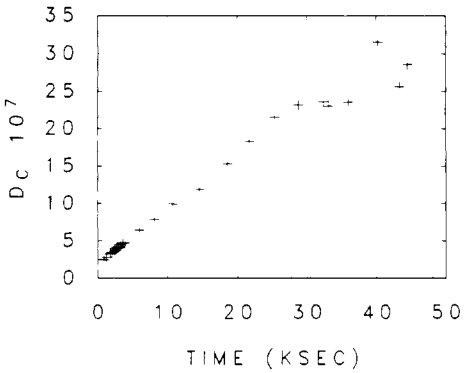

Figure 1. Plot of the mutual diffusion coefficient D_c vs. elapsed time for the thermal copolymerization of styrene and divinylbenzene.

because the gelation reaction leads to permanent inhomogeneities in the sample, the data near the end of the run are probably partially heterodyned by the scattering from these gel defects. The results after 30 ks are probably affected by this problem.

The values of D_c observed during the polymerization are plotted vs. elapsed time in Figure 1. Even though a gel is being formed, there is no indication of any significant change from the homopolymerization results,[1] at least during the homogeneous part of the reaction. The effect of the gel elasticity would be to increase D_c. There is no indication of an increase in D_c over the pure solution results. This is consistent with the prediction that the concentration fluctuations are sensitive to the overall polymer concentration and not to the topology for these gels. The swelling ratio at the end of the polymerization was approximately 5. This was determined by weighing the fresh gel and a dried gel.

A clear gel sample was cooled and studied between 9 and 90 °C. Although the results were slightly affected by the part of the sample that was observed due to the presence of the gel defects, the trend of D_c with temperature was clearly determined. The ranges of D_c determined for the gel are plotted against the temperature divided by the solvent viscosity in Figure 2. The error limits reflect the uncertainty caused by the spatial variation in D_c in the sample. The modulus E depends linearly on the temperature and in a more complicated way on the solvent quality. Styrene is expected to be a very good solvent at all temperatures studied in this work. The friction per unit volume will depend linearly on the solvent viscosity and in a more complicated way on the polymer concentration. The mutual diffusion coefficient for the gel is then expected to be proportional to the quantity T/η. This relation is obeyed very well by the gel sample used in this study.

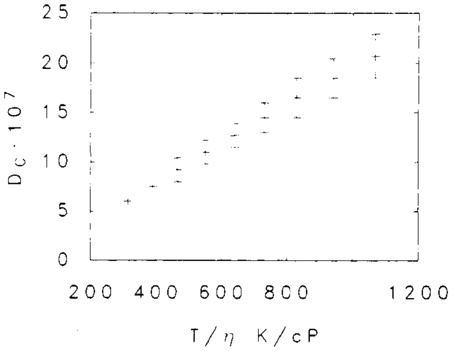

Figure 2. Plot of D_c vs. T/η for the polystyrene gel. The mutual diffusion coefficient is proportional to the absolute temperature divided by the solvent viscosity.

The present results suggest that no information about the detailed structure of the gel will be obtained from measurements of D_c under the conditions observed in this study. If the mutual diffusion coefficient is not measurably affected by the presence of a true network, then it should also not be affected by the presence of a pseudogel network. The actual value of D_c is determined by the balance of the osmotic restoring force, which depends on T and the solvent quality, and the friction, which depends on the solvent viscosity and the polymer concentration in this range. The present results do not support the notion that a dynamic screening length can be quantitatively extracted from measurements of the mutual diffusion coefficient in solutions and gels. Neither the solutions nor the gels obey the predicted[5] scaling law behavior in the range of concentrations observed here.

References and Notes

(1) Patterson, G. D.; Stevens, J. R.; Alms, G. R.; Lindsey, C. P.; *Macromolecules* **1979**, *12*, 658.
(2) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229.
(3) Patterson, G. D.; Jarry, J.-P.; Lindsey, C. P. *Macromolecules* **1980**, *13*, 668.
(4) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(5) de Gennes, P. G. *Macromolecules* **1976**, *9*, 587.
(6) Alms, G. R.; Patterson, G. D.; Stevens, J. R. *J. Chem. Phys.* **1979**, *70*, 2145.

