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On the Nonexistence of Crankshaft-like Motions in Dilute Solutions of Flexible-Chain Molecules[1]

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ABSTRACT: A poly(ethylene oxide) was prepared which had incorporated into the middle of the polymer chain a dichromophoric residue capable of intramolecular excimer formation. The ratio of excimer and monomer emission intensities, I_d/I_m, for the polymer and a low molecular weight analogue was measured over a range of temperatures. The apparent activation energies derived from these data were virtually identical for the polymer and its analogue, proving that conformational transitions in the backbone of polymer chains cannot involve two near-simultaneous hindered rotations ("crankshaft-like motions"). At low polymer concentrations, I_d/I_m for the labeled polymer is only slightly lower than for analogous low molecular weight compounds, but the factor by which excimer formation is decreased by incorporation of the dichromophoric residue into the polymer chain increases with the addition of unlabeled polymer. The decrease of the excimer yield of either polymer or analogue at increasing concentration of polymer for polymers with different chain length is similar for solutions with the same macroscopic viscosity.

Hindered rotation around a bond in the backbone of a flexible polymer molecule has been perceived to present the conceptual problem represented schematically in Figure 1. If rotation takes place around one bond only with no change in the conformation of the rest of the molecule (Figure 1a), then a large part of the chain has to move through the viscous medium with a prohibitive expenditure of energy. This difficulty was circumvented by proposing[2-5] that two hindered rotations take place simultaneously in what has been described as a "crankshaft-like motion" (Figure 1b) so that only a short section of the chain would have to move through the medium. This concept was originally meant to apply to conformational transitions of polymers in bulk, but it was

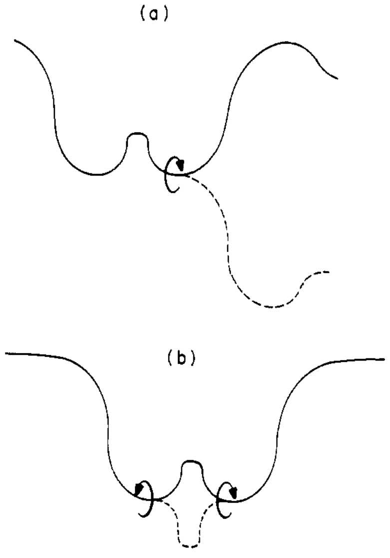


Figure 1. Schematic representation of conformational transitions in polymer chains: (a) a single rotation around a bond in the chain backbone; (b) two correlated rotations in a crankshaft-like motion.

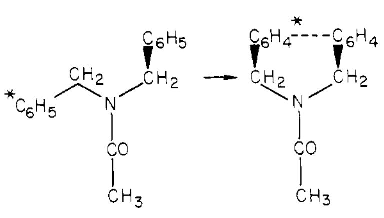
later also used in considerations of the conformational mobility of flexible-chain molecules in highly dilute solution[4,6] and it was applied to models used in computer simultations of the micro-Brownian motion of flexible polymer chains.[7]

If the two hindered rotations are to be strictly simultaneous, the activation energy of the process would be twice as large as in an analogous small molecule in which one hindered rotation only is required.[3,6c,8] Thus, assuming an energy barrier on the order of 3 kcal/mol, rotation around a specific bond in a polymer chain should be slower by 2 orders of magnitude. Even if the requirement of strict simultaneity for passage over the two energy barriers were to be somewhat relaxed, the rotation around bonds in a polymer backbone would have to be much slower than in small molecules if the concept of crankshaft-like motions were to be valid.

