Studies of Synthetic Polymers by Nonradiative Energy Transfer

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Nonradiative energy transfer between fluorescent labels attached to polymers has been used to characterize polymer miscibility, the interpenetration of chain molecules in solution, micelle formation in graft copolymers, the unfolding of collapsed chain molecules in polymer melts, and the transfer of energy absorbed by a large number of donor labels to a small number of acceptors by an "antenna effect." The change in the emission spectrum after ionomer solutions with different fluorescent counterions were mixed provided rate constants for counterion interchange. The fluorescence behavior of dispersions of donor-labeled polymers stabilized by a graft copolymer with acceptor fluorophores in the solution phase led to inferences about the morphology of the dispersed particles.

IN A SYSTEM CONTAINING TWO FLUORESCENT SPECIES SUCH that the emission spectrum of one (the "donor") overlaps the absorption spectrum of the other (the "acceptor"), the excitation energy of the donor molecules may be transferred by a resonance dipole-dipole interaction mechanism over relatively large distances to the acceptor molecules. According to a theory formulated by Förster (*1*), the efficiency E of such nonradiative energy transfer (NET) may be expressed by

$$E = [1 + (r/R_0)^6]^{-1}$$
$$R_0^6 = (8.8 \times 10^{-25})\, J\, n^{-4} \phi_D^0\, \kappa^2 \qquad (1)$$

where r is the distance between donor and acceptor, J is the overlap integral between the emission spectrum of the donor and the absorption spectrum of the acceptor, n is the dielectric constant, ϕ_D^0 is the fluorescence quantum yield of the donor in the absence of acceptors, and κ^2 is a function of the mutual orientation of the donor and acceptor transition moments. With many pairs of fluorophores, the distance, R_0, for which the probability of transfer of the excitation energy is 50%, lies in the range of 2 to 4 nm (*2*). Since E changes rapidly with the donor-acceptor spacing when r/R_0 is not far from unity (for example, E decreases from 0.65 to 0.36 as r/R_0 increases from 0.9 to 1.1), the relative emission intensity of donor and acceptor when the system is irradiated in the donor absorption band may be used as a "spectroscopic ruler" (*3*) to estimate the separation of these two moieties.

NET has been widely used to characterize distances within biological macromolecules or their complexes (*4, 5*). Since these macromolecules usually involve rigid structures, the estimation of donor-acceptor separation from the energy transfer efficiency depends on a knowledge of the mutual orientation of the chromophores. This difficulty can be overcome, in principle, by supplementing data on energy transfer with data on fluorescence depolarization (*6*), but Stryer (*5*) has argued that the uncertainty in the estimated distances is small even if this additional information is not available.

In the applications of NET to studies of synthetic polymers that I discuss in this article, fluorescent labels were attached to (or associated with) chain molecules at long spacings along the contour of the flexible polymer backbone, so that their mutual orientation could be considered to be random. Under these circumstances $\kappa^2 = 0.667$ in fluid media (*1*) and $\kappa^2 = 0.475$ in rigid media where the rotational diffusion constant is small compared to the rate constant for energy transfer (*7*). In such studies we are not concerned with a translation of NET data to donor-acceptor separations, but we use fluorophore-labeled polymers to gain insight into a wide variety of problems such as polymer compatibility, the interpenetration of polymer chain molecules as a function of solution concentration, the kinetics of the unfolding of collapsed chain molecules in polymer melts, the association of graft copolymers to micellar aggregates, the kinetics of ion interchange in solutions of polymers carrying ionized substituents that form ion-pairs with their counterions, the exploration of the "antenna effect" (by which quanta absorbed by a large number of chromophores along a polymer chain are transferred to an acceptor site), and the elucidation of the morphology of polymeric dispersions.

