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Order Parameter in Polymer Liquid Crystals. 1. Poly(*p*-benzamide) in *N*,*N*-Dimethylacetamide/Lithium Chloride[†]

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ABSTRACT: The order parameter, *s*, for nematic solutions of poly(*p*-benzamide) in *N*,*N*-dimethylacetamide + 3% LiCl was determined in the composition range extending from the lower limit for stability of the pure mesophase to the solubility limit of the polymer. *s* was obtained from the dichroic ratio by polarized IR spectroscopy at 860 cm^{-1}. The band is attributed to a CH out-of-plane bending vibration of the aromatic nucleus with a transition moment perpendicular to the ring and forming an 85° angle with the chain axis. Problems in obtaining lyotropic monoliquid crystals with homogeneous alignment may be severe. Macroscopically aligned samples were obtained by surface treatment of KBr cells and by a magnetic field. *s* increased from 0.76 to 0.83 with increasing polymer concentration. These values are smaller than, yet in not too serious disagreement with, predictions of the lattice theory, suggesting a change from 0.93 to 0.97 in the same composition range.

For rigid or semirigid macromolecules a spontaneous transformation from an isotropic to a nematic solution occurs when the polymer volume fraction v_2 is isothermally increased above a critical value v_2'. At fixed composition, the transition occurs at the isotropic → nematic transition temperature (T_{NI}). In recent years, several theoretical investigations have dealt with the phase behavior of rigid mesogenic polymers.[1–6] The dependence of the v_2' value upon persistence length, temperature, and molecular weight distribution was experimentally characterized.[6–10]

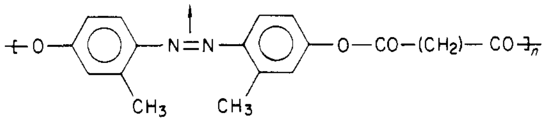
The various theoretical treatments mentioned above make specific predictions concerning the order parameter, *s*, usually defined as[11]

$$s = \tfrac{1}{2}(3\langle\cos^2\theta\rangle - 1) \qquad (1)$$

where θ is the angle between the molecular axis and the director, a vector representing the average molecular orientation at any point of the liquid. For instance, *s* calculated from Flory's disorientation parameter[1] *y* (cf. seq.) attains large values at v_2' and further increases with increasing concentration. At $v_2 = 1$, *s* is predicted to be = 0.95 at T°_{NI} for rigid rods with an axial ratio as small as $x = 6.4$.[3] The latter is the smallest axial ratio at which the mesophase is stable due to molecular asymmetry alone.[1] Partial stabilization by orientation-dependent attractions causes *s* to decrease with axial ratio.[3] For typical low molecular weight nematogens, $s = 0.2$ at T°_{NI}.

The order parameter is also affected by chain rigidity and by flow field. For instance, Ronca and Yoon[12] predicted values between 0.4 and 0.7, increasing with the persistence length. Khokhlov et al.[4] also arrived at similar conclusions and predicted smaller values of *s* for the wormlike chain than for the Kuhn chain. An elongational flow gradient is predicted[13–16] to increase *s*, the effect being more pronounced with less concentrated solutions and less rigid polymers. Doi[5] predicted an increase of *s* with the shear flow gradient using the molecular dynamics approach.

Measurements of order parameter have been performed, using different techniques, for semirigid polyesters. *s* is affected by chemical structure and decreases with temperature, varying between 0.3 and 0.75 at T°_{NI}.[17] For instance, Noël et al.,[18] from polarized FT IR spectroscopic studies, reported $s \sim 0.3$ for the copolyester $-(\mathrm{OC}\text{-}p\text{-}\mathrm{C_6H_4O})_{0.6}-[\mathrm{OOC}\text{-}p\text{-}\mathrm{C_6H_4OCH_2CH_2O}\text{-}p\text{-}\mathrm{C_6H_4COOCH_2CH_2}]_{0.4}-$. Blumenstein et al.[19] and Martins et al.[20] using NMR observed that *s* for the polyester



