(22) Antonietti, M.; Coutandin, J.; Grütter, R.; Sillescu, H. *Macromolecules* **1984**, *17*, 798.
(23) Callaghan, P. T.; Pinder, D. N. *Macromolecules* **1980**, *13*, 1085; **1981**, *14*, 1334; **1983**, *16*, 968.
(24) Amis, E. J.; Han, C. C. *Polymer* **1982**, *23*, 1403.
(25) Amis, E. J.; Han, C. C.; Matsushita, Y. *Polymer*, in press.
(26) Pohl, D. W.; Schwarz, S. E.; Irniger, V. *Phys. Rev. Lett.* **1973**, *31*, 32.
(27) Hervet, H.; Urbach, W.; Rondelez, F. *J. Chem. Phys.* **1978**, *68*, 2725.
(28) Coutandin, J.; Sillescu, H.; Voelkel, R. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 649.
(29) Brown, G. H., Ed., "Photochromism"; Wiley: New York, 1971.
(30) Chang, T.; Yu, H. *Macromolecules* **1984**, *17*, 115.
(31) Brown, W.; Johnsen, R. M.; Stilbs, P. *Polym. Bull.* **1983**, *9*, 305.
(32) Brandrup, J.; Immergut, E. H., Eds. "Polymer Handbook", 2nd ed.; Wiley: New York, 1975.
(33) Takaki, M.; Asami, R.; Kuwata, Y. *Polym. J.* **1979**, *11*, 425.
(34) Morton, M.; Fetters, L. J.; Inomata, J.; Rubio, D. C.; Young, R. *Rubber Chem. Technol.* **1976**, *49*, 303.
(35) Rubio, D. Ph.D. Thesis, University of Akron, Akron, OH, 1975.
(36) Van Rheenen, V.; Cha, D. Y.; Hartley, W. M. *Org. Synth.* **1978**, *58*, 43.
(37) Burns, J.; McCombie, H.; Scarborough, H. A. *J. Chem. Soc.* **1928**, 2928.
(38) Nanya, H. *Nippon Kagaku Zasshi* **1959**, *80*, 219.
(39) Wesson, J. A.; Takezoe, H.; Yu, H.; Chen, S. P. *J. Appl. Phys.* **1982**, *53*, 6513.
(40) Mandema, W.; Zeldenrust, H. *Polymer* **1977**, *18*, 835.
(41) King, T. A.; Knox, A.; Lee, W. I.; McAdam, J. D. G. *Polymer* **1973**, *14*, 151.
(42) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Macromolecules* **1975**, *8*, 804.
(43) Graessley, W. W. *Polymer* **1980**, *21*, 258.
(44) Jamieson, A. M.; Telford, D. *Macromolecules* **1982**, *15*, 1329.
(45) Ferry, J. D.; Grandine, L. D., Jr.; Udy, D. C. *J. Colloid Sci.* **1953**, *8*, 529.
(46) Beuche, F.; Cashin, W. M.; Debye, P. *J. Chem. Phys.* **1952**, *20*, 1956.
(47) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1; **1982**, *47*, 67.
(48) Landry, M. R.; Yu, H., unpublished results.

New Fluorescence Technique for Characterizing Polymer Self-Diffusion†

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ABSTRACT: Dilute solutions of a mixture of naphthalene donor and pyrene acceptor labeled polymers were freeze-dried so that the chain molecules collapsed into globular particles. Pellets pressed from this material were heated above the glass transition temperature, and the emission spectrum was followed as a function of heating time. The interdiffusion of the polymer led to an increase in the nonradiative energy transfer. Data are presented for three molecular weights of polydisperse poly(ethyl methacrylate) and one molecular weight of poly(methyl methacrylate). The method is believed to allow studies of self-diffusion rates smaller than those that can be investigated by other methods.

Introduction

The theoretical analysis of self-diffusion of long flexible-chain molecules by de Gennes[2] and by Doi and Edwards[3] has stimulated a number of workers to devise methods allowing experimental testing of theoretical predictions. Klein and Briscoe[4] followed the diffusion of deuterated polyethylene into normal polyethylene by infrared spectroscopy, and their results confirmed de Gennes' prediction that the self-diffusion coefficient D should be inversely proportional to the square of the chain length. On the other hand, Gilmore et al.,[5] who followed the diffusion of poly(vinyl chloride) into caprolactone by a combination of scanning electron microscopy and energy-dispersive X-ray analysis, found D to vary inversely as the first power of the molecular weight.