Polymer Compatibility

Whereas most organic liquids consisting of small molecules are miscible with each other, miscibility of long-chain molecules is much more restricted. To those unfamiliar with the behavior of polymers it will come as a surprise to learn that even such similar substances as the high molecular weight polymers of methyl methacrylate and ethyl methacrylate are completely immiscible. The cause of this peculiar behavior was clarified many years ago by Gee (*8*); with small molecules, the large entropy of mixing provides a sufficient driving force so that even a moderately unfavorable enthalpy change can be tolerated. By contrast, in the mixing of long-chain molecules, the entropy change per unit volume is negligible, so that even a slight endothermicity of mixing is sufficient to prevent the formation of a single phase. The mixing of molecules that does not involve specific interactions of the hydrogen bonding or acid-base type is almost always endothermic (*9*), and it follows that some form of specific interaction that will render the process exothermic is usually required for polymer miscibility. An exception to this generalization is provided by some blends of a homopolymer with a copolymer. In this case, energetically unfavorable contacts between

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unlike monomer residues in the copolymer are partially relieved as these residues are separated from one another by blending with a homopolymer and this provides the exothermicity needed for the formation of a stable blend (*10*). Shiomi *et al.* (*11*) have listed various systems in which this effect has been observed.

A number of techniques have been developed to characterize polymer miscibility (*12, 13*). The most widely used involves the determination of glass transition temperatures (T_g) by differential scanning calorimetry. If a blend exhibits two T_g values, each characteristic of one of the polymeric components, the presence of two phases may be inferred, whereas a single T_g at an intermediate temperature is taken as proof of polymer miscibility. This method is applicable only to blends of polymers whose T_g values are reasonably far from each other, and it yields only information concerning the miscibility in the temperature range of the glass transitions. To avoid these limitations, investigations in my laboratory introduced the study of blends of polymers labeled with donor and acceptor fluorophores, respectively. If two distinct phases are formed, the donor and acceptor labels will be too far from each other for efficient energy transfer, but the ratio of donor and acceptor emission intensities will exhibit a decrease as the two phases mix on a segmental level. The high sensitivity of fluorescence spectroscopy makes it possible to carry out such experiments with very small label concentrations, so that the properties of the polymers are not appreciably altered. In an example of a system in which this principle was used, blends of poly(methyl methacrylate) (PMMA) with copolymers of styrene with acrylonitrile were used (*14*). As shown in Fig. 1, the ratio of the emission intensities of the carbazole donor and the anthracene acceptor, I_C/I_A, drops to a low value for blends of copolymers containing 30 to 45 mol % acrylonitrile (with a somewhat broader range when PMMA of a shorter chain length was used). The high efficiency of energy transfer in this range of copolymer composition is indicative of the mixing of the two polymeric components and is consistent with results obtained on this system by neutron scattering (*15*). The value of I_C/I_A does not change abruptly but rather gradually, indicating that there is no sudden transition from an incompatible to a fully miscible system. With a small driving force for phase separation, some mixing of the two polymeric components occurs near the phase boundary, as suggested by the "fuzzy" appearance of these boundaries in electron micrographs (*16*) and by theoretical analysis (*17*).

The NET technique has been used most effectively by Albert *et al.* (*18, 19*) for the study of poly(vinyl chloride) (PVC) blends with syndiotactic PMMA (s-PMMA). The phase separation increases smoothly with an increasing content of s-PMMA in the blend, going through a maximum at a weight fraction 0.8 of s-PMMA (Fig. 2). Albert *et al.* concluded that the NET technique is able to detect compositional inhomogeneities on a shorter scale than differential scanning calorimetry, which had previously led to the view (*20*) that all blends up to a weight fraction 0.8 of s-PMMA are completely homogeneous. In all of these blends, energy transfer is fairly efficient, which indicates that the phase domains cannot be much larger than the R_0 value for transfer from the naphthalene donor to the anthracene acceptor [$\sim$2 nm (*14*)]. The location of the NET maximum, interpreted as the point of phase inversion, showed that s-PMMA is more soluble in PVC than PVC in s-PMMA.