In recent years, the dynamics of conformation transitions of polymers in dilute solution have been investigated by a number of experimental methods, such as depolarization of fluoresence,[9] dielectric dispersion,[10] NMR relaxation,[6e,11] and ESR spectral broadening of spin labels.[11e,12] However, while such measurements can be interpreted in terms of rates of conformational transitions in the case of high polymers for which rotational diffusion of the molecule as a whole is negligible, such effects will be dominated by molecular tumbling in the case of low molecular weight analogues,[6d] so that none of these techniques is suitable for a comparison of the conformational mobility of the large and the small species. Ultrasonic absorption is unaffected by molecular tumbling and this method might, in principle, be applicable to a comparison of the dynamics of polymers and their analogues. In fact, measurements have been reported on polystyrene[13] and on the analogous isomeric 2,4-diphenylpentanes.[14] However, the ultrasonic absorption spectrum of the polymer is complex and not easily interpretable.

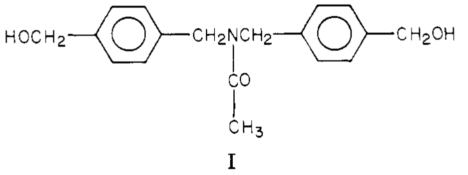
In this laboratory we have attempted for some years to compare rates of hindered rotation in the backbones of polymers and their low molecular weight analogues, using spectroscopic methods which are unaffected by rotational diffusion. NMR spectroscopy was used to study the rate of rotation around the amide bond in piperazine polyamides and their analogues,[15] and the rates of thermal cis–trans isomerization of polymers with azobenzene residues in the chain backbone were compared with rates observed in small azobenzene derivatives by UV spectroscopy.[16] In neither of these cases was any difference detected between the conformational mobility of the polymers and the small molecules, but it was realized that these systems are not very suitable for deciding the question of the existence of "crankshaft-like motions", since rotations around bonds with very high energy barriers[17] were observed in chains containing much more flexible bonds. To overcome this difficulty, we studied the photochemical cis–trans isomerization of azobenzene residues in polymers and their analogues.[18] Malkin and Fischer[19] had argued on the basis of the temperature dependence of the quantum yield of azobenzene photoisomerizations that the excited cis and trans states are distinct and separated by a potential barrier of 2–3 kcal/mol, similar to the barriers for rotation around the bonds of paraffinic hydrocarbons,[20] so that the result with the photochemical process was expected to be pertinent to the question whether incorporation of a given bond into a typical polymer chain impedes conformation transition. Once again, no significant difference was observed between the behavior of the polymer and its analogue as long as the solution was highly diluted. However, the interpretation of this experimental result must be considered somewhat uncertain in view of the study by Jones and Hammond[21] which suggests that *cis*- and *trans*-azobenzenes lead to a common excited state.

Intramolecular excimer formation from two chromophores connected by a three-atom bridge and the resultant change in the emission spectrum provides a powerful tool for the study of the rates of conformational transitions with relaxation times in the range of 1–100 ns.[22] For instance, if one of the phenyl groups of dibenzylacetamide is excited, the ratio of the emission intensity from the excimer and the "monomer" will depend on the probability that the conformational transition



"monomer" excimer

which brings the two phenyl residues into juxtaposition takes place during the excited lifetime of the molecule. The emission spectrum is, of course, independent of rotational diffusion of the fluorescing species and it is therefore tempting to utilize intramolecular excimer fluorescence for a comparison of the conformational mobility of polymer chains and their analogues. However, it is not possible to compare in this manner emission spectra of, e.g., polystyrene[23] and its low molecular weight analogue 2,4-diphenylpentane,[24] since the excitation energy in the polymer can migrate from chromophore to chromophore until it reaches a location favorable for excimer formation.[25] In the present study we have eliminated this difficulty by incorporating a single *N*,*N*-bis[*p*-(hydroxymethyl)benzyl]acetamide (I) group into the middle of a



I

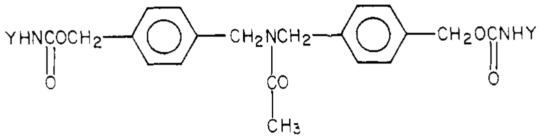
poly(ethylene oxide) chain so that a comparison of the emission spectrum of the polymer with that of a low molecular weight analogue could be interpreted in terms of the relative rates of the hindered rotations required for excimer formation.