Study of the Association of Anionic and Cationic Polymers by Nonradiative Energy Transfer[1]

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ABSTRACT: Nonradiative energy transfer was studied in aqueous solutions containing mixtures of naphthyl- and anthryl-labeled charged or uncharged polymers. An enhanced efficiency of energy transfer was observed when the donor and acceptor chromophores were attached to polymers carrying charges of the opposite sign. This effect decreased with an increasing ionic strength of the solution. However, in mixtures of an anionic copolymer of dimethylacrylamide and a cationic copolymer of vinylpyrrolidone, both hydrogen-bonding and hydrophobic interactions contributed to the stability of the polymer complex. Energy transfer was not found to reflect the repulsion between ionized poly(acrylic acid).

The phenomenon of nonradiative energy transfer between two fluorescing chromophores, discovered and subjected to theoretical analysis by Förster,[2] has been used extensively to characterize distances between donors and

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Table I

sample designation[a]	mol % monomer residues						[η]
	DMA	VP	AA	DAEM	NEM	AMM	
PDMA-N	99.46				0.54		1.35
PDMA-A	99.58					0.42	
PDMA-Nα1	80.23		19.3		0.47		1.37
PDMA-Nα2	88.82		10.7		0.48		1.50
PDMA-Aβ	91.09			8.49		0.42	0.96
PVP-A		99.45				0.55	0.75
PVP-Aβ1		82.84		16.6		0.56	1.50
PVP-Aβ2		89.74		9.66		0.60	0.83
PAA-N			97.85		2.15		1.35
PAA-A			99.0			1.0	0.43

[a] PDMA, PVP, and PAA are copolymers or terpolymers whose main components are dimethylacrylamide, vinylpyrrolidone, and acrylic acid, respectively. The symbols N and A stand for labeling with naphthyl and anthryl residues; α and β stand for acidic and basic terpolymers.

acceptors in rigid biological macromolecules.[3] Some studies have also been reported dealing with the intramolecular energy transfer in synthetic oligomers or polymers[4] and two reports from this laboratory[5] have shown that intermolecular energy transfer between donor- and acceptor-labeled polymers may be used to characterize polymer compatibility. Here we report on the effect of energetic interactions between chromophore-labeled polyions on the magnitude of intermolecular energy transfer. This study is thus designed to test the dependence of this phenomenon on the molecular association of polymers.

Experimental Section

Monomers and Polymers. Acrylic acid (Aldrich) was distilled at 39 °C under 10 torr. (*N*,*N*-Dimethylamino)ethyl methacrylate (DAEM) (Rohm and Haas) was distilled at 60 °C and 4 torr. *N*,*N*-Dimethylacrylamide (Kohjin) was distilled at 68 °C under 10 torr. *N*-Vinylpyrrolidone (Aldrich) was distilled at 55 °C under 3 torr. The two fluorescent monomers 9-anthrylmethyl methacrylate (AMM) and 1-(2-naphthyl)ethyl methacrylate (NEM) were prepared as in our previous study.[5a] Copolymers and terpolymers were obtained by using azobis(isobutyronitrile) as initiator. Polymers in which *N*-vinylpyrrolidone was the main component were prepared in bulk, *N*,*N*-dimethylacrylamide polymers in dioxane solution, and acrylic acid polymers in dimethylformamide solution. In all cases the reaction was stopped at low conversion to ensure a narrow distribution of copolymer compositions. The naphthyl and anthryl residues in the polymers were determined by UV spectroscopy, assuming that the extinction coefficients are the same as in 1-(2-naphthyl)ethyl acetate (NEA) (5.1×10^3 M^{-1} cm^{-1} at 276 nm) and 9-anthrylmethyl acetate (AMA) (8.3×10^3 M^{-1} cm^{-1} at 368 nm) in methanol. The concentration of acrylic acid residues in copolymers was determined by titration with sodium ethoxide in ethanol solution with phenolphthalein as the end point indicator, while the amine groups in the basic copolymers were analyzed for by titration of water solutions with HCl in the presence of 0.25 M NaCl to the methyl red end point. Intrinsic viscosities were obtained in methanol solution at 25 °C and are specified in dL/g.

