behavior where the Budiansky equation fit the experimental results well.[7] Another noteworthy factor in Figure 1 is that the volume resistivity data of the high percentage polyurethane IPN's (75 and 85% polyurethane concentration) fit well with the model. The modulus behavior of these IPN's did not follow this model and it was explained as being due to reduced crystallinity in the polyurethane phase, due to interpenetration. This supports this explanation since the effect of crystallinity is much smaller here than in the mechanical modulus (as evidenced by comparing UC 100 and UC75MC25 with the linear counterpart UL100, UL75ML25 in Figure 1).

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Fluorescence Studies of the Microviscosity of Polymer Solutions. 1. Microviscosity of Polymerizing Media

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ABSTRACT: Changes in microviscosity during polymerization of vinyltoluene have been studied using fluorescence polarization and intensity measurements. A variety of fluorescence probes were employed. "The" microviscosity of the polymerizing medium experienced by a fluorescent probe is dependent upon the size of the kinetic unit responsible for the variation in observed emission characteristic. No stepwise increments in microviscosity upon conversion to polymer were recorded in any of the systems studied.

The sensitivity of the photophysics of a molecule to changes in its microenvironment has prompted the use of fluorescence techniques in the investigation of such phenomena as energy migration, segmental relaxation, and microviscosity effects in polymers in bulk or solution. The attraction of the use of fluorescent probes in macromolecular systems derives from the fact that minimal perturbation of the sample is necessary due to the low concentrations of fluor involved and the absence of any externally applied constraints on the system. The study of microviscosities of polymer solutions by fluorescence methods can involve either (a) the use of the polarization characteristics of the emitted radiation or (b) the observation of changes in fluorescence intensity of suitable molecules, as discussed below.

(a) The degree of polarization, p, of fluorescence emitted by a molecule following excitation with polarized radiation reflects the extent to which the transition axes of the photoselected species can randomize by rotation during the time interval between absorption and emission of radiation. For spherical molecules, Perrin[1] has shown that

$$\left(\frac{1}{p}-\frac{1}{3}\right)=\left(\frac{1}{p_0}-\frac{1}{3}\right)\left(1+\frac{3\tau}{\rho}\right) \tag{1}$$

where p_0 is the intrinsic polarization (i.e., that observed in the absence of all external depolarizing factors), τ is the lifetime of the excited state, and ρ is the rotational relaxation time. If ρ may be approximated by

$$\rho = 3\eta V/RT \tag{2}$$

where η is the viscosity experienced by the molecule and V is the molar volume, the Perrin equation becomes

$$\left(\frac{1}{p}-\frac{1}{3}\right)=\left(\frac{1}{p_0}-\frac{1}{3}\right)\left(1+\frac{RT\tau}{\eta V}\right) \tag{3}$$

Hence the degree of polarization can be used to monitor changes in the microviscosity of the medium in which the probe is dispersed.

(b) The use of fluorescence intensity measurements in the study of phenomena involving microviscosity effects involves the dependence of quenching mechanisms upon the viscosity of the medium. In general external quenchers may be employed. However, certain molecules, notably flexible molecules capable of internal rotation, exhibit radiationless deactivation processes which are viscosity dependent.[2,3] A Stern–Volmer type treatment of internal quenching due to torsional deactivation leads to a relationship of the form[2,4]

$$\phi_f^0/\phi_f = 1 + A(\tau^0/\rho_i) \tag{4}$$

where ϕ_f and ϕ_f^0 are the fluorescence quantum yields in the presence and absence of internal quenching, respectively, A is a constant, τ^0 is the fluorescence lifetime in the absence of internal rotation, and ρ_i is the relaxation time characteristic of the rotation. If ρ_i is approximated by a Stokes–Einstein relationship as in eq 2, the fluorescence intensity, I_f, may be related to that at infinite viscosity, I_f^0, by eq 5[2,4]

$$\frac{1}{I_f} = \frac{1}{I_f^0} + B\left(\frac{T}{\eta}\right) \quad (5)$$

Molecules for which the above relationship is valid may be used in microviscosity investigations.

