Furthermore it should be possible to study reaction mechanism using this method not only to follow molecular weight changes but also the proportions of modified end units (free acid vs. methyl ester or ethylenic vs. hydroxylated) in the reaction product. When suitable calibrated oligomers are available the retention time is a useful measure of degree of polymerization.

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References and Notes

(1) (a) Université de Montréal; (b) Institut Pasteur.
(2) J. N. Baptist, U.S. Patent, 3 036 959.
(3) (a) M. Lemoigne, *Ann. Inst. Pasteur, Paris,* **41,** 148 (1927); (b) *ibid.,* **39,** 144 (1925)
(4) J. R. Shelton, D. E. Agostini, and J. B. Lando, *J. Polym. Sci.,* **9,** 2789 (1971).
(5) D. E. Agostini, J. B. Lando, and J. R. Shelton, *J. Polym. Sci.,* **9,** 2775 (1971).
(6) S. Akita, Y. Einaga, Y. Miyaki, and H. Fujita, *Macromolecules,* **9,** 774–780 (1976).
(7) J. Cornibert, R. H. Marchessault, H. Benoit, and G. Weill, *Macromolecules,* **3,** 741–746 (1970).
(8) B. Hauttecoeur, M. Jolivet, and R. Gavard, *C. R. Hebd. Seances Acad. Sci.,* **274,** 2729–2732 (1972).
(9) A. Képes and C. Peaud-Lenoël, *C. R. Hebd. Seances Acad. Sci.,* **234,** 756 (1952).
(10) K. Okamura, Ph.D. Thesis, College of Forery, SUNY, Syracuse, N.Y., 1967.
(11) B. Hauttecoeur, M. Jolivet, and R. Gavard, *C. R. Hebd. Seances Acad. Sci.,* **280,** 2801 (1975).
(12) B. Hauttecoeur, M. Jolivet, and R. Gavard, *C. R. Hebd. Seances Acad. Sci.,* **274,** 1957 (1960).
(13) L. D. Metcalfe and A. A. Schmitz, *Anal. Chem.* **33,** 363 (1961).

Communications to the Editor

A New Method for the Study of Polymer Compatibility[1]

It is well known that most polymer pairs form incompatible mixtures.[2] The cause of this phenomenon has been clarified by Gee[3] who pointed out that for the mixing of two polymeric species the entropy of mixing per unit volume is negligible, so that only pairs of polymers which mix with an evolution of heat will form thermodynamically stable mixtures.

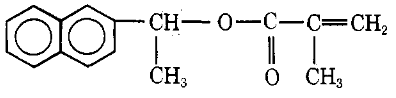
A number of methods have been employed for the characterization of polymer compatibility. Optical clarity of mixtures[4] is frequently used as a test but it suffers from the obvious limitation that light scattering will only be observed if the two polymers have significantly different refractive indices. A comparison of the heat of solution of the components of a mixture and the mixed polymers yields the heat of mixing and this experimentally exacting method has been shown to give results which correlate with other criteria of compatibility.[5–7] DSC measurements of glass transition,[8,9] measurements of dynamic mechanical properties,[9,10] and electron microscopic studies[11] are the methods used most frequently for compatibility studies. Various aspects of studies of multicomponent polymer systems have been reviewed in a recent monograph.[12] It should be noted that different methods have different powers of resolution. For instance, blends of poly(2,6-dimethyl-1,4-phenylene ether) and isotactic polystyrene exhibit two-phase behavior by dynamic mechanical testing, while DSC studies give results typical of a single phase.[9] On the other hand, dynamic mechanical testing was found to be less sensitive than electron microscopy which will reveal separate phases even if their domains have dimensions as small as 10 nm.[11]

We have found that the phenomenon of nonradiative energy transfer[13] is a powerful tool for the study of polymer compatibility. If the emission spectrum of a donor (D) overlaps the absorption spectrum of an acceptor chromophore, light absorbed by D may be emitted by A. The dependence of the efficiency of this process on the distance r between the two chromophores is of the form

$$\mathrm{Eff} = [1 + (r/R)^6]^{-1} \qquad (1)$$

when R is a characteristic distance depending on the refractive index of the medium and the mutual orientation of the chromophores, with R^6 proportional to the overlap integral of the emission spectrum of D and the absorption spectrum of A. In favorable cases R may be as large as 4 nm. Thus, if two polymers are labeled with D and A, respectively, the efficiency of energy transfer in a system containing both polymers characterizes the extent of their interpenetration.

We have employed in our studies copolymers of I and II.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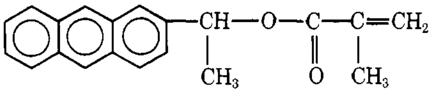
II

The naphthyl group has an absorption maximum at 287 nm and its emission spectrum has maxima between 325 and 336 nm, which overlap the absorption spectrum of the anthryl group. The anthryl group emission has maxima at 388, 408, and 432 nm, with the central peak most intense. Nonradiative transfer efficiencies were determined by recording the reflectance fluorescence spectrum of films cast from a mixed polymer solution irradiated at 278 nm. The results were characterized by I_D/I_A, the ratio of the fluorescence intensity of the donor at 336 nm and the acceptor at 408 nm.