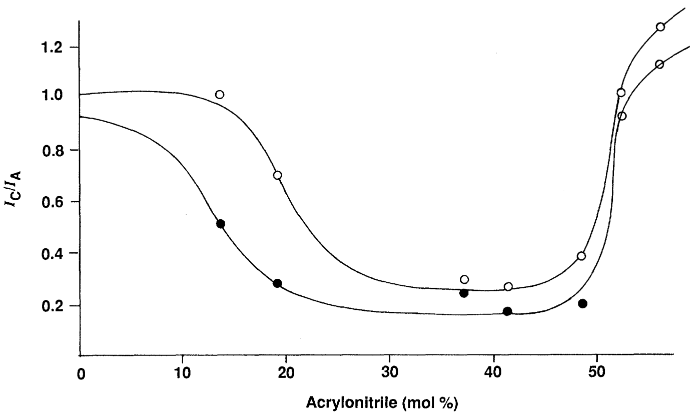


Fig. 1. Ratio of carbazole donor and anthracene acceptor emission intensities, I_C/I_A, in blends of equal weights of carbazole-labeled styrene-acrylonitrile copolymer and anthracene-labeled PMMA, as a function of the acrylonitrile (AN) content of the copolymer. The intrinsic viscosities of the PMMA in benzene at 25°C were 106 ml/g (○) and 18 ml/g (●). [Adapted from (*14*) with permission of the American Chemical Society, Washington, D.C.]

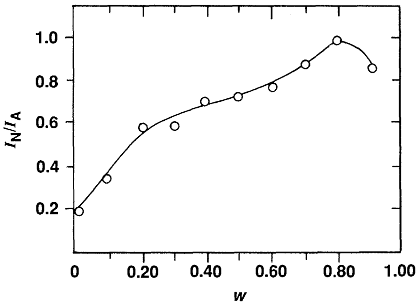


Fig. 2. Ratio of emission intensities of naphthalene donors and anthracene acceptors, I_N/I_A, in blends of naphthalene-labeled s-PMMA and anthracene-labeled PVC as a function of the weight fraction *w* of s-PMMA. All blends contained $10^{-2}M$ donors and acceptors, respectively. [Adapted from (*18*) with permission of the American Chemical Society, Washington, D.C.]

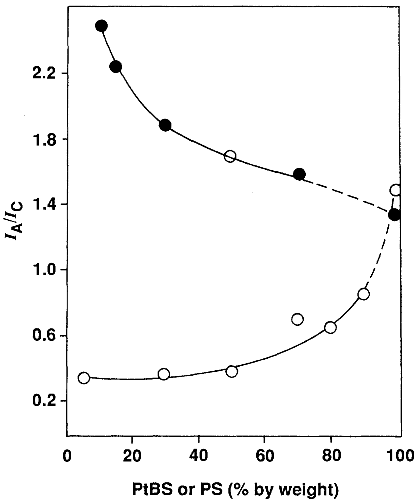


Fig. 3. Ratio of anthracene and carbazole emission intensity in blends of PS-PtBS (carbazole-labeled in the PS block) with anthracene-labeled PS (●) or PtBS (○) as a function of the composition of the blend. Labeled polymers were diluted with unlabeled polymers to label concentrations of $10^{-2}M$. [Adapted from (*21*) with permission of the American Chemical Society, Washington, D.C.]

In the case of block copolymers, the blocks can be selectively labeled, so that NET data provide information about the mixing of the labeled block with the second component of that blend. This approach was used (*21*) to study blends of polystyrene (PS) and poly(*tert*-butylstyrene) (PtBS) with a block copolymer PS-PtBS carrying a donor fluorophore in the PS block (Fig. 3). As expected, NET was much more efficient when this block copolymer was blended with PS than when it was mixed with an acceptor-labeled PtBS, which is incompatible with PS. A similar experiment carried out by Albert *et al.* (*19*) on blends of an acceptor-labeled PVC with a PMMA-PS block copolymer donor-labeled in the PMMA block led to the same efficiency of NET as in blends of the homopolymers PVC and PMMA; these results suggested that the PS block in the PMMA-PS does not interfere with the exothermic interaction of the PMMA block with PVC.

The most vexing aspect of studies of copolymer compatibility concerns the effect of sample preparation. Film casting from a solution containing a mixture of two polymers may, in some cases, lead to homogeneous or phase-separated products depending on the casting solvent that is used (*22*). Such phase separation in a mixture of polymers that should form a single phase at equilibrium is caused by a preferential solvation of one of the polymeric components by the solvent used in the film casting (*23*). A striking demonstration of this effect was observed in a recent study in which NET was used to characterize the compatibility of poly(ethyl methacrylate) (PEMA) with styrene copolymers that carried hydrogen bond–donating carboxyl groups (*24*). We expected the exothermic hydrogen bonding of the carboxyls with the carbonyls of PEMA to counteract the unfavorable energy for the mixing of PS with PEMA and to lead to improved compatibility. The results showed that the extent of phase separation was sharply dependent on the solvent used for film casting (Fig. 4). Dioxane apparently competed with PEMA as a hydrogen bond acceptor, and chloroform was such a strong hydrogen bond donor that the NET was completely insensitive to the carboxyl content of the styrene copolymer.