The purpose of the current work is the study of microviscosity changes in concentrated polymer solutions. In particular we report the results of studies on polymerizing vinyltoluene systems incorporating a variety of fluorescent probes. Microviscosities have been determined from polarization and internal quenching data allowing variation of the molecular dimensions of the kinetic rotor which samples the microenvironment.

Fluorescence depolarization has been used by several authors in the study of microviscosity effects in polymer solutions. Nishijima et al. examined solutions of polystyrene in benzene[5] and polyacrylamide in water.[6] Stepwise increases in local viscosity in the ranges of 20 to 30% and 60 to 70% concentration, ascribed to the development of "internal structure", have been reported for solutions of polystyrene in benzene.[5] Molar mass effects have been examined in solutions of polystyrene in di-*n*-butyl phthalate.[7] Other studies include those on poly(γ-benzyl L-glutamate) in dioxane and dimethylformamide[8] and in hydroxyethyl cellulose in aqueous solution.[9] Fluorescence polarization measurements have also been used to measure local viscosities in polyethylene melts.[10]

Fluorescent molecules capable of internal rotation, notably auramine O, have been used mainly in the study of transitions in bulk polymer systems.[11]

Studies of phenomena affected by microenvironmental variations in polymerizing media have included reports of energy transfer[12] and radioluminescence[13,14] changes with polymer content and an NMR line-width investigation of molecular motion in polystyrene–styrene solutions.[15] An early paper by Kryszewski and Grosmanova[16] suggested the use of fluorescence polarization to study polymerization kinetics.

Experimental Section

Materials. 2,5-Diphenyloxazole (PPO), bis-1,4-[2-(5-phenyloxazolyl)]benzene (POPOP), and 1,1',4,4'-tetraphenylbutadiene (TPB) (Nuclear Enterprises, Scintillation Grade) were used without further purification. 9-Methylanthracene (MAN) (Aldrich) was purified by multiple recrystallization from 40–60 °C petroleum ether.

Vinyltoluene monomer (Dow Chemical Company) was purified by washing with 5% sodium hydroxide solution followed by prepolymerization and fractional, high-vacuum distillation. Toluene (BDH scintillation grade) and paraffin (BDH) were used without further purification.

Techniques. Fluorescence intensities and polarizations were determined using a Perkin-Elmer 203 spectrofluorimeter equipped with Polaroid HNP'B polarizers. Correction of fluorescence polarization data to account for parallel diffraction anomalies[17] of the instrument and verification of the accuracy of the data have been described.[18]

Polymerizations were performed at 60 °C on degassed solutions of fluor (10^{-5} M) in monomer sealed under high vacuum in fluorescence microcells as previously described.[12] Fluorescence data were measured at 20 °C following careful annealing from the polymerization temperature. Degrees of conversion of monomer to polymer were determined by weighing following purification of the poly(vinyltoluene) by multiple reprecipitation.

Results and Discussion

The local viscosity experienced by a fluorescent probe will be characteristic of the macroviscosity of the medium when the probe is dispersed in a "molecularly homogeneous" solvent. In systems such as polymer solutions where the solvent is markedly heterogeneous at the molecular level the microviscosity sensed by the probe will be very different from the macroviscosity. Calibration plots relating fluorescence polarization or intensity data to the viscosity of the medium may be constructed with solvent mixtures, the components of which are of reasonably comparable molecular dimensions.

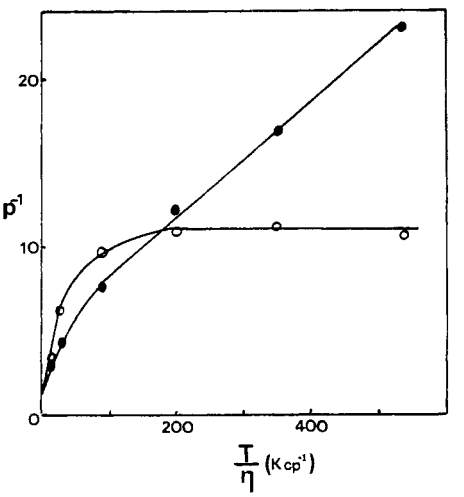

Figure 1. Polarization data for POPOP (●) and TPB (○) solutions.