Experimental Section

N,*N*-Bis[*p*-(hydroxymethyl)benzyl]acetamide (I) (mp 86 °C) was prepared by converting α-bromo-*p*-tolunitrile (Aldrich) to bis(*p*-cyanobenzyl)amine (mp 105 °C) (excess ammonia in methanol/benzene), hydrolyzing the dinitrile in KOH solution to the dicarboxylic acid (mp 275 °C), converting the diacid to the diethyl ester (mp 274 °C), reducing the diester to bis[*p*-(hydroxymethyl)benzyl]amine (mp 84 °C) ($LiAlH_4$ in refluxing THF), acetylating to *N*,*N*-bis[*p*-(acetoxymethyl)benzyl]acetamide (mp 45 °C), and hydrolyzing the ester groups in 50% ethanol containing 0.5 M KOH at 80 °C for 15 min.

The diol I was incorporated into the center of a poly(ethylene oxide) by the following procedure: One mole of I was reacted with 2.1 mol of hexamethylene diisocyanate (Aldrich) overnight in chloroform solution. The completion of this reaction was characterized by the disappearance of the hydroxyl peak at 3605 cm^{-1}. The diisocyanate product was then treated with 2.5 mol of poly(ethylene oxide) (J. T. Baker Chemical Co.) with a nominal molecular weight of 3000 (PEO-3000) which had been dissolved six times in chloroform and reprecipitated in diethyl ether. Completion of the reaction was monitored by the disappearance of the isocyanate band at 2270 cm^{-1}. The polymer (P) had $[\eta] = 0.10$ dL/g in benzene at 25 °C, corresponding[26] to $M \sim 6.5 \times 10^3$.

The following low molecular weight compounds forming intramolecular excimer analogous to that in P were used. *N*,*N*-Bis[*N*-(*n*-propyl)-*p*-carbamatoxylyl]acetamide (mp 102 °C) (A)



$$\mathrm{P,\ Y = (CH_2)_6NH\underset{\underset{O}{\|}}{C}(OCH_2CH_2)_{68}OH}$$

$$\mathrm{A,\ Y = CH_2CH_2CH_3}$$

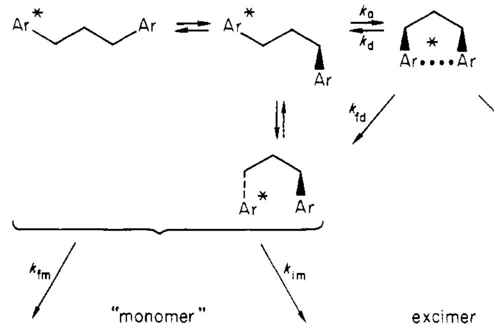
was obtained by reaction with I with *n*-propyl isocyanate (Aldrich). *N*,*N*-Dibenzylacetamide was obtained by acetylation of dibenzylamine (Pfaltz and Bauer) as an oil boiling at 191–192 °C (1.5 torr). *N*,*N*-Bis(*p*-methylbenzyl)acetamide was obtained as a viscous liquid by reacting 1 mol of α-bromo-*p*-xylene (Aldrich) with 2 mol of (4-methylbenzyl)amine (Aldrich) in benzene solution, purifying the product by vacuum distillation [bp 190 °C (0.5 torr)], and acetylating the amine. In addition to the acetate of I described above, the valeric acid ester was obtained as an oil and the palmitic acid ester as crystals melting at 47 °C.

Fluorescence spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrophotometer equipped with a thermostated sample cell compartment. Concentrations of the fluorescing species were 10^{-3} M, corresponding to a concentration of polymer P of about 0.5 g/dL. The excitation wavelength, 256 nm, gave maximum emission intensity and minimum interference from the scattering peak. Oxygen was excluded by passing prepurified nitrogen through the solutions for 20 min. Excimer formation was characterized by I_d/I_m, the ratio of the emission intensities of the excimer at its maximum (330 nm) and the monomer at its emission maximum (284 nm). The observed I_d was corrected for the contribution from monomer emission and I_m was similarly corrected for a contribution from the excimer.

