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Time-Resolved Fluorescence and Emission Depolarization Studies on Polystyrene: Photochemical Processes in Polymeric Systems. 9[1]

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ABSTRACT: The prompt fluorescence emission from polystyrene has been studied in the solid phase (thin film) and in dilute CH_2Cl_2 solution. Measurements of lifetime and polarization have been performed as a function of wavelength in the region 278–380 nm. These studies demonstrate that two emissive species may be characterized in this wavelength range, the monomer (isolated single phenyl groups), emitting at wavelengths shorter than 320 nm, and the excimer, emitting in the range 300–380 nm. Emission in the wavelength region 335–380 nm is characterized by a single-exponential decay in dilute solution as well as in the solid state. No measurable delay is observed in time evolution of any emission. Steady-state polarization measurements show that the fluorescence excimer emission from pure films recorded at 330 nm is essentially completely depolarized. These steady-state measurements are in agreement with polarization measurements on the prompt fluorescence. Total prompt fluorescence following the laser flash is similarly completely depolarized at 335 and 365 nm. Excimer emission from oriented (stretched) films was also found to be depolarized. Polystyrene films that were photodegraded showed less depolarization.

Introduction

Kinetics of decay of singlet excimers are frequently complex and require functions with two or three separately variable exponents for acceptable fits for several polymers in which chromophores are farther apart than the optimal distance required for the formation of 1,3 excimers.[2–6] Guillet and co-workers[2–5] analyzed excimer emission kinetics to obtain rates of dissociation and formation of excimers in several of these systems. In these systems, it is commonly observed that (1) formation of excimers in fluid solution is delayed, the rise time approximately corresponding to the rate of rotation of the pendant groups, and (2) the rate of singlet energy migration is relatively slow, as monitored by the gradual rise in the acceptor's fluorescence over more than 100 ns in poly(1-naphthyl methacrylate). Since the rate of rotation of pendant groups in these systems is fast relative to the rate of excited singlet energy migration in fluid solution, it is to be anticipated that the predominant mechanism of excimer formation involves rotational alignment of an excited state to a neighboring chromophore.

It is our contention that polymers capable of forming 1,3 excimers belong to a distinct class, at least in terms of their photophysical characteristics. Thus in poly(1-vinylnaphthalene)[6] and poly(vinylcarbazole)[7,8] the kinetics of decay of excimer fluorescence are best interpreted in terms of formation of multiple excimer species, which once formed, do not revert back to the monomeric state prior to deactivation. Formation of excimers is observed to be rapid relative to the rate of rotation of pendant groups, even in fluid solution, being essentially complete within 2 ns. In pulse radiolysis experiments on P1VN films doped with anthracene[10] it was found that transfer of singlet excitation of anthracene was complete within 5 ns, an observation that yielded a lower limit of the rate of singlet energy migration in this system. Thus, energy migration to "preformed" parallel pairs of chromophores may be viewed as the major contributor to excimer formation in these systems; rotational alignment subsequent to excitation plays a minor role.

Polystyrene would be expected to belong to the second group of polymers; hence we proposed to investigate two crucial features of the photophysical behavior of this polymer. Specifically, we attempted to determine if the prompt fluorescence from the singlet excimer is depolarized, since observation of depolarized fluorescence from the excimer would strongly indicate energy migration prior to excimer formation.[9] Measurements of polarization as a function of time in the 0–100-ns range would also (a) yield estimates of the rate of energy migration and (b) verify whether a sequential rotational alignment mechanism proposed to interpret data on energy transfer to acceptors[11] can operate in the solid state. The other aspect of the photophysics we report here is the kinetics of fluorescence emission in fluid solution as well as in the solid state. We found a single well-characterized (in terms of spectral resolution of emission) excimer in both cases, decay of which may be satisfactorily fitted to a single-exponential decay function and the formation of which is complete within 2 ns following the laser pulse. Data reported by Ghiggino[12] indicate that the rate constant of excimer formation is greater than or equal to $k = (3\ \text{ns})^{-1}$, consistent with our results and with expected rates of singlet energy transfer in this system.

