangle^{1/2}$ with respect to that of the θ-condition, causing chromophore separations to increase. Thus, even prior to a quantitative analysis of the data, it is clear that PS2VN expands

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TABLE 2: Comparison of the Values for $\langle R_g^2 \rangle^{1/2}$ of PS2VN Measured by EET Fluorescence Depolarization Experiments with That of Polystyrene Measured by Light Scattering[a]

actual M_w	$\langle R_g^2 \rangle^{1/2}$ (Å)[b]	$[\langle R_g^2 \rangle^{1/2}/\sqrt{M_w}] \times 10^4$, $\langle R_g^2 \rangle^{1/2}$ in nm	host	technique	ref
113 000	102	303	polystyrene	fluorescence depolarization	this work
1 260 000	101	303	34.7 °C cyclohexane	light scattering	28
6 400 000	98	292	34.5 °C cyclohexane	light scattering	29
186 000	98	291	15 °C decalin, 61.7% cis	light scattering	30

[a] The polystyrene literature data have been scaled to match the molecular weight of the copolymer. [b] Corresponding to M_w of 113 000.
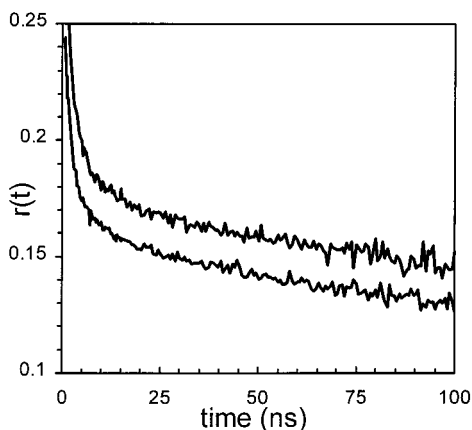
Figure 4. Fluorescence anisotropy, $r(t)$, for a sample of PS2VN dissolved in PVME (upper curve). The lower curve corresponds to the $r(t)$ for a sample of PS2VN dissolved in PS. The slower decay in the PVME host results from slower excitation transport, demonstrating that the copolymer expands in PVME relative to θ-conditions.
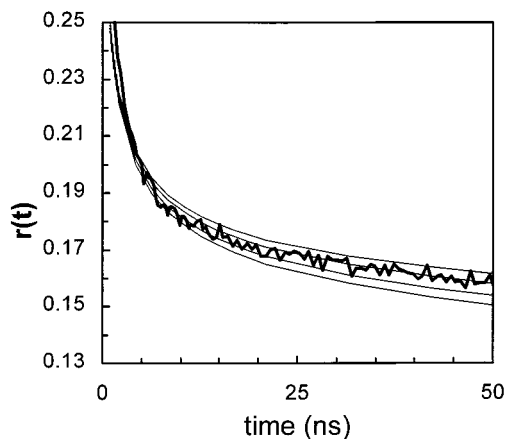
Figure 5. Fluorescence anisotropy, $r(t)$, for a sample of PS2VN dissolved in PVME (heavy line) and decay curves calculated from eq 1 (thin lines) for copolymer rms radius of gyration values, from highest to lowest curve, of 170, 138, 119, and 110 Å.

in PVME relative to θ-conditions. The very light tagging fraction of naphthyl groups, and the fact that the PS2VN has a $\langle R_g^2 \rangle^{1/2}$ consistent with θ-conditions in PS, strongly suggests that the observed chain expansion is not significantly influenced by the presence of the naphthyl groups.

To determine the extent of PS2VN copolymer expansion in PVME, additional calculations were performed using eq 1, varying $\langle R_g^2 \rangle^{1/2}$. Figure 5 displays the results of the calculations, along with the anisotropy decay for the PS2VN/PVME polymer blend sample. The calculated curves, from top to bottom, correspond to $\langle R_g^2 \rangle^{1/2}$ of 170, 138, 119, and 110 Å. The data mainly fall between the 138 and 119 Å curves. Thus, the value of $\langle R_g^2 \rangle^{1/2}$ is 129 Å. The error is estimated to be ±5 Å. The copolymer chain expansion, relative to θ-conditions, is large. The precision of the measured $\langle R_g^2 \rangle^{1/2}$ is substantially

lower than that for PS2VN/PS. The decreased precision is a reflection of the low chromophore tagging fraction employed in these studies. Chain expansion causes the average chromophore−chromophore separation to increase, which reduces the rate of excitation transport. The reduced rate of excitation transport reduces the sensitivity of the observable to changes in size. The 1.25% tagging fraction used in this study could have been greater. While it is desirable to use a small tagging fraction to avoid significant perturbation to the chain structure, given the extent of the chain expansion observed, a tagging fraction of 3 or 4% would have provided a more accurate determination of the expanded $\langle R_g^2 \rangle^{1/2}$ for PS2VN in PVME.