Results and Discussion

Hirayama found[27] that emission spectra of 1,3-diphenylpropane are independent of concentration and concluded that the observed excimer emission must be due entirely to an intramolecular excimer formation. It has also been observed[28] that bimolecular excimer formation, which is observable in neat toluene, is virtually absent in *p*-xylene. We are, therefore, well justified in assuming that excimer emission observed in this study in highly dilute solutions of species containing two para-disubstituted phenylene residues arises exclusively from an intermolecular process. Nevertheless, we satisified ourselves that this assumption is valid.

Scheme I



The kinetic analysis of a steady-state excitation of a substance containing two fluorescing residues linked by a three-atom bridge is based on Scheme I.[22b,e] Here k_a and k_d are rate constants for the conformational transitions by which an excimer is formed or decomposed, k_{fm} and k_{fd} are rate constants for the emission from the "monomer" and the excimer, and k_{im} and k_{id} are rate constants for nonradiative deactivation of the excited monomer and excimer species. This scheme leads to a ratio I_d/I_m of the intensities at the wavelength maxima of excimer and monomer emissions in the steady state (eq 1), where Z is a proportionality constant relating I_d/I_m to the ratio of the areas under the excimer and monomer emission spectra and α is the fraction of the "monomer" which exists in the conformation from which the excimer can be formed by a single conformational transition.

$$I_d/I_m = Z\alpha(k_a/k_{fm})\left[1 + \frac{k_{id} + k_d}{k_{fd}}\right]^{-1} \qquad (1)$$

In our previous studies,[22e] we found that dibenzylacetamide yields much stronger excimer emissions than 1,3-diphenylpropane or dibenzyl ether, probably due to the geometry of the amide bond, and we used, therefore, dibenzylacetamide residues as fluorescent labels in the polymer backbone to overcome the unfavorable influence of the para disubstitution of the phenyl rings on excimer formation.

Figure 2 shows emission spectra of the polymer P at −15, 0, and 20 °C. It is seen that an increasing temperature leads to a decreasing emission intensity of the "monomer" band and to a lesser reduction of the excimer emission. This is due to two effects: an increasing importance of nonradiative deactivation of both the excited monomer and the excimer[22b,29] and an acceleration of the excimer formation from the excited monomer. The analogue A behaves in a similar manner. Figure 3 shows an Arrhenius plot of I_d/I_m over the temperature range −15 to +20 °C. It may be seen that I_d/I_m is slightly lower for the polymer than for the analogue, but the apparent activation energies, 3.8 and 3.7 kcal/mol, are the same within experimental error.

Since the rate constants for radiative emission may be considered to be temperature independent and α is relatively insensitive to temperature, eq 1 indicates that the dependence of I_d/I_m on temperature should yield the activation energy for the conformational transition required for excimer formation provided $(k_{id} + k_d)/k_{fd} \ll 1$. This condition is satisified for a number of dichromophoric substances below −50 °C,[22e] where the decrease in "monomer" emission is compensated by increasing excimer

Table I
I_d/I_m Ratios for $CH_3CON(CH_2C_6H_4Y)_2$ in Methylene Chloride at 20 °C

	Y						
	H	CH_3	CH_2OCOCH_3	$CH_2OCOC_4H_9$	$CH_2OCOC_{15}H_{31}$	A	P
I_d/I_m	3.5	0.78	0.95	0.90	0.73	0.69	0.57

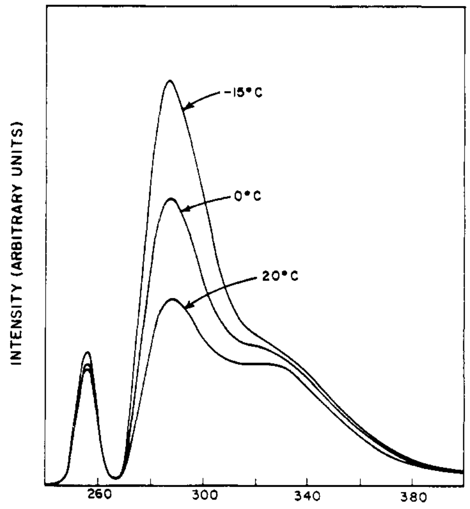


Figure 2. Emission spectra of polymer P in dichloromethane solution.