In general, two different experimental approaches have been utilized in order to seek evidence of singlet energy

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migration in polystyrene and similar systems. Johnson[8] proposed a random walk model of energy migration involving a Förster-type dipole–dipole resonance transfer by measuring fluorescence decay rates on doped polymers. A similar approach was also used by Fox et al.,[14] who measured fluorescence of a series of copolymers of styrene and vinylnaphthalene, in which naphthalene acted as the acceptor. Fluorescence depolarization measurements have also been used to study energy migration as well as molecular motion in polymers. Reid and Soutar[15] studied energy migration and intramolecular excimer formation in a series of copolymers of 1-vinylnaphthalene, 2-vinylnaphthalene, styrene, and methyl methacrylate using the fluorescence depolarization technique. MacCallum and co-workers[11,16] reported fluorescence depolarization studies on styrene–phenylacetylene copolymers using perylene as an acceptor. They also studied the depolarization of excimer emission from polystyrene film cast from methylene chloride solution and concluded that excimer fluorescence from polystyrene is essentially completely polarized. Photophysical properties of polystyrene have also been investigated by Klöpffer,[17] Geuskens,[18] and others. Among these, Hirayama[19] and Ishii[20] demonstrated efficient energy transfer to several classes of acceptors incorporated in polystyrene. In a preliminary communication[13] we have reported on monomer/excimer fluorescence intensity ratios in polystyrene and demonstrated that both emissions are efficiently quenched by the products of photodegradation.

Experimental Section

A. Steady-State Measurements. Polystyrene ($\bar{M}_n = 125000$, $\bar{M}_w/\bar{M}_n \simeq 2.0$) purchased from Polysciences, Inc., was purified by repeated precipitations from CH_2Cl_2 solutions by addition of methanol. Emission spectra were recorded on a Perkin-Elmer MPF3A spectrofluorimeter. Polystyrene films were stretched 300% in an Instron tensile machine. Samples were heated to 112 °C in a nitrogen atmosphere and then were stretched up to 300% at a rate of 12.5 cm/min. The elongated samples were cooled under tension in a stream of dry nitrogen for a few minutes. Photodegradation was induced in films by suspending freestanding films at a certain distance from a low-pressure Hg arc lamp. Fluorescence polarization was measured on the Perkin-Elmer MPF3A spectrofluorimeter using Polacoat (3M Co.) and HNP'B (Polaroid Corp.) polarizers.

B. Flash Spectroscopy. Polystyrene, purified as above, was dissolved in methylene chloride (0.5 g/L) and deoxygenated by bubbling high-purity argon through the solution for 2–5 min. It was then excited with the fourth harmonic (266 nm) of a Nd:YAG pulsed laser. Collected fluorescence was spectrally resolved by a McKee-Pederson 0.45-m monochromator. Slit widths corresponding to 4–10-Å spectral resolution were used. The spectrally resolved optical signal was incident on a EMI 9829QB photomultiplier, the output of which was digitized in real time on a Biomation 6500 transient recorder with a 2-ns gate. Data were averaged and analyzed on a Z-80-based microcomputer. Laser scatter was used for the reference pulse shape for iterative deconvolutions. Data were analyzed by deconvolution with a single-exponential lifetime. This yielded a "residual error", which is the sum of the absolute values of the difference of the data and fit at each channel divided by the sum of the data. Good fits were obtained by averaging 100 pulses. Lifetime measurements at 300 nm were obtained by averaging 1000 pulses. Time-resolved polarization measurements were made on PS films by mounting a Glan-Taylor polarizer in the fluorescence beam path. Films were placed in 1-mm quartz cuvettes and continuously purged with N_2 during excitation. Fresh films were used after every 200 shots. The exciting laser power was attenuated to approximately 100 μJ in order to avoid photodegradation and formation of quenchers. A dilute solution of naphthalene in CH_2Cl_2 was used to determine the instrumental bias for polarization measurements at 335 and 365 nm and a solution of benzene in cyclohexane at 285 nm. The instrumental correction factor was expressed as $[I_H/I_V]_{instr}$. Instrumental bias was found to be relatively independent of wavelength in the range 320–380 nm and was equal to 2.04 ± 0.04. The use of naphthalene and benzene in dilute solution in order to determine the instrumental constant is justified by the fact that the rotational time constant (τ_{rot}) for small molecules in fluid solvents is of the order of 100 ps.[24] It increased sharply at wavelengths less than 310 nm.