Polymer Behavior in Solution

When flexible polymer chains are entangled with one another, their conformation becomes interdependent, which causes a loss of entropy. This produces a strong resistance of polymer coils to overlap in dilute solution. However, as the polymer concentration is increased, a point is eventually reached at which all of the space is taken up by the swollen polymer coils and any further increase in solution concentration forces the polymers to interpenetrate. The critical point at which this occurs is commonly denoted by c^*, and it marks the transition from a "dilute" to a "semidilute" solution with characteristic changes in the dependence of the solution properties on the concentration and the chain length of the polymer (*25*).

Whereas c^* may be located by a variety of experimental methods, the question arose whether the extent of overlap of the polymer coils in the semidilute regime may be characterized by a spectroscopic technique. Chang and Morawetz approached this problem (*26*) in the following manner. Solutions containing PS tagged with donor and acceptor fluorophores, respectively, were rapidly frozen and the solvent was removed by sublimation. The resulting polymer samples were pressed into pellets and their emission spectra were recorded. Although all of these samples had identical compositions, their fluorescence exhibited a marked dependence on the concentration of the solution from which they were derived. This was interpreted as reflecting the extent of chain entanglement, which was assumed to have remained unchanged during the fraction of a second required for the freezing of the solution.

Figure 5 illustrates the results obtained. The NET observed in samples freeze-dried from very dilute solutions is small and independent of the nature of the solvent. This characterizes, presumably, a situation in which unentangled polymer chains collapsed into compact spherical globules, such as had been observed for freeze-dried dilute solutions of glassy polymers by electron microscopy (*27*). Once the original solution exceeded c^*, the NET increased, reflecting an increasing chain entanglement. We obtained data for samples derived from solutions with the solvent power decreasing in the order benzene > dioxane > cyclohexane. Unexpectedly, the NET data demonstrated that the degree of chain overlap increases with an increasing solvent power of the medium, although a decreasing solvent power increases the mutual attraction of polymer segments. It appears that an increasing entropic resistance to the interpenetration of less expanded chains is the dominant factor governing the extent of chain overlap. The second unexpected phenomenon was the relative insensitivity of NET to the concentration c of the original solution beyond $c \sim 3c^*$. This was interpreted as indicating that the inner core of the polymer coils resists strongly interpenetration by other chain molecules, so that semidilute polymer solutions would have to be viewed as microscopically heterogeneous.

The basic assumption of this study, that molecular chain entanglement remains unchanged during the rapid freezing of polymer solutions, cannot perhaps be proved rigorously. However, several considerations give us confidence in its validity. First, the NET of freeze-dried samples is independent of the original solvent concentration and the nature of the solvent below the critical concentration c^*, and it increases beyond this point where chain entanglements have been demonstrated by other methods. Second, the dependence of the degree of chain entanglement on the solvent power of the medium, deduced from the study in which the freeze-drying method was used, is identical with that derived from the NET on solutions of fluorophore-labeled PS (*28*). Finally, the data are highly reproducible.

The NET phenomenon has also been exploited for the study of solutions of a graft copolymer in which donor-labeled PS backbones carried acceptor-labeled PMMA branches (*29*). In acetonitrile solution, in which the PMMA grafts are soluble but the PS backbones collapse, the NET efficiency increases sharply above polymer concentrations that have been interpreted as critical concentrations for polymer micelle formation.

Kinetics of the Unfolding of Collapsed Chain Molecules in Polymer Melts

The diffusion of long-chain molecules in polymer melts has been the subject of intensive study since it had been predicted that chains diffuse by a "reptation" mechanism that leads to a self-diffusion coefficient, D, inversely proportional to the square of the chain length (*30*). This results in extremely small values of D for a vinyl polymer chain comprising several thousand monomer residues and since $\langle x^2 \rangle = 2Dt$, where $\langle x^2 \rangle$ is the mean square translation in a given direction in time t, experimental methods with an extremely high spatial resolution are required if D is to be estimated from data collected over a reasonable time. Green *et al.* (*31*) surveyed the various approaches that have been taken toward the solution of this problem.