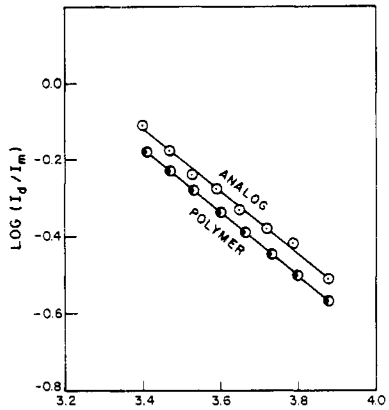


Figure 3. Arrhenius plot of the temperature dependence of I_d/I_m for polymer P and analogue A in dichloromethane.

emission, but such low temperatures could not be used in the present study because of the low excimer yield from compounds containing para-disubstituted phenylenes. We must, therefore, assume that the temperature dependence of k_{id} makes a negative contribution to the apparent activation energies. Nevertheless, since k_{id} should be independent of the incorporation of the chromophore into the polymer chain backbone, we may conclude that the activation energy for the hindered rotation required for excimer formation remains unchanged when the fluorescent label is placed into the middle of the polymer chain.

Since the analogue A contains a number of bonds around which hindered rotations can take place, we recorded emission spectra for *N*,*N*-dibenzylacetamide and a series of its *p*′-disubstituted derivatives. The results for these various compounds are compared with analogue A and polymer P in Table I. It is seen that a large decrease in excimer emission is produced by methyl substitution in the para positions of *N*,*N*-dibenzylacetamide. This is similar to the large decrease in the excimer yield of *p*-xylene as compared to toluene alluded to above. However, a lengthening of the para substituents has a strikingly small effect on excimer formation. Thus, the polymer P is characterized by an I_d/I_m value which is only 27% smaller than that of *N*,*N*-bis(*p*-methylbenzyl)acetamide which contains only two bonds around which hindered rotation can take place.

These results provide conclusive proof that the conformational transition required for excimer formation in the middle of the poly(ethylene oxide) chain does not require a second hindered rotation in the polymer chain as assumed in the "crankshaft-like motion" model. Moreover, previous studies of the excimer fluorescence of dibenzylacetamide[22a] have established the activation energy for excimer formation as 3.6 and 4.1 kcal/mol in heptane and ethanol, respectively, close to the energy barriers for trans–gauche transitions in alkanes,[20] and it may be assumed that similar barriers characterize hindered rotations in the poly(ethylene oxide) chain.[36] Thus, if hindered rotation of the fluorescent label is not correlated with a second hindered rotation, it may be inferred that neither can two near-simultaneous hindered rotations be required as a mechanism for conformational transitions of poly(ethylene oxide). The present work tends, therefore, to confirm our previous suggestions[18,30] that the concept of "crankshaft-like motions" of flexible chains is incompatible with the behavior of such chains in highly dilute solution. Though this denial of a widely held concept may seem shocking, it should be noted that activation energies for conformational transitions in polymers, obtained by a variety of experimental methods,[3b,9b,10d,12c] were in the range to be expected for a single hindered rotation. Also, recent computer simulation studies[31] led to results inconsistent with the concept of crankshaft-like motions. In fact, Schatzki, has even been led to question its validity for polymers in bulk.[32] He found that a transition similar to that occurring in amorphous regions of glassy polyethylene, which had led him to advance this mechanism for conformational change, is also observed in a polymer with bulky side chains where no such motion is possible.