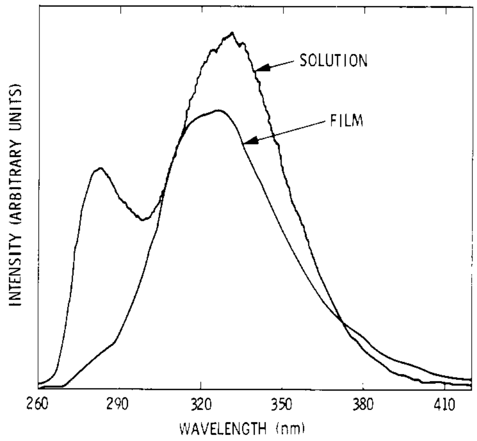

Figure 1. Fluorescence spectra of polystyrene in CH_2Cl_2 solution and of film cast from CH_2Cl_2 solution (λ_{ex} = 250 nm).

Results

A. Steady-State Measurements. Figure 1 shows the fluorescence spectra of polystyrene in CH_2Cl_2 solution and of polystyrene film cast from CH_2Cl_2 solution. Fluorescence polarization was calculated as

$$p = [I_{VV} - GI_{VH}]/[I_{VV} + GI_{VH}]$$

where I is the light intensity and $G = I_{HV}/I_{HH}$, the subscripts H and V referring respectively to the horizontal and vertical polarization of the exciting or analyzing polarizer. G represents the instrumental correction factor.[21] Polarization of fluorescence of a fluid solution of fluorescein (10^{-5} M, pH 7, 23 °C) was found to be $p = 0.016$, in good agreement with published data.[22] Fluorescence from rhodamine 6G in a polystyrene matrix was found to be completely polarized, p being approximately 0.49 at room temperature. Fluorescence polarization was measured on polystyrene film at room temperature. p was found to be 0.03 at 330 nm (λ_{ex} = 260 nm). Fluorescence polarization was also obtained on stretched polystyrene films. p was found to be 0.04 for a 300% stretched film when the axis of sample orientation was perpendicular to the plane of the incident beam and p was 0.03 when sample orientation was in the plane of the beam. Fluorescence polarization values obtained for photodegraded samples are shown in Figure 2. The value of p increased from 0.03 to 0.1 after 32 min of irradiation with a low-pressure Hg arc lamp (total photons incident 2.6×10^{-6} einstein/cm^2) while the excimer fluorescence intensity dropped by a factor of 7.

B. Time-Resolved Spectroscopy. Figure 3 shows time profiles of emission from PS in CH_2Cl_2 solution recorded at 285, 300, 335, and 380 nm. Additional spectra were monitored at 278, 320, 350, and 365 nm. Table I gives the lifetime and residual errors for the film at some of these wavelengths. These data indicate that fits to single-exponential decay functions at 278 nm and in the wavelength range 335–380 nm are quite good. Residual errors in the wavelength range 285–335 nm are systematically higher. Figure 4 shows fluorescence decay plots obtained on the film. Table I gives the best fit lifetimes calculated on these data. Figure 5 shows the time evolution of fluorescence monitored at 365 nm with the polarization parallel and perpendicular to the plane of polarization of the incident laser beam. These decays are identical within our in-