It was mentioned above that the freeze-drying of dilute solutions of glassy polymers leads to compact globules containing a single polymer molecule. Since such globules produced from polymers with molecular weights as high as 10^6 will have a radius below 10 nm, the interdiffusion of polymer chains contained in them was expected to be relatively rapid once a pellet prepared from this material was heated above T_g. In the first experiments exploiting this concept (*32*) a mixture of polymers labeled with donor and acceptor fluorophores, respectively, was used and the increase in the NET was followed as a measure of the interdiffusion. Since D has the dimension cm^2 sec^{-1}, it was conjectured that the ratio of the square of the particle diameter d and the time $t_{1/2}$ required for the ratio of acceptor and donor emission to move half-way from its initial to its equilibrium value would be proportional to D. In later work (*33*), we used monodisperse PS doubly labeled with donor and acceptor, which was mixed with a large excess of unlabeled polymer. When pellets freeze-dried from a solution of this mixture were heated above T_g, the NET decreased as the labeled polymer expanded from the collapsed state into the unlabeled matrix to its equilibrium extension. In a typical experiment, in which PS with a molecular weight of 9.8×10^4 was used, $t_{1/2}$ was 1400 seconds at 180°C, so that $d^2/t_{1/2} = 3 \times 10^{-16}$, which may be compared to D near 10^{-12} cm^2 sec^{-1} estimated from data of Antonietti *et al.* (*34*). The value of $d^2/t_{1/2}$ had a dependence on polymer chain length similar to that of

Fig. 4. Ratio of carbazole and anthracene emission intensity, I_C/I_A, in blends of carbazole-labeled PS and styrene-methacrylyl glycine (MAG) copolymers with anthracene-labeled PEMA. Films were cast from toluene (○), dioxane (□), and chloroform (△).

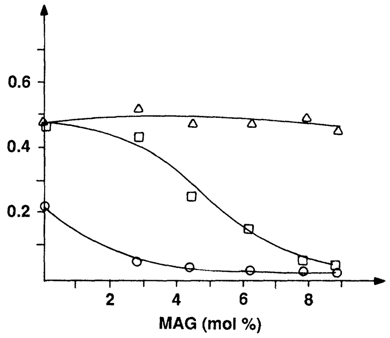
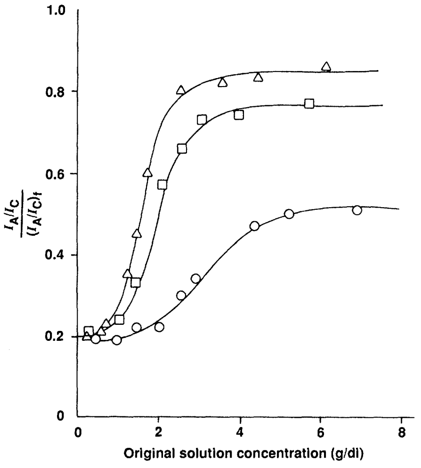


Fig. 5. Ratio of anthracene and carbazole emission intensity, I_A/I_C, in freeze-dried solutions of mixtures of labeled polystyrenes (molecular weight 4.1×10^5) referred to this ratio, $(I_A/I_C)_f$, in films cast from these solutions. [Adapted from (*26*) with permission of the American Chemical Society, Washington, D.C.]



the diffusion coefficient, but its temperature dependence differed from that expected for reptation. Thus the kinetics of the unfolding of collapsed polymer chains are not determined by the *D* value of the polymer melt. In retrospect, this is not surprising since the chain ends, which are buried within the labeled globules, must diffuse to their surface before they can penetrate by reptation into the surrounding unlabeled matrix.

Ion-Pair Interchange in Ionomer Solution

Although factors affecting the equilibrium of ion-pair formation in media of low dielectric constant have been explored in great detail (*35*), no studies of the kinetics of such processes seem to have been reported. The polymer chemist is interested in this problem for two reasons. (i) In the anionic polymerization of vinyl compounds, the rate constant for chain propagation is different for chains terminated by "contact ion pairs" and by "solvent-separated ion pairs." Thus a slow ion-pair interchange will lead to a bimodal chain length distribution (*36*). (ii) The interaction between ion pairs in polymers carrying ionized substituents associated with their counterions (designated as "ionomers") leads to a sharp increase in viscosity both in bulk and in solutions of moderate concentration (*37*), and the rheology of such systems should depend on the rate of counterion interchanges leading to temporary breaks in ion-pair associations linking different chain molecules (*38*).