We are then faced with a dilemma: On one hand we have excluded the possibility of two hindered rotations correlated in time as shown schematically on Figure 1b. On the other hand, we cannot consider the possibility of a large portion of the chain moving through the viscous medium due to a single hindered rotation. To resolve this difficulty we note that the energy requirement for the distortion of a bond angle or an internal angle of rotation is proportional to the square of the distortion. Thus, if the stress introduced into a molecular chain by a hindered rotation is relieved by many small distortions rather than a second compensating hindered rotation, the additional energy requirement may be very small.[33]

It should be noted at this point that in a process of a very different nature two or more simultaneous hindered rotations are necessarily involved and that such a mechanism is strongly suggested by experimental data. In globular proteins the polypeptide backbone exists in a precisely defined conformation, but transitions involving small regions of the globular structure have been observed. Unless such changes take place at the chain end, they must be due to a short section of the chain, *both ends of which are anchored in the globular structure.* Clearly, such transitions are impossible with a single hindered rotation.

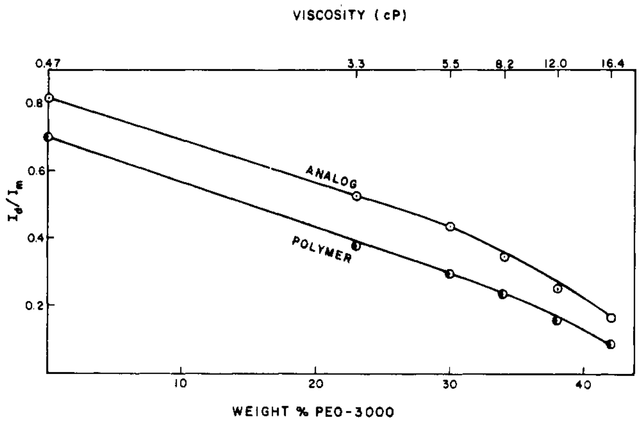


Figure 4. Dependence of I_d/I_m for polymer P and analogue A in dichloromethane at 20 °C on the concentration of added PEO-3000.

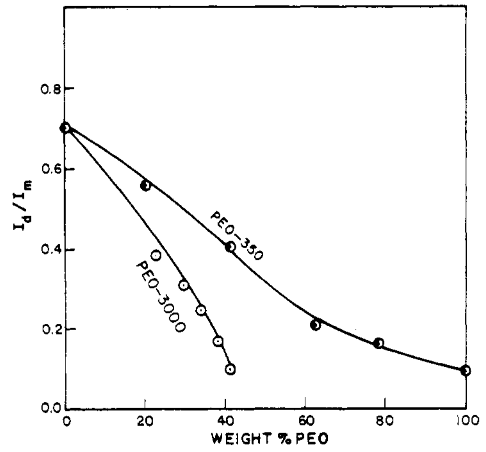


Figure 5. Dependence of I_d/I_m for polymer P in 1,2-dimethoxyethane at 20 °C on the concentration of added PEO-350 and PEO-3000.

In fact, relaxation times for such processes are typically in the millisecond range,[30a] but a process with a half-life as long as 90 s has also been reported.[34] This is in striking contrast with the transition rates in flexible chains where ultrasonic and dielectric dispersion data led typically to a relaxation time on the order of 10^{-8} s.[30b]

It was also of interest to find how the rate of the conformational transition required for excimer formation is affected by the addition of unlabeled poly(ethylene oxide) to the solution of the polymer bearing the fluorescent label. Figure 4 shows the variation of I_d/I_m for the polymer and the analogue in dichloromethane solutions containing added PEO-3000 as a function of the solution viscosity and the polymer concentration. Although excimer emission decreases for both P and A as the solution becomes more viscous, the ratio of the I_d/I_m values for the polymer and the analogue decreases sharply as the polymer concentration is increased. This is not suprising since conformational transitions of polymers must become cooperative in concentrated systems. Similar observations were made earlier[18] concerning photoisomerization rates of polymers and analogues in solutions of varying polymer concentration.