increases with increasing molecular weight from ~0.5 to a plateau value of ~0.7. For the same polymer mixed with a low molecular weight liquid crystal,[21] values of *s* vary from 0.75 to 0.4 when the amount of solvent in the mixture is increased. Moreover, an oscillation of *s* in the range 0.35–0.75 depending on the number *n* of flexible spacer segments was reported.[22] Iannelli et al.[23] using X-ray diffraction methods, found a similar odd–even effect, with *s* ranging from 0.5 to 0.6 for the polyesters $-[(\mathrm{OOC(CH_2)}_{n-2}\mathrm{COOR})_{0.5}-(\mathrm{OOC(CH_2)}_{n'-2}\text{-}\mathrm{COOR})_{0.5}]_x-$ with R = $-p\text{-}\mathrm{C_6H_4C(CH_3){=}CH}\text{-}p\text{-}\mathrm{C_6H_4}-$, *n* ranging from 7 to 10, and *n′* ranging from 10 to 13. From magnetic susceptibility study of the polyester $-[(\mathrm{CH_2})_{10}\mathrm{O}\text{-}p\text{-}\mathrm{C_6H_4COO}\text{-}p\text{-}\mathrm{C_6H_4O}\text{-}(\mathrm{CH_2})_{10}\mathrm{O}\text{-}p\text{-}\mathrm{C_6H_4OOC}\text{-}p\text{-}\mathrm{C_6H_4O}]_x-$ Sigaud et al.[24] observed $s = 0.6$. For the same polymer Yoon et al.[25] reported a higher value of the order parameter ($s = 0.75$) measured from NMR spectra.

Quantitative studies of the order parameter for rodlike molecules in solution have been reported for poly(γ-benzyl L-glutamate) (PBLG) but not for the rigid aromatic polyamides. For nematic PBLG,[26,27] *s* determined from X-ray diffraction and susceptibility measurements was found to decrease from ~0.8 to ~0.6 with increasing dilution. In fact, the determination of *s* for lyotropic systems is of particular interest since the comparison with theoretical prediction can be performed over a large composition range involving a single anisotropic phase having $v_2 \geqslant v_2''$. v_2'' is the composition of the conjugated anisotropic phase which appears[1] at the slightly lower critical volume fraction v_2'. In fact, one of the problems attending the determination of *s* for the thermotropic polyesters is the occurrence of a biphasic region close to T°_{NI}. On the other hand, several of the techniques used for the thermotropic systems lose sensitivity when a diluent is present. Infrared dichroism,[28] which may be applied to lyotropic systems provided the solvent bands do not mask the region of interest, was selected for the present investigation of the order parameter of poly(*p*-benzamide) solutions. The use of this particular technique requires samples with a macroscopic orientation of the director. As expected, this

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proved to be the most crucial problem of this investigation. Some polymers have been found to preferably orient homeotropically (e.g., PBLG), and others homogeneously (e.g., thermotropic polyesters). Preliminary data with poly(*p*-benzamide) indicated an easiness of planar orientation. Several of the techniques used for homogeneously aligning low molecular weight liquid crystals tend to give poor results in the case of polymers. Nevertheless, some satisfactory results, which however apply mostly to thermotropic systems, have been reported. Noël et al.[18] used the orientating effect of freshly cleaved mica surfaces or directed oblique SiO_2 evaporation.[29] Casagrade et al.[30] and Sum Zheng-Min and Kleman[31] used rubbing with a diamond paste. For lyotropic nematic PBLG, Taratuta et al.[32] coated the glass surface with a plasma-polymerized polyethylene film. However, they did not report a conoscopic image. In most of these cases the orientation was enhanced by an *H* field. Here we tried several of the above techniques (but not the elaborate one of Taratuta et al.) and found satisfactory results with treated KBr cells and a magnetic field.