Since the dependence of the mean square diffusion distance in a specified direction $\overline{x^2}$ on time, t, is given by $\overline{x^2} = 2Dt$, the ability to measure the very small diffusion coefficients of high polymers depends critically on the spatial resolution of the analytical technique employed. In the method of Klein and Briscoe this resolution was on the order of 10^{-2} cm, allowing estimates of D down to 7×10^{-10} cm^2-s^{-1}, i.e., those of polyethylene with $\overline{M_w} = 23\,000$ at 176 °C. Gilmore et al. were able to estimate D on the order of 10^{-15} cm^2-s^{-1}. In an ingenious method suggested by Sillescu and Zimmer,[6] polystyrene deuterated in the main chain only was to be precipitated, the particles were to be imbedded in perdeuterated polystyrene and the diffusion was to be followed by an NMR technique. With particles having a diameter of 10^{-5} cm (isolated by size fractionation), this technique was expected to allow measurements of D on the order of 10^{-16} cm^2-s^{-1}. Recently, Smith[7] has described the application of fluorescence redistribution measurement after photobleaching for the study of the diffusion at 25 °C of a dye of low molecular weight in poly(methyl methacrylate) containing 18% residual solvent characterized by $D = 1.6 \times 10^{-13}$ cm^2-s^{-1}. The same technique has been used to study the self-diffusion of polymers.[8]

We have used a principle similar to that suggested by Sillescu and Zimmer but which employs a different analytical technique and allows, we believe, even smaller diffusion coefficients to be studied. It has long been known[9] that on freeze-drying dilute solutions of polymers that are glassy at ambient temperatures the individual polymer chains collapse into spherical globules. In a previous study from this laboratory[10] it was shown that if part of the polymer is labeled with a fluorophore (the "donor") whose emission spectrum overlaps the absorption spectrum of a fluorophore (the "acceptor") carried by a second portion of the polymer solute, the fluorescence of the freeze-dried material reflects the original solution concentration, i.e., the extent of the interpenetration of the chain molecules. Thus, when a mixture of donor and

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† Dedicated with affection and admiration to W. H. Stockmayer on his 70th birthday.

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Table I
Characterization of the Polymers Used in This Study

polymer desig[a]	[η], dL/g	$10^{-5}\overline{M}_\eta$	label conc, mol/kg
PMMA	0.60	0.94	
PMMA-P	0.60	0.94	2.05×10^{-3}
PMMA-N	0.60	0.94	2.38×10^{-3}
PEMA (1)	0.93	5.30	
PEMA-P (1)	0.93	5.30	1.35×10^{-3}
PEMA-N (1)	0.93	5.30	1.92×10^{-3}
PEMA (2)	0.54	2.60	
PEMA-P (2)	0.54	2.60	1.97×10^{-3}
PEMA-N (2)	0.54	2.60	1.82×10^{-3}
PEMA (3)	0.18	0.65	
PEMA-P (3)	0.18	0.65	1.37×10^{-3}
PEMA-N (3)	0.18	0.65	2.30×10^{-3}

[a] "P" and "N" indicate a pyrene and naphthalene label, repsectively.

acceptor labeled polymers is freeze-dried from highly dilute solution and a pellet pressed from this material is heated above the glass transition, the interdiffusion of the polymer chains will gradually increase the efficiency of nonradiative energy transfer so that the process may be followed by the change in the emission spectrum.

The present report covers a preliminary exploration of this technique using polydisperse polymers of poly(ethyl methacrylate) and poly(methyl methacrylate).

Experimental Section

4-(1-Pyrenyl)butyl Methacrylate (PBM). 4-(1-Pyrenyl)butanol was prepared from 1-pyrenylbutyric acid (Polysciences) by reduction with $LiAlH_4$ in ether solution. The product (mp 76 °C) was obtained in 55% yield after recrystallization from benzene/hexane. It was converted to the methacrylic ester by treatment with methacrylyl chloride in the presence of triethylamine under nitrogen for 20 h at 70 °C. The ester (mp 79.5 °C) was recrystallized from benzene/hexane.