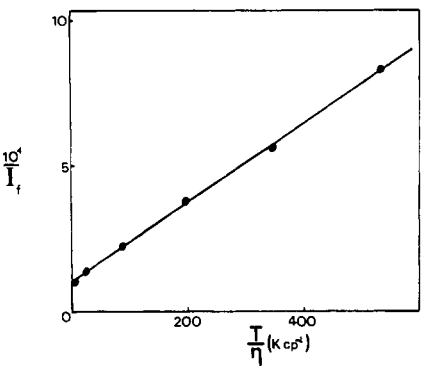

Figure 2. Viscosity dependence of TPB emission intensity.

Figure 1 shows the reciprocal degree of polarization of POPOP and TPB as a function of T/η for a series of toluene/paraffin mixtures at 20 °C. Both Perrin plots are nonlinear. The curvature of the POPOP plot is a consequence of the nonspherical nature of the molecule. Elliptical molecules are not characterized by a single rotational relaxation time and yield Perrin plots which are concave to the T/η axis.[19]

The Perrin plot of TPB is markedly nonlinear. The curvature of the plot results both from the elliptical shape of the molecule and the influence of the internal rotational quenching process upon the lifetime of the excited state. The fluorescence lifetime of TPB will decrease with decreasing viscosity of the medium. Inspection of eq 3 shows that this has the effect of increasing the observed value of p^{-1}. The polarization data must be corrected for the influence of lifetime variations. The appropriate modified Perrin plot is one of p^{-1} against $(T/\eta)(\tau/\tau^0)$. It is not necessary to determine the fluorescence lifetimes at each viscosity provided emission intensity data are available, as $\tau/\tau^0 = I_f/I_f^0$. The ability of eq 5 to describe the influence of solvent viscosity upon TPB fluorescence intensity is illustrated in Figure 2. Figure 3 shows the Perrin plot modified to account for variations in the lifetime of the excited state. The residual curvature of the plot may be ascribed to the nonspherical nature of the molecule.

The changes in p^{-1} with increasing degree of conversion during polymerization of vinyltoluene at 60 °C are shown in Figure 4. The fluorescent probes employed were PPO, POPOP, MAN, and TPB. Specific microviscosity data, obtained from the polarization calibration plots (Figure 1), are also shown for systems incorporating POPOP and TPB as

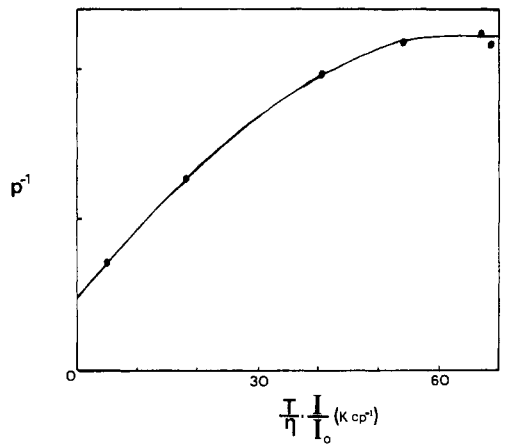

Figure 3. Polarization data for TPB corrected for the influence of viscosity upon the excited state lifetime.

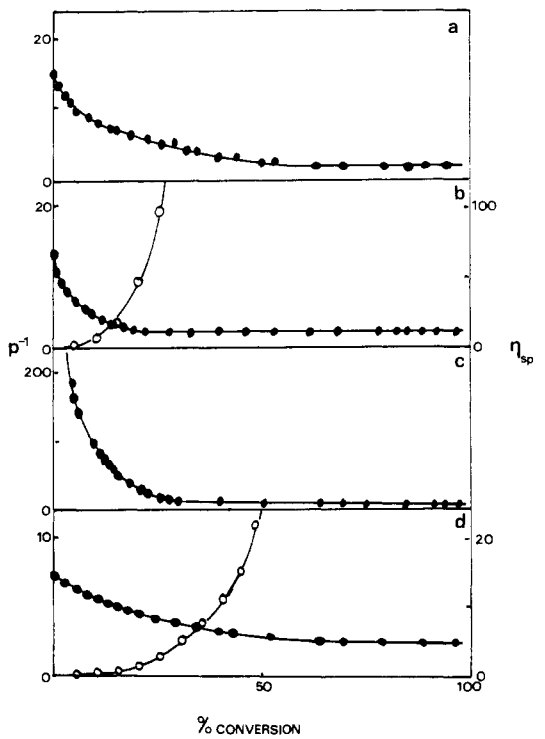

Figure 4. Polarization (●) and specific microviscosity (○) data as a function of percent conversion to polymer. Fluorescent probes are (a) PPO, (b) POPOP, (c) MAN, and (d) TPB.