Aside from the fundamental relevance of the order parameter to the detailed description of the mesophase, the dependence of *s* upon chemical structure and external fields points out its relevance to the processing behavior of polymer liquid crystals.[33]

Experimental Section

Materials and Solutions. Poly(p-benzamide) (PBA) was synthesized following the method of Yamazaki et al.[34] The polymer was purified by dissolution in *N,N*-dimethylacetamide (DMAc) containing 3% LiCl and reprecipitation with CH_3OH. The dissolution was repeated three times, performing the final precipitation with H_2O, washing until LiCl was eliminated. PBA was dried at 50 °C under vacuum for 24 h. Intrinsic viscosity, measured at 25 °C in 96% H_2SO_4,[9] was 1.44 dL/g, corresponding to a molecular weight $\bar{M}_v = 11\,000$, in terms of the relationship $[\eta] = 1.9 \times 10^{-7} \bar{M}_w^{1.7}$ reported by Schaefgen et al.[35] The solvent was analytical DMAc (Hoechst), dried over molecular sieves and containing 3% (w/v) dried LiCl. A saturated PBA solution was prepared by stirring the components for about 1 month at room temperature in a sealed container. The supernatant was separated by centrifugation and the soluble PBA determined by precipitation with H_2O on an aliquot of the solution. Polymer concentration C_p (w/w) was 12.5%, in line with previously reported results.[9] Three additional solutions having C_p = 11.4, 10.5, and 10.2% were prepared by dilution. The polymer volume fraction v_2 was calculated from C_p using a value of 0.754 mL/g for the partial specific volume ($\bar{v}_2$) of PBA and of 1.0356 mL/g for the specific volume of diluent. These values were determined pycnometrically.[9] Following preparation, each solution was centrifuged at 28 000 rpm for 48 h to eliminate dust or residual impurities and to ascertain that no isotropic phase was present. Traces of the latter were evident only for the most dilute solution (C_p = 10.2). The composition of the latter was therefore identified with v_2'', the minimum concentration of the pure anisotropic phase. Best results in the determination of *s* were obtained with freshly centrifuged solutions.

Infrared Spectroscopy. Infrared spectra were taken at room temperature with a Perkin-Elmer Model 983 spectrometer equipped with a wire grid polarizer which ensured 99.8% polarization. The dichroic ratio *R* was determined from the ratio of the absorption coefficients $\epsilon_\parallel$ and $\epsilon_\perp$, measured with the IR radiation polarized parallel to and perpendicular to, respectively, the optical axis of the sample using the band at 860 cm^{-1}. $\epsilon_\perp$ was considerably larger than $\epsilon_\parallel$, but both values could be determined with precision by using an appropriate cell thickness. It was verified that the Beer–Lambert law described the measured absorbance up to OD ~ 0.9. Cells consisted of two KBr windows with a 45-μm Teflon spacing held together by an aluminum frame (Al prevented distortion of the magnetic field). The Teflon spacing included a channel ~4 × 20 mm long to allow filling of the cell. The latter operation was performed by capillarity, placing a drop of solution at the opening of the channel. The filled cell was closed with a cyanoacrylic glue. Before the cell was assembled, the KBr windows were carefully polished according to the standard procedure used for IR measurements. Windows were also treated with a 0.25% solution of poly(vinylformal) in dichloroethane. The latter was allowed to flow along the direction of the filling channel. Such treatment, which has been used to improve the orienting effect of the surface for low molecular weight liquid crystals,[36] appeared to improve the alignment of the solution under the magnetic field. No evidence of a solubilization of KBr or poly(vinylformal) in our solution was detected. The dichroic ratio *R* was determined at various times following the filling of the cell. The corresponding evolution of the nematic texture was followed with a polarizing microscope using both normal and convergent light. In another set of experiments, cells were exposed to a magnetic field of ~10 kG for lengths of time between 30 min and 8 h (the long axis of the cell was parallel to the field). The cells were then quickly transferred to the IR spectrometer; the transfer operation took about 90 s and an additional 75 s was needed for the registration of the spectra. Duplicate measurements of *R* a few minutes after the cell was removed from the magnet gave concordant results, revealing a very slow relaxation of the alignment. The recovery of the texture at longer times was not investigated.