Sample Preparation. Buffers were prepared from glycine–glycine hydrochloride for pH 2–3, acetic acid–sodium acetate for pH 4–5, KH_2PO_4–Na_2HPO_4 for pH 6–8, and glycine–sodium glycinate for pH 9–10. Ionic strengths from 0.025 to 0.3 were adjusted by the buffer concentration. Solutions of higher ionic strength were prepared by addition of NaCl to the buffer with an ionic strength 0.3. Films of mixed polymers were cast from 10% methanol solution onto silicone-coated plates after bubbling nitrogen through the solution for 5 min. After drying in a vacuum oven at 40 °C, the films were kept under vacuum before fluorescence measurement.

Fluorescence Measurements. Emission spectra were recorded on a Hitachi Perkin-Elmer MPF-2A spectrophotometer equipped with a 150-W xenon lamp, an R-106 photomultiplier, and a PQD recorder. Solutions were purged with nitrogen before recording the reflectance fluorescence spectrum with the exciting beam at 60° and the observation of the emission at 30° to the surface of the quartz cell holding the sample. Similar measurements were carried out for polymer films mounted between quartz plates. The excitation wavelength was set at 285 nm to minimize the fraction of the light absorbed by the acceptor anthryl groups (the extinction coefficients at 285 nm for the naphthyl and anthryl groups were 3.30×10^3 M^{-1} cm^{-1} and 1.62×10^3 M^{-1} cm^{-1}, respectively). The energy transfer was characterized by I_N/I_A, the ratio of the emission intensity of the naphthyl groups at 340 nm and the anthryl groups at 420 nm. Unless otherwise specified, I_N/I_A of mixed polymers was measured in pH 7 phosphate buffers at 25 °C with a 3.08×10^{-4} M naphthyl and 3.28×10^{-4} M anthryl concentration.

Results and Discussion

Characteristic Energy Transfer Distance R_0. According to the Förster theory,[2] the characteristic distance R_0 between donor and acceptor at which half of the excitation energy is transferred is given by

$$R_0^6 = \frac{9000(\ln 10)\kappa^2\phi_D^0}{128\pi^5 n^4 N}\int_0^{\mathrm{inf}} (F_D(\nu)\epsilon_A(\nu)/\nu^4)\,d\nu \qquad (1)$$

where κ^2 is a function of the mutual orientation of donor and acceptor with $\kappa^2 = {}^2/_3$ for random orientations in fluid media, ϕ_D^0 is the emission quantum yield of the donor in the absence of acceptors, $F_D(\nu)$ and $\epsilon(\nu)$ are the normalized emission intensity of the donor and the extinction coefficient of the acceptor as a function of the wavenumber ν, n is the refractive index, and N is Avogadro's number. Using NEA and AMA as analogues of the chromophore-bearing residues in the copolymers, $\phi_D^0 = 0.13$,[5a] and the overlap integral was evaluated as 4.31×10^{-15} cm^6 mol^{-1}, very close to 4.08×10^{-15} cm^6 mol^{-1} given by Berlman for the 2-methylnaphthalene donor and the 2-methylanthracene acceptor.[6a] In an aqueous medium, these data correspond to $R_0 = 2.16$ nm with a critical acceptor concentration 0.0045 M, at which 76% of the energy absorbed by the donor would be transferred to the acceptor[6b] if the chromophores were randomly distributed and if their diffusion during the excited lifetime of the donor could be neglected.