In the determining the $\langle R_g^2 \rangle^{1/2}$ of PS2VN/PVME, it was assumed that the decay of the fluorescence anisotropy arising from orientational relaxation is the same as the orientational anisotropy decay for PS2VN/PS (Figures 1 and 2). At room temperature, PS is below its glass transition temperature, T_g. PVME is just above its T_g, and it is an extremely viscous liquid. In both hosts, the time scale of the fluorescence measurements is too short for significant backbone motion. The orientational anisotropy arises from motion of the naphthyl side group with fixed backbone geometry. In studies of poly(methylphenyl-siloxane) (PMPS) it was found that the fast phenyl side-group orientational relaxation was independent of the viscosity/temperature of the PMPS melt, even though this ratio changed dramatically.[32,33] It was also determined that the phenyl side-group relaxation was almost unchanged in going from the PMPS melt to dilute carbon tetrachloride solution. A study of the fast orientational relaxation of the naphthyl side group of poly(2-vinylnaphthalene) in carbon tetrachloride[32] demonstrated that orientational dynamics were independent of viscosity/temperature even when this ratio changed by a factor of 40. The results of these studies show that fast side-group orientational relaxation, occurring on a time scale that is short compared to backbone motion, is controlled by local, on-chain steric interactions and is little influenced by the nature or viscosity of the solvent. Thus, the assumption that the orientational relaxation of the naphthyl group of PS2VN is the same in PS and PVME is reasonable. (We are currently testing this assumption experimentally with polymers specially prepared for this purpose.) However, this assumption does increase the uncertainty in the magnitude of the chain expansion of PS2VN in PVME. If going from the glassy host (PS) to the very viscous liquid host (PVME) increases the rate of orientational relaxation, then the analysis of the data presented in Figure 5 underestimates the magnitude of the chain expansion. If the orientational relaxation is for some reason slower, then the extent of chain expansion is overestimated. Given the arguments made above, and the fact that the orientational relaxations of the naphthyl groups in PS2VN/PS and in poly(methyl methacrylate-*co*-2-vinylnaphthalene)/PMMA are very similar, uncertainty in the extent of orientational relaxation should not greatly increase the error in the determination of the magnitude of the PS2VN chain expansion in the PVME host.

Using small-angle neutron scattering, Briber, Bauer, and Hammouda performed an extensive study of deuterated PS in low concentration in blends with PVME and PS hosts.[20] From the SANS data, they determined the radius of gyration of deuterated PS (MW = 193 000) in PVME from 353 to 433 K at 20 deg intervals. Their results indicate that the deuterated PS is larger in PVME than in PS, especially at lower temperatures. It also suggests that deuterated PS expands in PVME, and collapses in PS, as the temperature is lowered, but they acknowledged that these temperature dependences fell within the error bars for their data. In an effort to determine whether our 298 K data confirmed their temperature dependence, we found that their guest polymer was always collapsed relative to ours. For example, if we determine the size/weight relationship (expressed in the *Polymer Handbook*[27] as $[\langle R_g^2 \rangle^{1/2}/\sqrt{M_w} \times 10^4]$ for $\langle R_g^2 \rangle^{1/2}$ in nanometers) from their data for deuterated PS in PS, we obtain a range from 258 to 264, while that for PS in θ-conditions[27] ranges from 280 to 306. Extrapolation of the best fit line to their data for deuterated PS in PVME predicted that their guest would further expand, but only to the PS θ-condition size at room temperature. Furthermore, their data indicate that deuterated PS is not in θ-conditions in PS. While Briber et al. have performed a careful study of deuterated PS in these hosts, the deuteration of a model compound can affect the phase behavior of its blends.[10]

According to Flory theory, a polymer chain should expand relative to its θ-condition size in a good solvent. Since PS/PVME blends are compatible and exhibit lower critical solution temperature behavior,[34] PVME acts as a good solvent for PS at low temperature and is a poorer solvent for PS as the temperature rises, leading to macroscopic phase separation. Therefore, the observation made here with EET, that PS2VN is significantly expanded in PVME at room temperature relative to θ-conditions, is consistent with expectations.

V. Concluding Remarks

Polymer chain configurations in polymeric blends were studied using electronic excitation transport among chromophores lightly tagged on polystyrene. The tagged PS is a copolymer, poly(styrene-*co*-2-vinylnaphthalene). By measuring the EET using time-resolved fluorescence depolarization and comparing the data to theoretical calculations of the EET, the radii of gyration of PS2VN in PS and in poly(vinyl methyl ether) were determined. In PS, the copolymer $\langle R_g^2 \rangle^{1/2}$ corresponded to that of θ-conditions, as is anticipated for a blend with the homopolymer. This is consistent with the very light tagging fraction, which does not substantially change the copolymer properties from those of PS. The PS2VN is essentially the same as the PS homopolymer. The measurements in PVME showed substantial chain expansion compared to θ-conditions at 295 K.

The EET measurements presented here and previous measurements of the $\langle R_g^2 \rangle^{1/2}$ of naphthyl-tagged PMMA[1,2,4] demonstrate that EET can be used as a quantitative method for the determination of $\langle R_g^2 \rangle^{1/2}$ or, equivalently, the statistical segment length. The type of SANS study used to determine the temperature dependence of $\langle R_g^2 \rangle^{1/2}$ in a blend can also be performed using properly designed EET experiments, with the following advantage: in producing contrast between blend components for neutron-scattering studies, deuteration affects every monomer in the model polymer and is likely to make the phase behavior of the model compound different from that of its hydrogenated counterpart. Model compounds for EET

studies can be less different chemically than their untagged counterparts, behaving as if in θ-conditions in blends with the untagged compounds. However, care must be taken to assess the influence of the chromophore labeling. It may be necessary to make a series of chains with different tagging fractions and extrapolate results to zero tagging. Recent detailed Monte Carlo simulations[35] demonstrate that the analytical EET theory used to analyze the experimental data is quantitatively accurate. In addition, the theoretical study, which will be published subsequently, gives insights into the proper design of the EET experiment. In light of these recent theoretical results, it is clear that the accuracy of the study reported above could be substantially improved by an increased tagging fraction for both the EET copolymer and the rotation-only copolymer. Nonetheless, the data reported here are of sufficient accuracy to yield insights into polymer chain structure in blends.

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