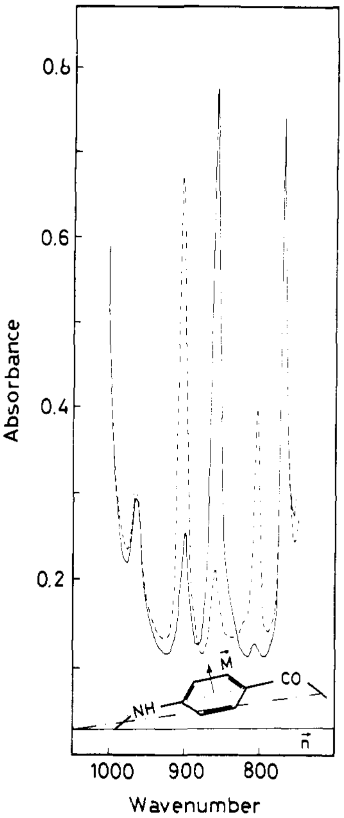

Figure 1. Polarized IR spectra of PBA in DMAc + 3% LiCl, C_p = 12.5%. The broken and the full lines indicate respectively the electric vector of radiation parallel to and perpendicular to the optic axis.

Results

The salient features of the polarized IR spectra of PBA solutions are illustrated in Figure 1. In the frequency region between 1000 and 750 cm^{-1} the absorption of the solvent is negligible and does not interfere with the polymer, as ascertained from the unreported spectra of the pure components. The three prominent bands in Figure 1 occur at 805, 860, and 902 cm^{-1}. We have used the band at 860 cm^{-1} for the evaluation of *R* and *s* (the other two bands have polarization opposite to that of the 860-cm^{-1} band).

Platonov et al.[37] attributed the 860-cm^{-1} band to a vibration perpendicular to the chain axis. A more detailed analysis was performed by Kross et al.[38] for several aromatic compounds, including *p*-aminobenzoic acid. They concluded that the frequency of one of the CH out-of-plane bending vibrations of the benzene ring (which falls in the range of 775 cm^{-1} for typical monosubstituted benzenes) is shifted to higher frequency for certain monosubstituted compounds such as benzoic acid and, particularly, for para-disubstituted benzenes. For *p*-aminobenzoic acid the frequency is shifted to 841 and 848 cm^{-1} respectively for the solid and for an acetone solution. The small difference between the latter figures reveals the intramolecular nature of the shift, which they attributed to a depletion of the π electronic charge of the aromatic nucleus caused by the electrophilic substituent. The transition moment of the above vibration is known to be perpendicular to the ring.[39] In Figure 1 we have schematized the attributed direction of the 860-cm^{-1} vibration. Being perpendicular to the axis of the ring, it forms an 85° angle with the chain axis.[40] The other bands in Figure 1 could not be unambiguously assigned. Had such an assignment been possible, the determination of the corresponding s would have allowed an alternative evaluation of α and the chain axis.

For a nematic uniaxial system the dichroic ratio is given by[28]

$$R = \frac{\cos^2\alpha\langle\cos^2\theta\rangle + \frac{1}{2}\sin^2\alpha\langle\sin^2\theta\rangle}{\frac{1}{2}\cos^2\alpha\langle\sin^2\theta\rangle + \frac{1}{4}\sin^2\alpha\langle 1 + \cos^2\theta\rangle} \qquad (2)$$

where θ is defined in eq 1 and α, the angle between the transition moment and the chain axis, is 85° in our case. The relationship between R and s then is given by[28]

$$s = \frac{2(1 - R)}{(R + 2)(1 - 3\cos^2\alpha)} \qquad (3)$$

The dichroic ratio should include the so-called "Lorentz inner field correction" arising from the anisotropy of the local field.[41] As done by most investigators,[18,42] this correction was neglected, due to lack of data for the refractive indices $n_\parallel$ and $n_\perp$ in the IR region of interest. For homogeneously aligned low molecular weight liquid crystals, the correction was found to strongly depend upon the theoretical treatment used to evaluate it. Some approaches gave a positive correction and others a negative one.[43]