If there is no energy transfer, I_N/I_A will be given by $(\epsilon_N/\epsilon_A)(C_N/C_A)X$, where ϵ_N/ϵ_A is the ratio of the donor and acceptor optical densities of the excitation wavelength, C_N/C_A is the ratio of their concentrations, and X is the ratio of the donor fluorescence intensity at 340 to the acceptor fluorescence intensity at 420 from solutions of NEA and AMA, respectively, of low equal optical density. With $\epsilon_N/\epsilon_A = 2.04$ and $X = 1.23$, this leads, for solutions of equal donor and acceptor concentration, to $I_N/I_A = 2.51$ in the absence of energy transfer.

Intermolecular Energy Transfer in Solutions of Donor- and Acceptor-Labeled Polymers. Table I lists the composition and the intrinsic viscosities of the polymeric samples used in this study. In solutions containing the same chromophore concentration, the emission in-

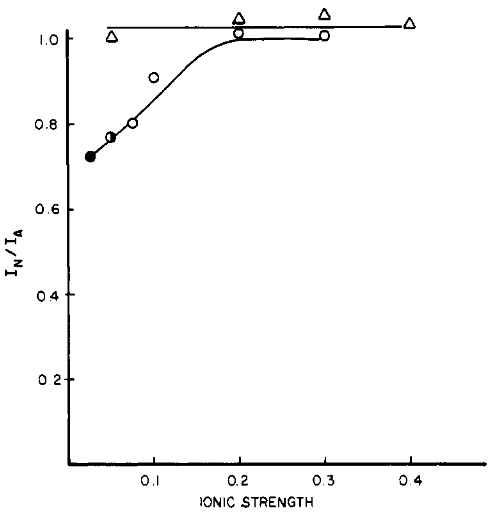

Figure 1. Energy transfer in solutions containing PDMA-Nα2 and PDMA-Aβ (○) or PDMA-N and PDMA-A (△). The half-filled point represents incipient phase separation.

tensity was the same in the uncharged copolymers and in the acidic or basic terpolymers, showing that in our case the introduction of carboxyl or amine groups into the polymer chain did not produce fluorescence quenching.[7]

First we compared energy transfer in solutions containing a mixture of naphthyl donor and anthryl acceptor labeled dimethylacrylamide copolymers with the energy transfer in solutions containing mixtures of chromophore-labeled acidic and basic dimethylacrylamide terpolymers. The results (Figure 1) show that I_N/I_A, the ratio of the emission intensities of the naphthyl donor and the anthryl acceptor, increases for mixtures of the oppositely charged polyions with an increasing ionic strength, reaching eventually a limiting value very close to that observed for mixtures of the uncharged copolymers. The results suggest that energy transfer between the polycation and polyanion is favored by molecular complex formation which increases the probability of a mutual approach of the donor and acceptor chromophores. Apparently, such complex formation is almost completely eliminated, in this case, at high ionic strength. In the case of the mixture of uncharged dimethylacrylamide copolymers, I_N/I_A is independent of ionic strength, showing that electrolyte addition in itself does not affect the efficiency of energy transfer as it would if it affected the excited lifetime of the donor.

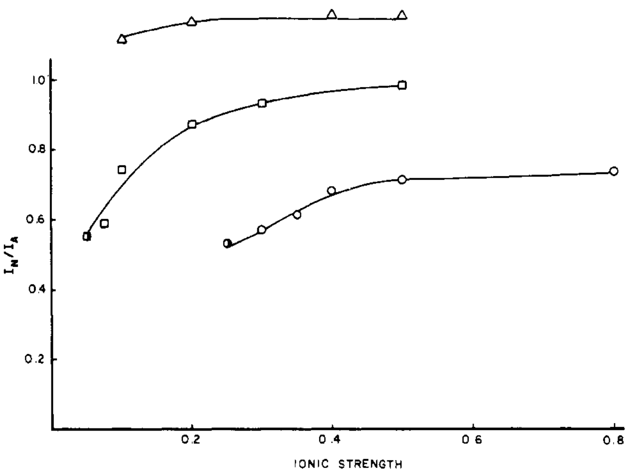

Figure 2. Energy transfer in solutions of PDMA-Nα1 and PVP-Aβ1 (○), PDMA-Nα2 and PVP-Aβ2 (□), and PDMA-N and PVP-A (△). The half-filled points represent incipient phase separation.