Rate constants have been obtained for ion-pair interchange in a stopped-flow apparatus monitoring the change in emission intensity after the mixing of solutions of two slightly sulfonated polystyrenes partially neutralized with 2-aminomethyl naphthalene (AMN) and 9-aminomethyl anthracene (AMA), respectively (*39*). As long as AMN and AMA are associated with different polymer chains, their spacing is too large for efficient NET. However, as these counterions interchange and come to be associated with the same polymer chain, their spacing becomes comparable with the characteristic transfer distance R_0 and irradiation in the donor AMN absorption band leads to an increasing AMA emission. Rate constants obtained in dioxane and in a mixture of equal volumes of dioxane and cyclohexane as a function of the ionomer concentration are plotted in Fig. 6. In highly dilute solution, the reaction is slower in the mixed solvent, since the stability of ion pairs increases in a medium of lower polarity. However, as the ionomer concentration increases, its solubility limit in this medium is approached and the polymer aggregation leads to a rapid increase in the rate of ion-pair interchange.

The "Antenna Effect"

In polymers with closely spaced aromatic residues, NET leads to a migration of excitation energy. If a small number of acceptor fluorophores are also attached to the molecular backbone, they will act as traps and light absorption by a large number of donor residues will result in emission from the acceptor. This "antenna effect," in which radiant energy absorbed over a relatively large volume is channeled to a specific moiety, is of particular interest because it may be thought of as "modeling the light-harvesting function of the photosynthetic process" (*40*, p. 224). In dilute solution the NET takes place within the isolated polymer chain, but the expansion of the chain produced in strongly solvating media reduces the NET efficiency (*41*) and this shows that energy migration does not proceed exclusively along the contour of the chain molecule. The "antenna effect" is remarkably efficient. Thus, in a solution of a 1-naphthylmethyl methacrylate copolymer with only one anthracene unit appended for every 160 monomer residues, 30% of the energy absorbed by the naphthalene chromophores was transferred to the anthracenes (*42*).

An interesting result was obtained in a study of acrylic acid copolymers with aromatic comonomers (*40*). Whereas their chains are extended in organic solvents, in basic aqueous solutions the hydrophobic aromatic groups tend to aggregate and this leads to a greatly enhanced NET efficiency. In a copolymer containing 7.5 mol % 1-naphthylmethyl methacrylate and 0.25 mol % anthracene residues, the fraction of energy transferred from naphthalene to anthracene moieties increased from 12% in dioxane to 69% in basic aqueous solution.

Morphology of Polymer Dispersions

When a vinyl monomer is polymerized in a medium in which the polymer is insoluble, stable polymer dispersions may be obtained in the presence of a block or graft copolymer that contains chain segments miscible with the precipitated macromolecules and chain segments miscible with the solvent. The morphology of the disperse phase of such systems has frequently been assumed to have a "core-shell structure" in which a globule of the insoluble polymer is surrounded by a stabilizing layer of the graft copolymer.

This concept has been subjected to a critical examination, with NET used to provide insight into the structure of the disperse phase. Typical studies dealt with dispersions prepared by copolymerizing methyl methacrylate with a small amount of naphthylmethyl methacrylate in an isooctane solution of polyisobutene. Some of the polymethacrylate is grafted to the polyisobutene, and this graft copolymer stabilizes the dispersion of the polymethacrylate, which is insoluble in the hydrocarbon medium (*43*). When anthracene was