probes. In all of the cases studied, the values of p^{-1} decrease monotonously to a limiting value at high viscosity. No stepwise increases in local viscosity are evident. This would appear to contradict earlier reports of microviscosity trends in concentrated polystyrene/benzene systems.[5,20] The smooth polarization data of the present work would not indicate drastic changes in excited state lifetime of the fluorescent solute. Grodel and Polacki[14] have observed marked changes in the scintillation lifetime during polystyrene polymerization. However, the latter data would contain contributions from energy migration and transfer processes and are not only a measure of solute fluorescence decay. The limiting values of the degree of polarization are listed in Table I and compared with those obtained by extrapolation of the Perrin plots for POPOP and TPB (Figures 1 and 3, respectively). The agreement obtained is good evidence for the noninterference of strain effects or variation of refractive index upon polymerization in the determination of polarization data from the

Table I
Limiting Polarization Data of Fluorescent Probes

Solute	Limiting polarization in rigid matrix (±0.005)	p_0^{-1} (Perrin plot) (±0.02)
POPOP	0.400	0.42
TPB	0.417	0.40
PPO	0.500	
MAN	0.222	

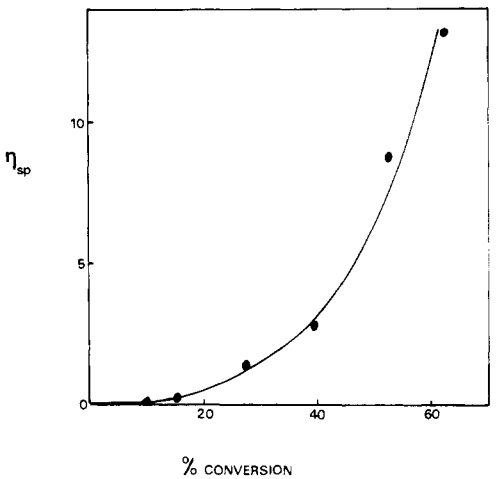

Figure 5. Specific microviscosity (as estimed from TPB intensity data) as a function of percent conversion to polymer.

polymerizing samples. Thus, the limiting polarization values are estimates of p_0. PPO shows a p_0 of 0.5, the theoretical maximum value for a fluor whose transition vectors of absorption and emission are parallel.

While we have previously shown that none of the fluorescent probes employed in this study affect the rate of vinyltoluene polymerization, MAN and TPB are involved in the kinetic scheme as chain-transfer agents.[21] Thus the total polarization characteristics of the emission from the latter probes will contain an increasing contribution from species which are bound to polymer chains. As the fraction of fluors which are bound to macromolecules is small the contribution to the overall emission characteristic may be ignored. Furthermore, it has been shown that chain attachment of TPB does not affect the observed polarization in dilute fluid solutions[21] (although this would not be the case in concentrated polymer solutions). Somewhat surprisingly, the limiting polarization of MAN agrees well with that obtained for MAN/polystyrene conjugates using fluorescence quenching techniques.

The limiting polarization is attained when the micro-Brownian rotational relaxation time of the fluor greatly exceeds the fluorescence lifetime. Hence the degrees of conversion at which p_0^{-1} is attained for the various probes should reflect the relative sizes of the molecules and associated solvent sheaths. Thus the minimum p^{-1} value for POPOP is reached at much lower polymer concentration than when PPO is employed as probe. Furthermore, it is evident that vinyltoluene solvated TPB is of the same order of molar volume as solvated PPO. [The polarization data rank the fluors according to V/τ. However, as the excited state decay rates of the molecules concerned are comparable (at least in cyclohexane as solvent[22]) the data may be used to discriminate qualitatively in terms of molar volumes.]