2-(1-Naphthyl)ethyl Methacrylate (NEM). 1-Naphthylacetic acid (Aldrich) was reduced to 2-(1-naphthyl)ethanol by $LiAlH_4$ in ether solution. The product, obtained in 78% yield, was a colorless liquid that gave a single spot on TLC with silica gel the stationary phase and ethyl ether the carrier. It was converted to the methacrylic ester by the same procedure as specified above. The product was chromatographed on silica gel, using a mixture of hexane and ethyl ether as eluent. The pure fractions were checked by TLC on silica gel and combined to give a 54.5% yield after pumping for 18 h t 10^{-2} torr.

Polymers. Methyl methacrylate (MM) and ethyl methacrylate (EM) copolymers containing about 2.1×10^{-3} mol of PBM or NEM were prepared by free radical initiated polymerization in bulk or in ethyl acetate solution at 70 °C. The molecular weight of the polymer was controlled by monomer dilution or by addition of hydroxyethane thiol as chain-transfer agent. Homopolymers of MM and EM were prepared under conditions similar to these of the labeled copolymers. Average molecular weights were estimated from intrinsic viscosities (dL/g) at 25 °C. For MM homopolymers and copolymers in chloroform the viscosity-average molecular weight was estimated from[11] $[\eta] = 2.52 \times 10^{-5}\overline{M}^{0.80}$, and for EM homopolymers and copolymers in butanone[12] $[\eta] = 2.83 \times 10^{-5}\overline{M}^{0.79}$. The content of the fluorescent labels in the copolymers was obtained from UV absorption using for standards methyl 1-naphthaleneacetate ($\epsilon = 7.67 \times 10^3$ at 281 nm) and 4-(1-pyrenyl)butanol ($\epsilon = 4.19 \times 10^4$ at 345 nm). Table I lists the labeled polymers employed in this study.

Sample Preparation and Fluorescence Measurements. A mixture of naphthalene- and of pyrene-labeled copolymers containing the same molar amount of the label was diluted with the methacrylate homopolymer to a label concentration of 7.9×10^{-5} mol/kg. A solution of 0.5 g of this polymer mixture was dissolved in 50 mL of benzene and rapidly frozen by swirling this solution in a round-bottom flask immersed in dry ice–acetone. The solid benzene was then sublimed under vacuum. A sample of the fluffy powder obtained (4–5 mg) was pressed into a pellet (with a thickness of 50–70 μm) using a pressure of 1000 atm. These pellets were heated for varying periods to temperatures above the glass transition, T_g, and cooled to room temperature. The reflectance fluorescence was then determined with a Hitachi Perkin-Elmer MPF-2A spectrometer equipped with a 150-W xenon lamp. Samples were irradiated at 282 nm (where the extinction coefficients of the naphthalene and pyrene labels were 7.6×10^3 and 10.4×10^3, respectively), and changes in the nonradiative energy transfer[13] were characterized by the relative emission intensity of the pyrene label at 395 nm and the naphthalene label at 339 nm. Control experiments were carried out in which homogeneous samples were prepared by film casting. These samples had the same overall composition as the freeze-dried samples.

Results and Discussion

The carbazole donor and anthracene acceptor fluorophores that were used in our previous studies[10,14] proved to be unstable at elevated temperatures and, therefore, could not be employed in this investigation. The naphthalene donor and the pyrene acceptor were found to be acceptable. The characteristic distance R_0 at which the nonradiative energy transfer between 1-methylnaphthalene and pyrene has a 50% efficiency has been given[15] as 2.86 nm, and we assumed that this would correspond closely to the behavior of our labels. Unfortunately, at the naphthalene label absorption peak at 282 nm the pyrene acceptor has a larger extinction coefficient than the naphthalene donor, so that anthracene emission is prominent even in the absence of energy transfer. Nevertheless, the ratio of pyrene and naphthalene emission as characterized by the ratio of fluorescence intensities at 395 and 339 nm, I_{395}/I_{339}, was found to be sufficiently different in cast films in which the labeled polymers are distributed at random ($I_{395}/I_{339} \approx 4$) and in freeze-dried mixtures containing separated donor and acceptor labeled polymers (I_{395}/I_{339} ranging from 1.95 to 2.15) to allow us to characterize the polymer interdiffusion by the changes in this ratio.