Figure 2 illustrates values of s determined for the C_p = 10.2% solution under the following conditions: (1) R determined within 20 min after filling of the cell; (2) R determined within 24 h after filling of the cell; (3) R determined following alignment in an H field for 1 h. Typical micrographs under the polarizing microscope (Figure 2) reveal the texture prevailing under the three above conditions. The block diagram represents the distribution of the measured values of s respectively for 30, 30, and 10 independent determinations. It is seen that under condition 1 a very disordered texture corresponds to a large scatter and low values of s. Standing (condition 2) improves the alignment, and the distribution of s shows a shift to larger values. The magnetic field (condition 3) is particularly effective in eliminating disinclinations, and the scatter around large values of s is significantly decreased. Measurements of s in the H field as a function of time revealed that a maximum asymptotic limit of s was reached 1 h after the application of the field. In these cases it was possible to measure R in areas of the sample which were apparently free of defects when viewed under the polarizing microscope with normal illumination (last block in Figure 2). Moreover, four positions of extinction were clearly observed upon rotation of the stage. The size of extinguishing areas was certainly above 0.5 mm^2. However, using convergent light we did not detect the conoscopic image consisting of hyperboles centered at the axis of the beam reported for homogeneously aligned low molecular weight liquid crystals.[44] Our observations with *p*-methoxybenzylidene-*p*-*n*-butylaniline (MBBA) indicated, however, that the conoscopic image for planar alignment did not so easily develop as in the case of homeotropic samples. Thus, while the lack of disinclinations in relatively large areas and the asymptotic limit of s in the H field are indicative of very good alignment, the formation of a perfect, large monoliquid crystal may be questioned. The difficulty in completely eliminating the disinclinations for liquid crystalline polymers is in line with theoretical considerations put forward by Marrucci.[45]

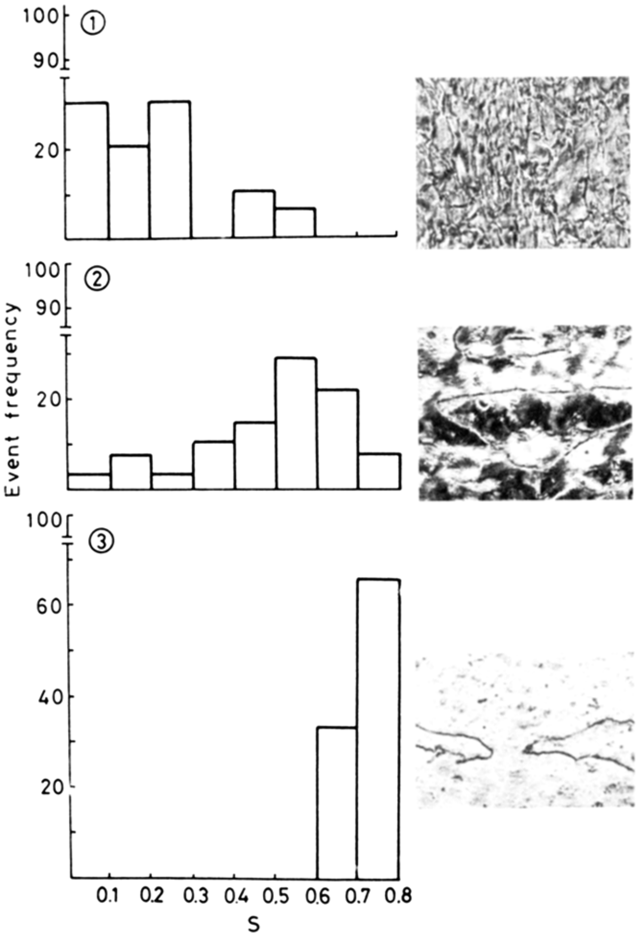

Figure 2. Event frequency of values of the order parameter measured within (1) 20 min and (2) 24 h from cell preparation and (3) after at least 1 h of alignment in a 10-kG H field. PBA/DMAc + 3% LiCl, C_p = 10.2%. Magnification of the micrographs ~62×.