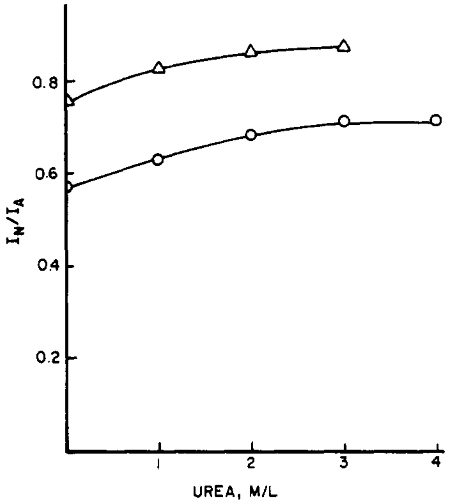

Figure 3. Energy transfer between PDMA-Nα1 and PVP-Aβ1 in pH 7 buffer and ionic strength 0.5 (○) and 0.3 (△) as a function of the concentration of urea.

It is well-known that most pairs of dissimilar polymers are incompatible[8] and it was, therefore, expected that complex formation between anionic and cationic polymers will become more difficult if the uncharged monomer residues constituting most of the two chain molecules are different from each other. In an attempt to demonstrate such an effect, we studied energy transfer in solutions containing copolymers or terpolymers of dimethylacrylamide with copolymers or terpolymers of vinylpyrrolidone (Figure 2). The I_N/I_A ratio for solutions containing uncharged dimethylacrylamide and vinylpyrrolidone copolymers was only very slightly higher than in solutions in which both the donor and the acceptor were appended to chains containing mostly dimethylacrylamide residues (Figure 1), indicating that the difference between the mutually excluded volume of similar and dissimilar monomer residues has only a marginal effect on the efficiency of energy transfer between two polymer chains in our systems. In the case of solutions containing acidic terpolymers of dimethylacrylamide and basic terpolymers of vinylpyrrolidone, energy transfer is again enhanced by complex formation at low ionic strength, but I_N/I_A remains substantially lower than in the mixture of the neutral copolymers even at high electrolyte concentration. We must assume, therefore, that other than Coulombic interactions contribute in this case to complex formation. Poly(*N*-vinylpyrrolidone) is known to form complexes with poly(acrylic acid)[9] and we believe that the relatively low I_N/I_A values in solutions of PDMA-Nα1 and PVP-Aβ1 or of PDMA-Nα2 and PVP-Aβ2 at high ionic strength reflect similarly an interaction of carboxyl groups off the dimethylacrylamide terpolymer with the vinylpyrrolidone terpolymer. As would be expected, the reduction of I_N/I_A at low ionic strength becomes more pronounced with an increasing density of charged groups along the polyion chains. However, I_N/I_A has about the same value for both polyion pairs as phase separation (characterized by a visible solution turbidity) is reached on decreasing the ionic strength, suggesting that a polymer-rich phase is formed when the polyanion–polycation aggregates exceed a critical size.