Figure 1 shows plots of I_{395}/I_{339} as a function of heating time for poly(ethyl methacrylate) with three average molecular weights at various temperatures, and Figure 2 shows results obtained with a sample for poly(methyl methacrylate). The results show that the energy transfer does increase with time, indicating a gradual interdiffusion of donor- and acceptor-labeled polymers. Since polydisperse polymers were used in this preliminary study and the diffusion coefficient of chain molecules in bulk is a steep function of chain length, quantitative interpretation of the results is not possible. Nevertheless, some qualitative observations may be made: (1) For poly(ethyl methacrylate) with $\bar{M}$ equal to 0.70×10^5, 2.6×10^5, and 5×10^5, the self-diffusion rates seem to be similar when the three samples are heated to 100, 120, and 140 °C, respectively. (2) Poly(methyl methacrylate) with a very small molecular weight ($\bar{M} = 0.94 \times 10^5$) exhibited much slower self-diffusion than poly(ethyl methacrylate) with a 5 times longer chain length. The low mobility of PMMA relative to PEMA would be expected because of the much closer proximity of PMMA to its glass transition temperature in the temperature range of this study. Using the parameters given by Berry and Fox,[16] one expects the ratio of the frictional coefficients per monomer residue of PMMA and PEMA, respectively, to be 37 at 120 °C and 12 at 140 °C.

Assuming that the spatial resolution of our method is characterized by the diameter of the spherical polymer particle, d, on the order of 10^{-6} cm, and if we limit the experimental time to 10^5 s, then diffusion coefficient, D,

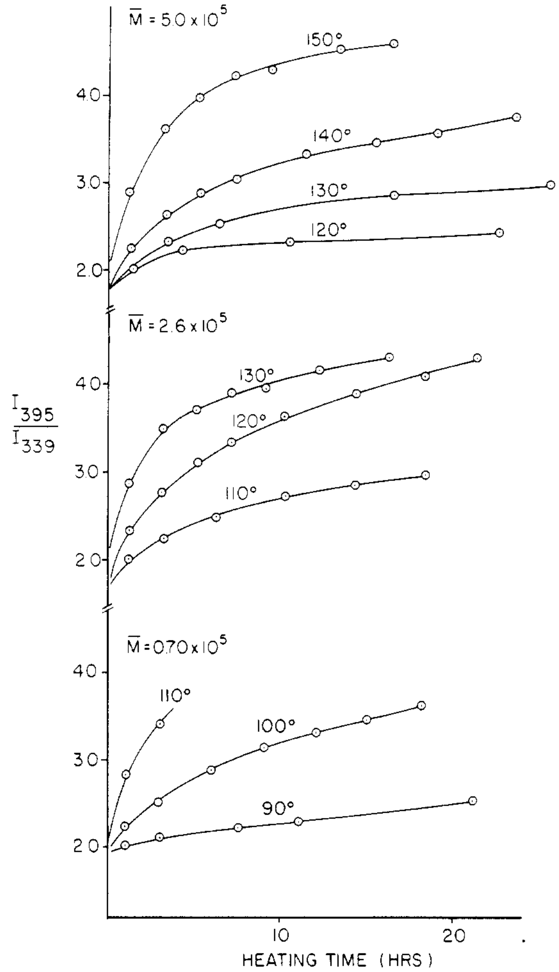

Figure 1. Dependence of the ratio of the emission intensity at 395 and 339 nm on the heating time of freeze-dried mixtures of naphthalene- and pyrene-labeled poly(ethyl methacrylate).