Table I
Order Parameter for PBA/DMAC + 3% LiCl Solution Aligned in an *H* Field

sol	C_p, %	v_2	$R_{860\text{cm}^{-1}}$	$s_{\text{exptl}}{}^a$	$s_{\text{theor}}{}^b$
1	12.5	0.094	0.13	0.83	0.961
2	11.4	0.086	0.14	0.82	0.948
3	10.5	0.078	0.17	0.78	0.930
4	10.2	0.076	0.19	0.76	0.927

[a] Equation 3 with α = 85°. [b] Theoretical values calculated for x = 148.

The averages of the largest values observed in the H field (last block in Figure 2) as a function of polymer concentration are collected in Table I. In view of the difficulties in completely eliminating the disinclinations, the s values in Table I could be regarded as lower limits.

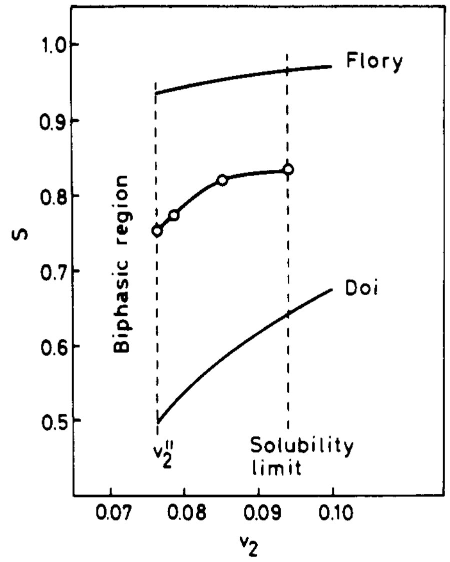

Figure 3. Experimental variation of the order parameter (open points) with polymer volume fraction compared with theoretical predictions by Doi (eq 4) and Flory (eq 5).

Comparison with Theory. We analyze Flory's theory, which, among virial and mean field theories previously considered, offers the best representation of various features of the lyotropic behavior, and Doi's theory, which we had not considered before. A variation of s with polymer concentration is predicted by the Doi and Flory theories. According to Doi[5]

$$s = \frac{1}{4} + \frac{3}{4}\left(1 - \frac{8v_2}{9v_2''}\right)^{1/2} \qquad (4)$$

for $v_2 > {}^8/_9\, v_2''$. This relationship is represented in Figure 3 in the composition range extending from the pure anisotropic phase (v_2'') to the solubility limit of PBA in DMAc + 3% LiCl. The increase of s with v_2 is in line with the experimental data reported (open points) in Figure 3. However, Doi's theory, essentially a virial theory, seriously underestimates the actual value of the order parameter.

Flory's theory is cast in terms of the disorientation parameter y, which is 1 for complete orientation and coincides with the axial ratio x for complete disorientation.[6] The recent Flory and Ronca theory[3] allows a correct approach to a relationship between s and y. Here s may be written as

$$s = 1 - {}^3/_2\langle\sin^2\theta\rangle \qquad (5)$$

$$\langle\sin^2\theta\rangle = f_3/f_1$$

where f_3 and f_1 may be determined by solving the system

$$f_3 = \int_0^{\pi/2} \sin^3\theta \exp(-\beta\sin\theta)\, d\theta$$

$$f_1 = \int_0^{\pi/2} \sin\theta \exp(-\beta\sin\theta)\, d\theta$$

$$\beta = -\left(\frac{4}{\pi}\right)x \ln\left[1 - v_2\left(1 - \frac{\bar{y}}{x}\right)\right]$$

$$\bar{y} = \left(\frac{4}{\pi}\right)x f_2/f_1$$

$$f_2 = \int_0^{\pi/2} \sin^2\theta \exp(-\beta\sin\theta)\, d\theta$$

The system was solved by an iterative calculation by assigning $x = 148$ as obtained by fitting the experimental v_2'' to the theoretical dependence of v_2'' upon x. The theoretical values v_2'' were evaluated according to the "exact treatment" described by Flory and Ronca.[3]