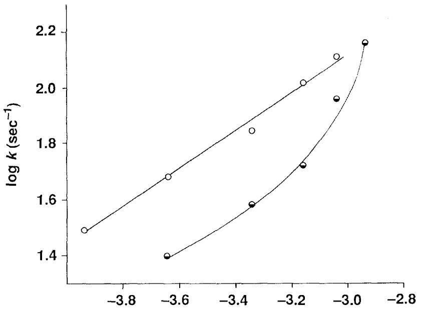


Fig. 6. Rate constants, *k*, for the counterion interchange after the mixing of solutions of PS with 6.9% of the monomer residues sulfonated and with 32% of these sulfonic acid groups neutralized with AMN and AMA, respectively. Solutions in dioxane (○) and a 1:1 mixture of dioxane and cyclohexane (◒) at 17°C. The abscissa specifies the logarithm of the base molarity of the ionomer solutions. [Adapted from (*39*) with permission of the American Chemical Society, Washington, D.C.]

added to the solvent and the system was irradiated in the naphthalene absorption band, the time dependence of the emission intensities indicated that the majority of the naphthalene labels transferred their excitation energy with equal probability to the anthracene acceptors. This observation is inconsistent with the core-shell model, since the time required for the anthracene molecules to diffuse to the center of the polymethacrylate particles is much larger than the excited lifetime of the naphthalene label. The results suggest that the stabilizing graft copolymer, swollen with isooctane, is interlaced throughout the polymethacrylate, so that the anthracene acceptor can penetrate within a distance comparable to R_0 from the naphthalene donors.

Future Research

When a polymer is doubly labeled with a donor and acceptor fluorophore, a change in the expansion of the chain molecule in solution will be reflected in a changing NET. This effect may be used to monitor the kinetics of the expansion of poly(methacrylic acid) after a *p*H jump (*44*). More information could be obtained by time-resolved spectroscopy after flash excitation, since conformational transitions during the excited lifetime produce a variation in the donor-acceptor spacing that leads to a perturbation of the time dependence of the emission spectrum. Haas *et al.* (*45*) have demonstrated this effect on a donor and acceptor end-labeled oligopeptide and interpreted their results in terms of the chain dynamics, but corresponding experiments on high polymers have not been reported.

Time-resolved fluorescence spectroscopy of blends of donor- and acceptor-labeled polymers should also be valuable in probing intermolecular correlations of macromolecules and their interfacial structure. The theoretical framework for such experiments is available (*46*) and awaits experimental exploitation.