In addition to hydrogen-bonding interactions between carboxyl groups and pyrrolidone residues, polymer complex formation could also be stabilized by hydrophobic bonding. Such aggregation would be opposed by addition of urea. Figure 3 shows indeed that an increasing urea concentra-

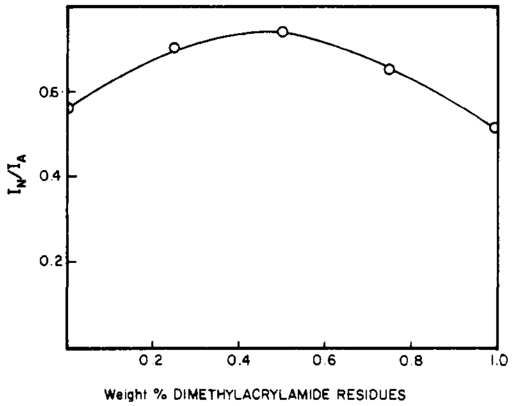

Figure 4. Energy transfer in films containing varying ratios of dimethylacrylamide and vinylpyrrolidone polymers with a constant concentration of 10^{-2} M naphthyl and 0.8×10^{-2} M anthryl labels.

tion tends to decrease the efficiency of energy transfer between PDMA-Nα1 and PVP-Aβ1. Since the effect of urea addition increased with a decreasing ionic strength of the solution, we must conclude that in addition to hydrophobic interactions, Coulombic forces between the cationic and anionic polymers were also reduced by the urea. This may be understood as resulting from an increase in the dielectric constant of the solution (e.g., from 78.54 for water to 87.95 for 3.56 M aqueous urea).[10]

In view of the above evidence for attractive interactions between vinylpyrrolidone and dimethylacrylamide residues, it was of interest to find whether the two corresponding polymers were compatible with each other in bulk. To provide evidence concerning such compatibility, we prepared films contaianing PDMA-N, PVP-A, and unlabeled PDMA and PVP so that the concentration of the fluorescent labels was kept constant while the composition of the polymer blend was systematically varied. Figure 4 shows that I_N/I_A passes through a maximum for a blend containing an equal weight of vinylpyrrolidone and dimethylacrylamide residues, indicating a phase separation which impedes energy transfer between chromophores attached to the two polymers. As pointed out by Koningsveld et al.,[11] compatibility in relatively dilute solutions need not imply polymer compatibility in bulk.

Since the results detailed above showed that energy transfer between chromophore-labeled polymers is sensitive to intermolecular attraction, it was of interest to find whether a repulsion between polyions carrying charges of the same sign will also lead to observable effects. For this purpose we studied solutions of donor- and acceptor-labeled poly(acrylic acid) as a function of pH so as to vary the charge of the polyion. As shown in Figure 5, no change of I_N/I_A was observed between pH 3 and pH 10, although this range corresponds to a transition from a virtually uncharged to an almost fully ionized poly(acrylic acid). Only when the pH is reduced below 2.7, leading to an incipient precipitation of the polymer, is a sudden change of the emission spectrum observed, indicating an increase in the energy transfer efficiency. It should also be noted that I_N/I_A values for the homogeneous systems were similar to values observed with donor- and acceptor-labeled uncharged polymers.

This unexpected result shows that while the mutual attraction of polycations and polyanions enhances the probability that chromophores attached to such species will approach each other, the probability of encounters between polyanion-bound donors and acceptors is not affected to any demonstrable degree by their mutual repulsion. In the case of the polyanion–polycation interaction, we are dealing apparently with an extensive interpenetration of the molecular coils; the Coulombic repulsion between two polyanions, on the other hand, may not add significantly to the repulsion between two uncharged polymer coils in a good solvent medium due to the excluded-volume effect.

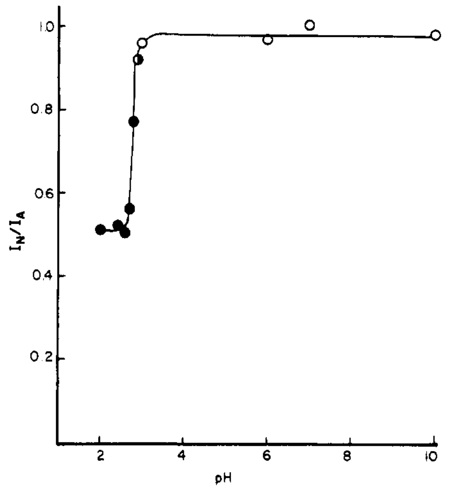

Figure 5. Energy transfer in solutions of donor- and acceptor-labeled poly(acrylic acid) at varying pH and an ionic strength of 0.025. The half-filled point represents incipient phase separation.