The values of the volume fraction v_2 used in the calculation were always larger than the critical value v_2'' for the stability of the anisotropic phase. The calculated values of s are included in Table I and reported in Figure 3. s is predicted to increase with concentration, but the theoretical values are very large, larger than experimentally observed. The difference between theory and experiment might be reduced if it were possible to completely eliminate all defects from the solution or if a smaller value of the angle α appearing in eq 3 were to apply. Virtual agreement between theory and experiment would be ensured by letting $\alpha = 76°$. However, we do not see any justification for such an assumption. Using a more simple equation, $s = 1 - (3/2)(y^2/x^2)$, derived operating some approximation on Flory's theory,[1] we obtained theoretical results very close to those reported in Table I and Figure 3.

Even though the local order exhibited by rigid nematogens in solution is smaller than theoretically predicted, it tends to be usually larger than that observed with the semirigid thermotropic polyesters mentioned in the introductory section. Moreover, a larger order occurs for lyotropic polyaramides than for PBLG.

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Effects of Chromophore Environment on the Photophysics of Poly(2-isopropenylnaphthalene)

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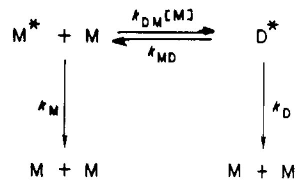
ABSTRACT: The fluorescence and phosphorescence decays of poly(2-isopropenylnaphthalene) (PIPN) samples of narrow polydispersity were measured in several solvents and in the neat film. In fluid solution at room temperature the excimer fluorescence decays are nonexponential, having rise times of less than 1 ns and two decaying components with characteristic lifetimes of 30 and 83 ns. Similar behavior is observed for the solid polymer except that the deviation of the excimer decay from exponentiality is even more pronounced. At 77 K, samples of PIPN dissolved in 2-methyltetrahydrofuran show no excimer emission at low excitation intensity, but the fluorescence decay of the free chromophore is biexponential, with typical decay times of 40 and 95 ns. The decay of naphthalene phosphorescence is exponential with a lifetime on the order of 2 s, whereas the 400- and 340-nm components of the delayed fluorescence give nonexponential decay, the latter having a considerably faster decay rate. These results are interpreted by using the concept of chromophores in inequivalent environments which do not interconvert during the time scales of the decay measurements. The proposed origin of the heterogeneity is the distribution of isotactic, heterotactic, and syndiotactic repeating units in the polymer samples.

Introduction

Reactions of functional groups attached to polymers exhibit complex kinetics because of the broad distribution of reactant separations and mobilities. These effects are particularly evident in studies of polymer photophysics, where the time scale of the experiment is on the order of the time scale of rotational and translational diffusion of polymers in fluid solution.[1,2]

The phenomenon of excimer fluorescence has some features which suggest that excimer formation between aromatic chromophores attached to a polymer chain might serve as a simple model for reactions on polymers. The excited-state complex has a well-defined structure: a sandwich dimer with a typical separation between aromatic rings of 0.3 nm. Excimer formation reflects segmental diffusion and a characteristic emission spectrum at a new wavelength is indicative of "product formation". Furthermore, since the excimer decays ultimately to two ground-state chromophores, the complications arising from depletion of reactants are absent. Nevertheless, recent studies of excimer decay kinetics in polymers have merely shown through the discovery of a number of new effects just how complex the problem of reactions on polymers can be.[3-10]

Scheme I



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