Table I
Lifetime Measurements on Polystyrene

	solution		film[c]			
			unpolarized		polarized	
					polarizer and analyzer parallel	polarizer and analyzer perpendicular
			unstretched	300% stretched		
λ, nm	τ[a]	residual error[b]	τ	τ	τ	τ
278	1.1	0.035				
285	1.3	0.071				
300		*d*	22.6			
335			22.0	21.1	20.6	21.4
365	12.7	0.031	21.0	22.6	22.2	22.2
380	12.9	0.059				

[a] τ ±1 ns. [b] Average fractional deviation. [c] Residual errors for data on films range from 0.056 to 0.033. [d] Decays were clearly biexponential; monoexponential fits produced residueal errors greater than 0.1.

Table II
Polarization Data Obtained in the 0-2-ns Time Gate[a]

λ, nm	$[I_H/I_V]_{\text{instr}}$	$[I_H/I_V]_{\text{PS}}$	p
335	2.04	2.03	−0.003 (±0.05)
365	2.04	1.9	−0.04 (±0.05)

[a] Apparent values of p as high as 0.12 (±0.05) were obtained on certain films after they were exposed to a large number (>500) of laser pulses.

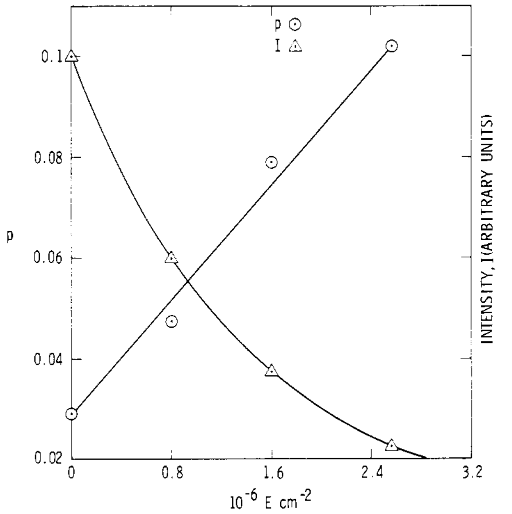

Figure 2. Change in polarization p and excimer intensity I with photodegradation in polystyrene film (λ_{ex} = 260 nm, λ_{em} = 330 nm).

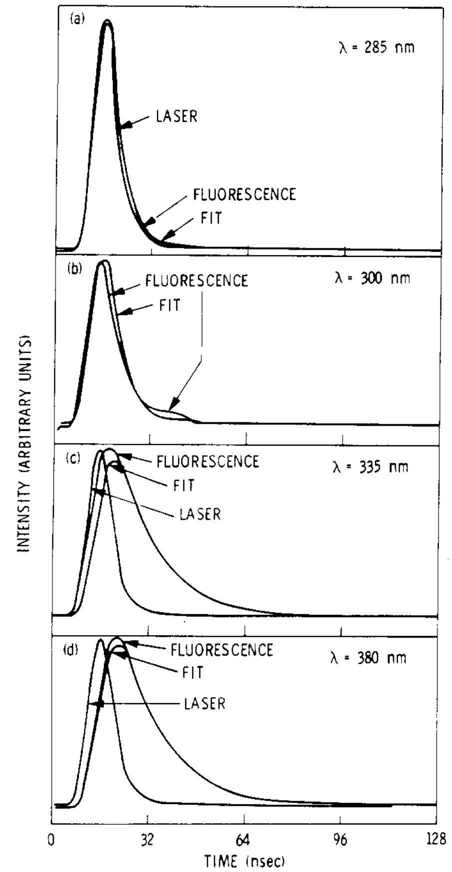

Figure 3. Fluorescence intensity decay curves for polystyrene in CH_2Cl_2 solution at different wavelengths of emission (λ_{ex} = 266 nm).