Figure 1 shows results obtained with blends, containing equal weights of poly(methyl methacrylate) labeled with 1.4 wt % of II and methyl methacrylate–butyl methacrylate copolymers labeled with 1.2 wt % of I. As expected, I_D/I_A increased with an increasing butyl methacrylate content of the copolymer, reflecting the decrease in energy transfer accompanying decreasing compatibility. The most striking result is the demonstration that the technique is able to characterize the decreasing interpenetration of the polymeric components, rather than make the merely qualitative distinction between a "compatible" and "incompatible" system. The high sensitivity of our technique may be illustrated by comparison with the use of dynamic mechanical measurements for the characterization of compatibility. In a study of the compatibility of methyl methacrylate–butyl acrylate copolymers,[10] the components of the system had to differ by 20 mol % in their composition before two damping maxima could be resolved. By contrast, in the similar system used by us, a change in I_D/I_A

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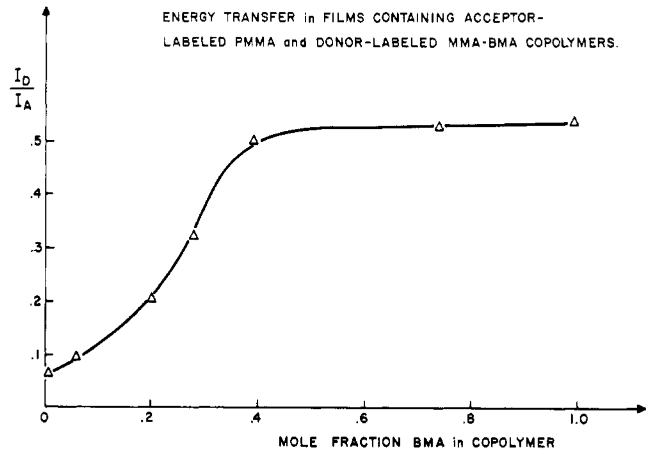

Figure 1. Nonradiative energy transfer in films containing a mixture of equal weights of an acceptor-labeled poly(methyl methacrylate) and donor-labeled methyl methacrylate–butyl methacrylate copolymers. The molecular weight of the polymers was estimated from solution viscosities as 380 000.

is easily observed with a difference of 5 mol % in the composition of the two polymers.

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References and Notes

(1) This work will form part of a Ph.D. dissertation to be submitted by F.A. to the Graduate School of the Polytechnic Institute of New York in June 1978.
(2) S. Krause, *J. Macromol. Sci., Rev. Macromol. Chem.*, **7**, 251 (1972).
(3) G. Gee, *Q. Rev., Chem. Soc.*, **1**, 265 (1947).
(4) T. Nishi, T. T. Wang, and T. K. Kwei, *Macromolecules*, **8**, 227 (1975).
(5) G. L. Slonimski, *J. Polym. Sci.*, **30**, 625 (1958).
(6) M. P. Zverev, L. A. Polovikhina, A. N. Barash, L. P. Mal'kova, and G. D. Litovchenko, *Vysokomol. Soedin.*, **16**, 2098 (1974).
(7) S. Ichihara, A. Kamatsu, and T. Hata, *Polym. J.*, **2**, 640 (1971).
(8) H. E. Bair, *Polym. Eng. Sci.*, **10**, 247 (1970).
(9) J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, 133 (1970).
(10) F. Kollinsky and G. Markert, *Adv. Chem. Ser.*, **No. 99**, 175–188 (1972).
(11) M. Matsuo, C. Nozaki, and C. Jyo, *Polym. Eng. Sci.*, **9**, 197 (1969).
(12) *Adv. Chem. Ser.*, **No. 99** (1972).
(13) I. Z. Steinberg, *Annu. Rev. Biochem.*, **40**, 83 (1971).

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CORRECTIONS

"Statistical Mechanical Treatment of Protein Conformation. 2. A Three-State Model for Specific-Sequence Copolymers of Amino Acids", by Seiji Tanaka* and Harold A. Scheraga, Volume 9, Number 1, January–February 1976, pages 165 and 166.

The upper limit of the product in eq 54, p 165, should be $i + n - 2$.

Equation 65 on page 166 should read:

$$P(i|n|\{\rho\}) \neq \left[\prod_{k=i}^{i+n-1} F_{k;\eta_k}\right]_{\{\rho\}}$$

or

$$P(i|n|\{\rho\}) \neq \left[\prod_{k=i}^{i+n-1} P(k|1|\eta_k)\right]_{\{\rho\}}$$

"Statistical Mechanical Treatment of Protein Conformation. 3. Prediction of Protein Conformation Based on a Three-State Model", by Seiji Tanaka* and Harold A. Scheraga, Volume 9, Number 1, January–February 1976, page 170.

The upper limit of the product in eq 9 should be $i + n - 2$.

"Statistical Mechanical Treatment of Protein Conformation. 6. Elimination of Empirical Rules for Prediction by Use of a High-Order Probability. Correlation between the Amino Acid Sequences and Conformations for Homologous Neurotoxin Proteins", by Seiji Tanaka* and Harold A. Scheraga, Volume 10, Number 2, March–April 1977, page 308.

The upper limit of the product in eq 5 should be $i + n - 2$.

These were typographical errors in printing. However, these errors were *not* made in the computations.

* Deceased November 8, 1977.

"Cross Relaxation in Poly(vinylidene fluoride) from Transient Overhauser Measurements", by V. J. McBrierty and D. C. Douglass*, Volume 10, Number 4, July–August 1977, page 855.

Due to a typographical error in our manuscript eq 4 and 5 are stated incorrectly. In eq 4 τ_c should be replaced by 10^{-8}. τ_c in eq 5 should read $S_z - S_0 = S_0[e^{-t/D_1} + e^{-t/T_1}]$.

The correct equations have been used in subsequent analysis.