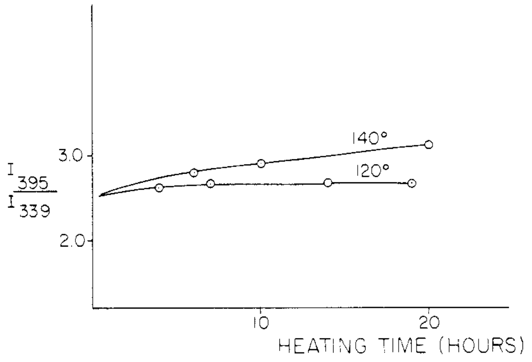

Figure 2. Dependence of the ratio of the emission intensity at 395 and 339 nm on the heating time of freeze-dried mixtures of naphthalene- and pyrene-labeled poly(methyl methacrylate).

on the order of 10^{-17} cm^2-s^{-1} should be accessible to characterization by this method. Specifically, if a time $t_{1/2}$ is required for the energy-transfer efficiency to change halfway from its initial value to the value corresponding to a uniform distribution of donor- and acceptor-labeled polymers, then it may be conjectured that $d^2/t_{1/2}$ is proportional to D. However, this assumption is somewhat uncertain since the unfolding of the original compact sphere to a random coil shape of the polymer chain is a complex process whose rate need not necessarily be proportional to D, which refers to the mobility of the unfolded chain.

Obviously, it will be important to assess the utility of this method using polymer samples with a narrow chain length distribution. Attachment of labels to preformed polymers has previously been used in this laboratory,[14b] and we plan to use polystyrenes with narrow chain length distributions labeled in this manner in future studies.

Note Added in Proof: The elegant paper by Antonietti et al. published in this issue (p 798) shows that the fluorescent labels reduce to a measureable extent the polymer diffusion coefficient.

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Registry No. PMMA, 9011-14-7; PMMA-P, 87450-41-7; PMMA-N, 87450-42-8; PEMA1, 9003-42-3; PEMA-P(1), 87450-43-9; PEMA-N(1), 87450-44-0; PBM, 71254-27-8; NEM, 72642-30-9; 4-(1-pyrenyl)butanol, 67000-89-9; 1-pyrenylbutyric acid, 3443-45-6; methacrylyl chloride, 920-46-7; 2-(1-naphthyl)ethanol, 773-99-9; 1-naphthylacetic acid, 86-87-3.

References and Notes

(1) Abstracted from a doctoral dissertation to be submitted by T. Y.-J. Shiah to the Graduate School of the Polytechnic Institute of New York.
(2) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(3) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789.
(4) Klein, J.; Briscoe, B. J. *Proc. R. Soc. London, Ser. A* **1979**, *365*, 53.
(5) Gilmore, P. T.; Falabella, R.; Laurence, R. L. Macromolecules **1980**, *13*, 880.
(6) Sillescu, H.; Zimmer, G. *Ber. Bunsenges. Phys. Chem.* **1979**, *83*, 396.
(7) Smith, B. A. *Macromolecules* **1982**, *15*, 469.
(8) Smith, B. A.; Samulski, E. T.; Yu, L.-P.; Winnik, M. A. *Phys. Rev. Lett.*, in press.
(9) (a) Siegel, B. M.; Johnson, D. H.; Mark, H. *J. Polym. Sci.* **1950**, *5*, 111. (b) Richardson, M. J. *Proc. R. Soc. London, Ser. A* **1964**, *279*, 50. (c) Reimlinger, H. *Naturwissenschaften* **1976**, *63*, 574.
(10) Jachowicz, J.; Morawetz, H. *Macromolecules* **1982**, *15*, 828.
(11) Baysal, B.; Tobolsky, A. V. *J. Polym. Sci.* **1952**, *9*, 171.
(12) Chinai, S. N.; Samuels, R. J. *J. Polym. Sci.* **1956**, *19*, 463.
(13) Förster, T. *Discuss. Faraday Soc.* **1959**, *27*, 7.
(14) (a) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649. (b) Mikeš, F.; Morawetz, H.; Dennis, K. S. *Ibid.* **1980**, *13*, 969. (c) Morawetz, H. *Ann. N.Y. Acad. Sci.* **1981**, *366*, 404.
(15) Berlman, I. B. "Energy Transfer Parameters of Aromatic Compounds"; Academic Press: New York, 1973; p 312.
(16) Berry, G. C.; Fox, T. G. *Adv. Protein Sci.* **1968**, *5*, 270.