strumental error; identical results were obtained at 335 nm. Table II gives the polarization ratios I_H/I_V obtained by recording the peak fluorescence amplitudes. Actual polarization ratios $[I_H/I_V]_{\text{act}}$ were calculated by ratioing $[I_H/I_V]_{\text{obsd}}$ to instrumental bias, $[I_H/I_V]_{\text{instr}}$. Polarization is then estimated as $([I_H/I_V]_{\text{act}} - 1)([I_H/I_V]_{\text{act}} + 1)$. Table II shows that the prompt fluorescence recorded at the peak (2-ns channel width) is essentially depolarized at 335 and 365 nm. These data, when considered along with steady-state polarization data and the observation that the fluorescence decay rate constants are the same when recorded at two mutually perpendicular positions of the polarization analyzer, imply that the polarization of the fluorescence contains little contribution from fluorescence at time delays more than 128 ns. In other words, fluorescence from PS films is essentially depolarized, whether it is collected over the first 2-ns interval of decay after the emission intensity reaches a maximum, collected over the total decay period (~110 ns), or monitored under steady-state conditions.

Discussion

Since fluorescence from polystyrene (film) is mainly from the excimer, it may be expected that the mechanism and kinetics of formation and decay of excimers can be probed by fluorescence analysis. Emission profiles monitored at 335–380 nm for PS in fluid solution or in the solid phase may be fitted to a single-exponential decay expression. This observation indicates that a single excimer-like emissive species is formed in PS, in contrast to results reported previously on poly(1-vinylnaphthalene) (P1VN).[7] In P1VN, three distinct emission profiles with characteristic emission wavelengths and lifetimes were identified and assigned to two different excimer geometries in addition to the monomer. In PS, single-exponential fits

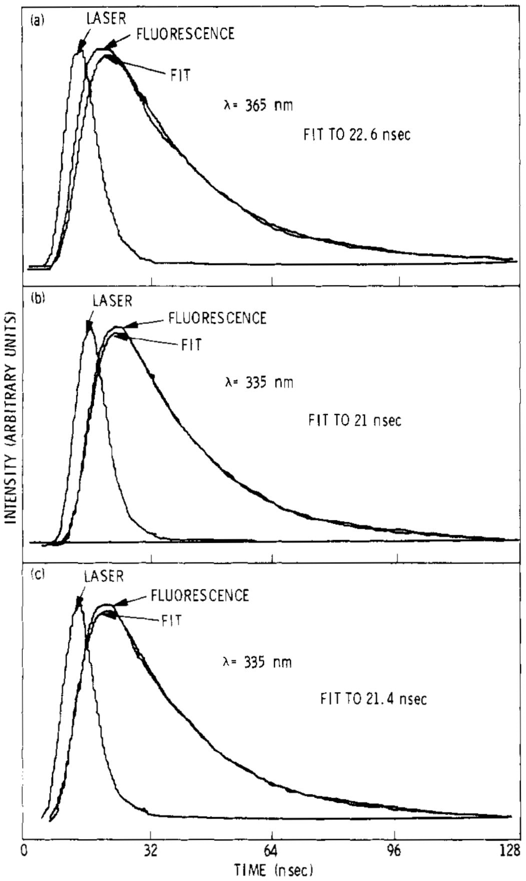

Figure 4. Fluorescence intensity decay curves for (a) polystyrene film (λ_{em} = 365 nm, λ_{ex} = 266 nm), (b) 300% stretched polystyrene film (λ_{em} = 335 nm, λ_{ex} = 266 nm), and (c) polystyrene film when polarizer and analyzer are perpendicular to each other (λ_{em} = 335 nm, λ_{ex} = 266 nm).