Another question of interest was the effect the chain length of the added polymer had on the excimer formation of the labeled polymer. Figures 5 and 6 give plots of I_d/I_m of polymer P in 1,2-dimethoxyethane solution containing varying concentrations of poly(ethylene oxide) with molecular weights of 350 and 3000, respectively. It may be seen that for any given concentration of PEO, the polymer with the higher molecular weight has a greater effect in reducing excimer formation. On the other hand, solutions of equal viscosity yield very similar I_d/I_m ratios whether they contain the low or the high molecular weight PEO. Similar results were obtained with analogue A in solutions of the two polymeric species. This seems surprising, since the rate of conformational transition, like the diffusion coefficient of small molecules in polymer solutions,[35] should depend on the microscopic viscosity which was expected to correlate with the polymer concentration and to be insensitive to the polymer chain length.

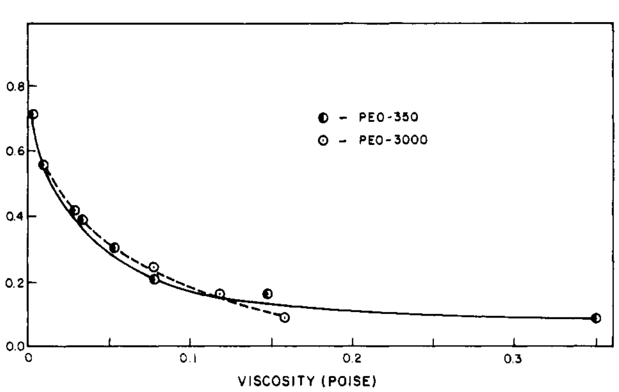


Figure 6. Dependence of I_d/I_m for polymer P on the viscosity of 1,2-dimethoxyethane solutions containing PEO-350 and PEO-3000.

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References and Notes

(1) Taken from the Ph.D thesis submitted by T.-P. Liao to the Graduate School of the Polytechnic Institute of New York, May 1980.

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Effect of Molecular Weight on Triplet Exciton Processes. 4. Delayed Emission of Solid Poly(2-vinylnaphthalene)

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ABSTRACT: The delayed emission of solid poly(2-vinylnaphthalene) has been studied at 77 K and has been found to depend on the molecular weight of the polymer. As molecular weight increases the intensity of the delayed fluorescence increases and the phosphorescence develops a new lower energy peak. Both spectra are broad and excimeric in nature. The delayed fluorescence is found to be red-shifted by $\sim$1800 cm^{-1} relative to the prompt fluorescence, which is taken to show that triplet–triplet annihilation occurs at traps. It is argued that at least part of this molecular-weight dependence arises from the partial localization of the triplet exciton on a single polymer chain.

Introduction

Since the work of Cozzens and Fox[1] in 1969 there have been a number of reports of triplet–triplet annihilation in polymers containing a high fraction of pendent aromatic chromophores. It has been demonstrated by a number of workers that the triplet annihilation occurs by an exciton mechanism involving either exciton–exciton annihilation or exciton-trapped triplet annihilation.[2] It has been found for several polymer systems in low-temperature glasses that the importance of triplet annihilation increases with molecular weight.[3] This dependence has been interpreted as arising from the increased probability of multiple excitations occurring in polymers with a larger number of chromophores. The present series of experiments was carried out to determine what molecular-weight dependence, if any, occurs in films or solid powders of poly(2-vinylnaphthalene) (P2VN). It was thought very likely that there would not be any molecular-weight dependence in solids for the following reason: if interchain contacts are extensive, then interpolymer excitonic migration should be facile and the size of individual polymer chains would be irrelevant. In fact, we have observed a molecular-weight effect that is qualitatively similar to that observed in isolated polymers in low-temperature glasses; i.e., increasing the molecular weight increases the delayed-fluorescence intensity. It will be noted that the delayed-emission spectrum (delayed fluorescence and phosphorescence) of the solid is quite different from that of isolated polymers, with an excimer-like delayed fluorescence and phosphorescence. We will also show that the delayed fluorescence is red-shifted relative to the prompt fluorescence, implying that triplet annihilation preferen-