Comparison of Energy Transfer between Free Chromophores and between Chromophores Attached to Polymer Chains. A dioxane solution containing 3.08×10^{-4} M NEA and 3.28×10^{-4} M AMA, the low molecular weight analogues of the donor- and acceptor-bearing monomers used in labeling the various polymers in this study, was characterized by $I_N/I_A = 0.66$. This corresponds to a substantially larger efficiency of energy transfer than $I_N/I_A = 1.05$, observed in an aqueous solution of PDMA-N and PDMA-A with the same chromophore concentration. The ratio of the refractive indices of dioxane and water is 1.066 and this should lead to a slightly less efficient energy transfer in dioxane. The observed higher efficiency may have contributions from three sources: (a) the small chromophore molecules may diffuse toward each other during the lifetime of the excited state. By contrast, in systems containing polymer-bound chromophores, diffusion of the polymers is negligible and the chromophore motions are limited by the rate of conformational transitions of the chain molecules. (b) The excluded-volume effect, as alluded to above, opposes the mutual interpenetration of the polymer coils and this might reduce interpolymer energy transfer. (c) The spheres of interaction of polymer-bound acceptors are more likely to overlap than those of acceptors distributed at random. This effect is believed to have been negligible at the low concentrations of acceptors in the polymers used in this work.

To assess the relative importance of the first two factors in reducing the efficiency of energy transfer between polymer-bound chromophores, we measured I_N/I_A in solutions of PDMA-N and PDMA-A to which increasing concentrations of unlabeled poly(dimethylacrylamide) were added. The initial polymer concentration was 1.66 g/100 mL; addition of the same concentration of unlabeled PDMA increased I_N/I_A from 1.05 to 1.12. We see then that a partial elimination of the excluded-volume effect by an increase in the polymer concentration has a small unfavorable effect on energy transfer. Unfortunately, this result does not lend itself to a reliable interpretation since the forced interpenetration of the molecular coils is accompanied by a reduced mobility of the chain segments.

Concluding Remarks. Association of globular proteins has been studied by nonradiative energy transfer between labels which were either covalently attached or adsorbed to specific binding sites.[12] Because of the well-defined geometry of the interacting molecules, the experimental results permit a precise interpretation, particularly if the labels are known to be situated at specific sites of the proteins. In fact, Fairclough and Cantor report[13,14] the reconstruction of the geometry of the relative positioning of *six* protein subunits of a ribosome from fluorescence data.

By contrast, the changes produced by the association of flexible-chain molecules are much more complex. Such association may change the extension of the chain, lead to a varying degree of interpenetration of the molecular coils, and reduce the micro-Brownian motion of the chain segments. Clearly, the single parameter obtained from energy-transfer data does not allow us to draw conclusions as to the extent of complexation or the nature of the complex.

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References and Notes

(1) Abstracted from the Ph.D. dissertation submitted by I. Nagata to the Graduate School of the Polytechnic Institute of New York in June 1980.

(2) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.

(3) (a) Steinberg, I. Z. *Annu. Rev. Biochem.* 1971, *40*, 83. (b) Schiller, P. W. In "Biochemical Fluorescence"; Chen, R. F., Edelhoch, H., Eds.; Marcel Dekker: New York, 1975; Vol. 1, p 285.

(4) (a) Stryer, L. *Science* **1961**, *162*, 526. (b) Hass, E.; Katchalski-Katzir, E.; Steinberg, I. Z. *Biopolymers* **1978**, *17*, 11. (c) Aspler, J. S.; Guillet, J. E.; Hoyle, C. E. *Macromolecules* **1978**, *11*, 925.