to fluorescence decay curves (Table I) show that only two emissive species are present, emissions from which overlap in the region 280–335 nm in fluid solution (CH_2Cl_2). Lifetime measurements in the wavelength region 300–335 nm are not well described by a single-exponential decay, as indicated by larger residual errors. This is probably due to overlap of monomer and excimer emission. Satisfactory fit to a single-exponential decay function could be obtained at 278 nm in this solvent with a lifetime of 1.1 ± 0.3 ns.[23] Fewer wavelengths were probed on the film, with similar results. The monomer emission is much weaker in the solid state and probably does not persist at λ >300 nm, because good fits to monoexponential decay curves are obtained at wavelengths greater than 300 nm on films, while biexponential decay behavior persists in fluid solutions up to 335 nm. The excimer lifetime in fluid solution is measured to be 12.5 ± 1 ns and in the solid state to be 22 ± 2.5 ns. These results imply that dissociation of excimers is not an important contributor to the 278-nm emission nor to the rate of depletion of excimers. Profiles of emission intensities recorded at 335, 365, and 380 nm also show that the emission is prompt (Figures 3–5); in other words, formation of excimers in PS is fast relative to the time resolution of our apparatus (1–2 ns) in fluid solution as well as in the solid state. Of the two possible mechanisms of excimer formation, rotation of a pendant phenyl group neighboring the excited chromophore and energy migration to a "preformed" excimeric trap, the second mechanism is clearly preferred on the basis of results from the polarization measurements. Steady-state polarization measurements show that the excimer emission monitored at 330 nm is highly depolarized. Prompt emission at the same wavelength collected at the peak of the decay curve over a 2-ns period is also found to be almost completely depolarized. Emission decay profiles measured on the film with no polarizer and with the polarizer placed parallel and perpendicular to the plane of polarization of the excimer laser beam (Figure 5) have identical lifetimes, within error. This result is consistent with the fact that there is no delay in excimer emission; in other words, excimer formation is complete within 1–2 ns, and once formed, excimers do not dissociate to form monomers, implying that migration of excitation energy to excimeric traps is complete within 1–2 ns. The proposed migration of excitation energy is also accompanied by an essentially complete loss of polarization; hence it probably involves a multiple-step hopping process. A simple kinetic scheme may therefore adequately represent all the experimental results on polystyrene reported here in the solid state as well as in dilute fluid solution, which is as follows:

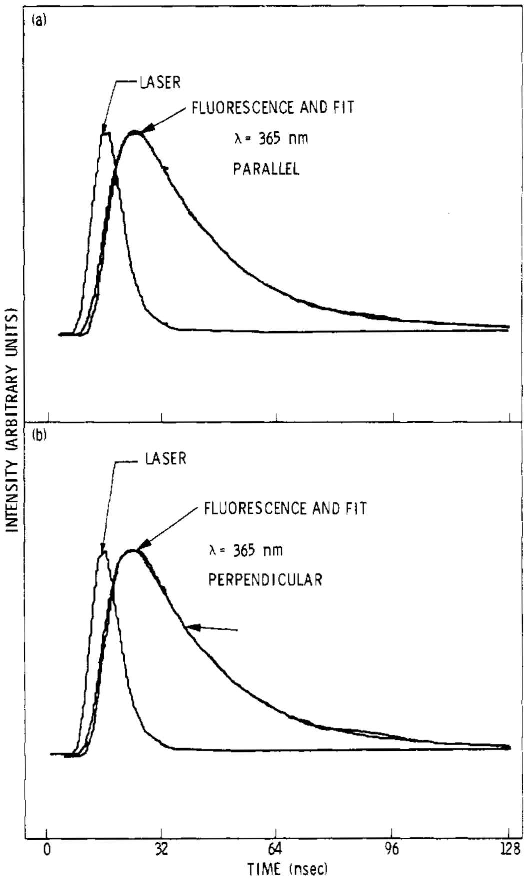

Figure 5. Fluorescence intensity decay curves for (a) polystyrene film when polarizer and analyzer are parallel (λ_{em} = 365 nm, λ_{ex} = 266 nm) and (b) polystyrene film when polarizer and analyzer are perpendicular to each other (λ_{em} = 365 nm, λ_{ex} = 266 nm).