REFERENCES AND NOTES

1. T. Förster, *Ann. Phys. (N.Y.)* **2**, 55 (1948); *Z. Naturforsch. Teil A* **4**, 321 (1949); *Discuss. Faraday Soc.* **27**, 7 (1959).
2. I. Berlman, *Energy Transfer Parameters of Aromatic Compounds* (Academic Press, New York, 1973).
3. L. Stryer, *Science* **162**, 526 (1968).
4. I. Z. Steinberg, *Annu. Rev. Biochem.* **40**, 83 (1971).
5. L. Stryer, *ibid.* **47**, 819 (1978).
6. R. E. Dale and J. Eisinger, in *Biomedical Luminescence*, R. F. Chen and H. Edelhoch, Eds. (Dekker, New York, 1975), vol. 1, p. 115.
7. M. Z. Maksimov and I. M. Rotman, *Opt. Spektrosk.* **12**, 237 (1962).
8. G. Gee, *Q. Rev. Chem. Soc.* **1**, 265 (1947).
9. H. Morawetz, *Macromolecules in Solution* (Wiley, New York, ed. 2, 1975), pp. 39–46.
10. R. Kambour, J. T. Bendler, R. C. Bopp, *Macromolecules* **16**, 753 (1983).
11. T. Shiomi, F. E. Karasz, W. J. MacKnight, *ibid.* **19**, 2274 (1986); *ibid.*, p. 2644.
12. D. R. Paul and S. Newman, *Polymer Blends* (Academic Press, New York, 1978), vol. 1.
13. O. Olabisi, L. M. Robeson, M. T. Shaw, *Polymer-Polymer Miscibility* (Academic Press, New York, 1979).
14. F. Amrani, J.-M. Hung, H. Morawetz, *Macromolecules* **13**, 649 (1980).
15. W. A. Kruse *et al.*, *Macromol. Chem.* **177**, 1145 (1976).
16. F. Kollinsky and G. Market, *ibid.* **121**, 117 (1969).
17. E. Helfand and Y. Tagami, *J. Polym. Sci. B* **9**, 741 (1971).
18. B. Albert *et al.*, *Macromolecules* **18**, 388 (1985).
19. B. Albert *et al.*, *J. Polym. Sci. Polym. Chem. Ed.* **24**, 2577 (1986).
20. J. W. Schürer, A. de Boer, G. Challa, *Polymer* **16**, 201 (1975).
21. F. Mikeš, H. Morawetz, K. S. Dennis, *Macromolecules* **17**, 60 (1984).
22. M. Bank, J. Leffingwell, C. Thies, *ibid.* **4**, 43 (1971); R. Gelles and C. W. Frank, *ibid.* **15**, 747 (1982); J. W. Barlow and D. R. Paul, *J. Polym. Sci. Polym. Phys. Ed.* **25**, 1459 (1987).
23. A. Robard and D. A. Patterson, *Macromolecules* **10**, 1021 (1977).
24. C. T. Chen and H. Morawetz, unpublished results.
25. M. Daoud *et al.*, *Macromolecules* **8**, 804 (1975).
26. L. P. Chang and H. Morawetz, *ibid.* **20**, 428 (1987).
27. R. M. Siegal *et al.*, *J. Polym. Sci.* **5**, 111 (1954); M. J. Richardson, *J. Polym. Sci. C* **3**, 21 (1963); H. Reimlinger, *Naturwissenschaften* **63**, 574 (1976).
28. J. M. Torkelson and S. R. Gilbert, *Macromolecules* **20**, 1860 (1987).
29. A. Watanabe and M. Matsuda, *ibid.* **18**, 273 (1985); *ibid.* **19**, 2253 (1986).
30. P. G. de Gennes, *J. Chem. Phys.* **55**, 572 (1971); M. Doi and S. F. Edwards, *J. Chem. Soc. Faraday Trans. 2* **74**, 1789 (1978).
31. P. F. Green *et al.*, *Macromolecules* **18**, 501 (1985).
32. T. Y.-J. Shiah and H. Morawetz, *ibid.* **17**, 792 (1984).
33. C.-Y. Liu and H. Morawetz, *ibid.* **21**, 515 (1988).
34. M. Antonietti, J. Coutandin, R. Grütter, H. Sillescu, *ibid.* **17**, 798 (1984).
35. U. Mayer, *Coord. Chem. Rev.* **21**, 159 (1976).
36. G. Löhr and G. V. Schulz, *Makromol. Chem.* **77**, 240 (1964); D. N. Bhattacharya, C. L. Lee, J. Smith, M. Szwarc, *Polymer* **5**, 54 (1964); R. V. Figini, *J. Polym. Sci. C* **16**, 2049 (1967).
37. N. Z. Erdi and H. Morawetz, *J. Colloid Sci.* **19**, 708 (1964); R. D. Lundberg and H. S. Makowski, *J. Polym. Sci. Polym. Phys. Ed.* **18**, 1821 (1980); R. D. Lundberg and R. R. Phillips, *ibid.* **20**, 1143 (1982).
38. N. Misra and M. Mandal, *Macromolecules* **17**, 495 (1984); M. Hara, A. Eisenberg, R. F. Storey, J. P. Kennedy, *Am. Chem. Soc. Symp. Ser. 302* (1986), p. 176.
39. H. Morawetz and Y. Wang, *Macromolecules* **21**, 107 (1988).
40. J. E. Guillet and W. A. Randall, *ibid.* **19**, 224 (1986).
41. J. S. Aspler, C. E. Hoyle, J. E. Guillet, *ibid.* **11**, 925 (1978).
42. D. A. Holden and J. E. Guillet, *ibid.* **13**, 289 (1980).
43. O. Pekcan, M. A. Winnik, L. Egan, M. D. Croucher, *ibid.* **16**, 699 (1983); M. A. Winnik, in *Photophysical and Photochemical Tools in Polymer Science*, vol. 182 of the North Atlantic Treaty Organization Advanced Study Institutes, Series C, M. A. Winnik, Ed. (Reidel, Dordrecht, 1985), p. 611.
44. J. Horský and H. Morawetz, *Makromol. Chem.*, in press.
45. E. Haas, E. Katchalski-Katzir, I. Z. Steinberg, *Biopolymers* **17**, 11 (1978).
46. G. H. Fredrickson, *Macromolecules* **19**, 441 (1986); ______ and E. Helfand, *ibid.*, p. 2601.
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