Figure 5 shows the increase in specific microviscosity with percent conversion as sensed by the internal rotors of the TPB molecule and estimated from the intensity calibration graph (Figure 2). Comparison of the microviscosity data presented

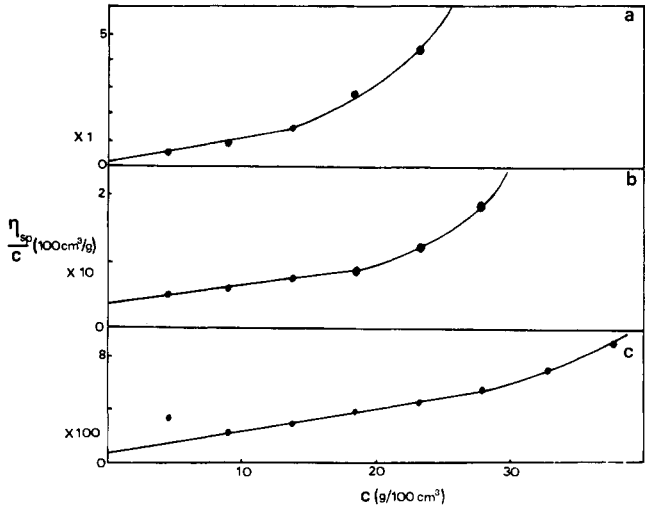

Figure 6. Plot of (a) η_{sp}/c vs. c from POPOP polarization data; (b) 10 η_{sp}/c vs. c from TPB polarization data; and (c) 100 η_{sp}/c vs. c from TPB intensity data.

in Figure 5 with those from polarization measurements of Figure 4 confirms the fact that the use of molecular probes will not furnish microviscosity values uniquely. Obviously the microviscosity experienced by a molecule is dependent upon the volume, lifetime, and nature of the species employed. The local viscosity experienced by the fluor is a measure of the extent to which the polymer coils encroach upon the volume occupied by the luminescent moiety. The greater the concentration of polymer the more dramatic will be its effect upon the observed local viscosity. Such a trend is apparent from the polarization-based data of Figure 4 for POPOP and TPB where the influence of the microenvironment upon whole molecule motion is relevant. As mentioned previously the concentration of polymer required to impede significantly rotational tumbling is lower for the case of POPOP than TPB. The microviscosity data of Figure 5 estimated from fluorescence intensity data involve short-range motions of much smaller kinetic units such as phenyl substituents. As is to be expected, significant increases in local viscosity occur at much higher polymer concentrations than for those corresponding to polarization data. It is of interest that no stepwise increases in local viscosity are apparent despite the large concentration range over which finite viscosities are recorded.

Polymer solution macroviscosity data are described by the Huggins equation and yield linear plots of specific viscosity per unit polymer concentration as a function of polymer concentration for dilute macromolecular solutions. Presentation of the microviscosity data of Figures 4 and 5 in this form (Figure 6) reveals that η_{sp}/c vs. c plots of microviscosities remain linear over surprisingly large ranges of concentration. Such observations have been recorded previously for fluorescence polarization data pertaining to poly(benzyl glutamate)/dioxane or dimethylformamide[8] solutions and polystyrene/di-*n*-butyl phthalate[7] solutions. 9,10-Diphenylanthracene was used as probe in both of these studies. (Values of polymer concentration in Figure 6 are expressed in g cm^{-3} and are corrected for contraction of the medium upon polymerization.) As expected the trend of polymer concentrations at which nonlinearity occurs follows the trend in molar volumes of the appropriate kinetic units. The decreasing influence in effect of the polymer chains upon the rotational freedom of the probe species is evident from the decreasing intercept of the plots the smaller the rotor. Further, deviations from linearity become apparent at low concentrations (in addition to those at high concentration) in a manner dependent upon probe size.[23]

Conclusions

The microviscosity sensed by a fluorescent probe in a macromolecular solution is a function of the molecular dimension of the kinetic moiety. No stepwise increases in local viscosity over the total polymer concentration range have been encountered for any of the molecular probes. This result, at variance with reported behavior in polystyrene/benzene solutions,[5,20] may be due to the greater homogeneity obtained in the polymerizing medium compared with systems involving mixing of concentrated polymer with solvent/fluor blends. Inhomogeneity in the latter case might lead to an effective partitioning of fluor in the solvent with regions of the mixture.

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