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}^{1*} \qquad \text{random excitation}$$

$$\mathrm{S}^{1} \rightarrow\rightarrow \mathrm{S}^{1*}(\text{trap}) \qquad \text{depolarization}$$

$$\mathrm{S}^{1*}(\text{trap}) \rightarrow \mathrm{S} + h\nu_0 \qquad 280\ \text{nm}$$

$$\mathrm{S}^{1*} \rightarrow\rightarrow \mathrm{E}^{1*}(\text{trap}) \qquad \text{complete depolarization}$$

$$\mathrm{E}^{1*} \rightarrow \mathrm{S} + \mathrm{S} + h\nu_1 \qquad 320\text{–}380\ \text{nm}$$

Polarization data on photodegraded films are given in Figure 2. These data show that as photodegradation proceeds, the emission intensity drops, while the unquenched remaining emission becomes more and more polarized. The photooxidation products that quenched the excited singlet state would be expected to more effectively quench excitation which migrates over several sites. It is therefore important to always use fresh film for these measurements. The quenching data reported previously[13] and the polarization ratios given in Table II may be used to calculate the number of "hops" required for a quenching encounter at a given probability, as well as the dependence of residual polarization of fluorescence on the number of hops taken by the migrating excitation prior to trapping.

The excimer formed in stretched films is found to have the same lifetime as that in annealed films, although the excimer fluorescence maximum is found to be considerably red shifted.[13] This is an unexpected result and our inclination is to postulate that the same excimer is formed (in other words, the distance between the chromophores is the same) in both cases, while the monomer emission is attenuated in stretched films relative to annealed films.[13] Analysis of the residual error of lifetime fits in fluid solution (Table I) shows that monomer emission may persist up to 335 nm in fluid solution. Fluorescence is found to be depolarized independent of the orientation of the exciting beam relative to the stretching direction. Formation of excimeric configurations or their population by the migrating excitation thus appears to be unaffected by orientation. Excimers may therefore be used as in situ probes for mechanical deformaton and fracture in quenched as well as annealed polymers.

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Initial Concentration Dependence of the Oscillatory Flow Birefringence Properties of Polystyrene and Poly(α-methylstyrene) Solutions

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ABSTRACT: The concentration dependence of the oscillatory flow birefringence (OFB) properties of narrow-distribution linear polystyrene ($\bar{M}_w = 390\,000$) or poly(α-methylstyrene) ($\bar{M}_w = 400\,000$ and $5\,000\,000$) Aroclor solutions has been obtained for concentrations in the range $c[\eta] \lesssim 3$. These data are compared with the predictions of the Muthukumar and Freed treatment of the concentration dependence of bead–spring model relaxation times, the Wang–Zimm theory, and the infinite dilution bead–spring model (hydrodynamic interaction varied to duplicate the apparent transition from nearly non-free-draining to free-draining behavior with increasing concentration). The data obtained show that the relaxation time spectrum is affected markedly by concentration. The longest relaxation time is affected most and appears to exhibit a nearly exponential dependence on concentration for the solutions examined; the shortest relaxation times are almost unaffected. The Muthukumar and Freed predictions provide the best OFB frequency dependence curve shapes and absolute positions on the frequency axis and predict the observed frequency dependence for a surprisingly large range in concentration. At the highest concentrations the OFB properties show behavior indicative of enhanced separation of the longest relaxation times due to the onset of significant entanglement effects.

Introduction

There have been several studies of the frequency dependence of the oscillatory flow birefringence (OFB) and linear viscoelastic (VE) properties of linear, monodisperse polymers in solutions sufficiently dilute to permit extrapolation to infinite dilution.[1-9] Bead–spring model[10-12] predictions (isolated-molecule theories) have been shown to be in very good agreement with the infinite dilution properties at low frequencies when exact eigenvalues are employed. The infinite dilution results exhibit behavior

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