(5) (a) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649. (b) Mikes, F.; Morawetz, H.; Dennis, K. S. *Ibid.* **1980**, *13*, 649.

(6) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973; (a) p 314, (b) p 29.

(7) Such quenching was observed in some polypeptides by Weber and Rosenheck (Weber, G.; Rosenheck, K. *Biopolymers Symp.* **1964**, *1*, 333) and by Fasman et al. (Fasman, G. D.; Bodenheimer, E.; Pesce, A. *J. Biol. Chem.* **1966**, *241*, 916).

(8) (a) Krause, S. *J. Macromol. Sci., Rev. Macromol. Chem.* **1952**, *C7*, 251–314. (b) In "Polymer Blends"; Paul, D. R., Newman, S., Eds.; Academic Press: New York, 1978; Vol. 1, Chapter 2.

(9) Ferguson, J.; Shah, S. A. V. *Eur. Polym. J.* **1968**, *4*, 343.

(10) Wyman, J., Jr. *J. Am. Chem. Soc.* **1933**, *55*, 4116.

(11) Koningsveld, R.; Kleitjens, L. A.; Schoffeleers, H. M. *Pure Appl. Chem.* **1974**, *39*, 1.

(12) (a) Gennis, L. S.; Gennis, R. B.; Cantor, C. R. *Biochemistry* **1972**, *11*, 2517. (b) Langlois, R.; Lee, C. C.; Cantor, C. R.; Vince, R.; Pestka, S. *J. Mol. Biol.* **1976**, *106*, 297. (c) Matsumoto, S.; Hammes, G. G. *Biochemistry* **1975**, *14*, 214.

(13) Huang, K.-H.; Fairclough, R. H.; Cantor, C. R. *J. Mol. Biol.* **1975**, *97*, 442.

(14) Fairclough, R. H.; Cantor, C. R. *Methods Enzymol.* **1978**, *18*, 347–79.

Triplet Luminescence Properties of Poly(1-vinylnaphthalene) Solid Films

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ABSTRACT: Both spectroscopic and kinetic studies of poly(1-vinylnaphthalene) (P1VN) in the solid film state have been carried out over the temperature range between 77 and 260 K. Luminescence decays with a chopper frequency of 30 Hz are nonexponential but with a frequency of 0.5 Hz two rather long-lived exponential components having lifetimes which are temperature invariant between 77 and 260 K have been observed. The phosphorescence emission is broad and red shifted compared with that of naphthalene itself or P1VN in rigid solution. With rising temperature the low-wavelength side of the emission preferentially loses intensity up to 180 K. Above this temperature a single emission band centered at 590 nm remains and is invariant in position to 260 K. The delayed-fluorescence emission retains essentially the same band shape and position from 77 to 260 K. The results suggest the existence of excimer-like triplet traps in these films which are populated by mobile triplet excitons. It is proposed that the delayed fluorescence arises primarily by interaction between mobile triplet excitons and trapped triplets.

Introduction

The photophysical properties of vinyl aromatic polymers have proved to be difficult to interpret in terms of simple mechanisms, and for many polymers only very general statements concerning the nature of the various luminescence processes may be made. Furthermore, mechanistic arguments applicable to dilute solutions of small molecules are often not at all appropriate for macromolecules where local high chromophore concentrations are found with varying degrees of conformational order. Thus, conventional interpretations of rate experiments are frequently not possible. A recent study of the lowest triplet properties of poly(2-vinylnaphthalene) (P2VN) in solution clearly points out the distinctive features associated with polymeric materials.[1]

Among the early investigations of poly(1-vinylnaphthalene) was a fluorescence study carried out by Vala and co-workers[2] in which it was shown that neighboring chromophore units of the chain form excimers. Triplet migration in this polymer was demonstrated by Cozzens and Fox,[3] who also showed that in rigid solutions at 77 K delayed fluorescence occurred by triplet–triplet annihilation. Both P1VN and P2VN, in rigid solutions, have delayed-emission spectra which are essentially identical with

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