

# Behavior of Azo Dyes Dispersed in Fluid Polymeric Matrices with Different Rheological Properties. A Kinetic Study of the *cis-trans* Isomerization of 3'-Nitro-4-Diethylamino Azobenzene in Polyethylenoxides

ERNESTINA DUBINI-PAGLIA,\* PIER LUIGI BELTRAME, and BRUNO MARCANDALLI, *Dipartimento di Chimica Fisica ed Elettrochimica, Università di Milano, 20133 Milano, Italy*, ALBERTO SEVES, *Stazione Sperimentale per la Cellulosa, Carta e Fibre Tessili Vegetali ed Artificiali, 20133 Milano, Italy*, and LOREDANA VICINI, *Stazione Sperimentale per l'Industria delle Conserve, 43100 Parma, Italy*

## Synopsis

The thermal *cis-trans* isomerization of 3'-nitro-4-diethylaminoazobenzene in seven polyethylenoxides at different molecular weight has been studied kinetically in the temperature range 35–70°C. The dependence of the reaction rate on the polymer polarity and viscosity is discussed. The kinetics of the isomerization of the dye dispersed in the fluid polymeric matrix was found to be a useful probe of the structural features of the polymer.

## INTRODUCTION

The thermal *cis-trans* isomerization of azobenzenes has been studied extensively with the aim to gain a deeper insight into the reaction mechanism that appears rather complex.

The dependence of this isomerization was examined on the presence and nature of substituents on the benzenic nuclei bound to the group  $-\text{N}=\text{N}-$ ,<sup>1-5</sup> on the length of some chains inserting azobenzenes,<sup>6,7</sup> on solvent effect,<sup>1-3,8</sup> on the nature of the polymeric matrices dispersing azobenzenes in the case of reactions carried out below and above the glass transition temperature,<sup>4-7</sup> and on temperature and pressure effect.<sup>3-5,9</sup>

On the other hand, the viscosity effect of the system surrounding the azobenzene on the kinetics of its isomerization has not been measured yet. However, it is known that the viscosity of a medium is correlated with its free volume<sup>10</sup> and this parameter can affect the kinetics of the *cis-trans* isomerization of dispersed azobenzene.<sup>4</sup> As a result, a dependence of such kinetics on viscosity of the medium could be expected. Analogously, some authors observed an influence of viscosity on the *trans-cis* photoisomerization of stilbenes even if the reverse reaction did not show such a dependence.<sup>11</sup>

\*To whom correspondence should be addressed.

In this work we have investigated the viscosity effect on the thermal *cis-trans* isomerization of 3'-nitro-4-diethylaminoazobenzene dispersed in various polyethylenoxides at different molecular weight. These fluid polymeric matrices allow a correlation of viscosity and other rheological properties with the kinetics of the isomerization. The kinetics of isomerization can be usefully employed as a probe of the interaction between a substance dispersed in a polymeric matrix and the polymer.

## EXPERIMENTAL

### Material

3'-Nitro-4-diethylaminoazobenzene (NDAB) was kindly supplied by ACNA S.p.A. Polyethylenoxides (PEO) at different molecular weight were purchased from Fluka A.G. Polymer with a declared molecular weight  $> 17,000$  gave  $M_v = 18,000$  by viscosity measurements in benzene at 20°C.

In every case polymers were dyed in bulk by adding such an amount of NDAB as to obtain dye concentrations  $\approx 2 \times 10^{-5}M$ . Colored polymers were found to be thermally stable up to 70°C.

Apparent viscosities were obtained by a Haake-Couette viscometer in the shear rate ( $\dot{\gamma}$ ) range 2.72–147 s<sup>-1</sup>. Some samples behaved as Newtonian melts in the investigated temperature range 35–70°C while others, with high molecular weight, showed pseudoplastic behavior (dependence of apparent viscosity  $\eta_a$  on  $\dot{\gamma}$ ). Zero shear viscosity ( $\eta_0$ ) for pseudoplastic melts was calculated by using a modified Cross-Bueche equation<sup>12</sup>

$$\eta_0/\eta_a = 1 + (\alpha\dot{\gamma})^m$$

where  $m$  gives a measure of the shear-thinning; the plot  $1/\eta_a$  versus  $\dot{\gamma}^m$  showed linearity for  $m = 2/3$  as usually found for polymer melts.<sup>13</sup>

### Kinetic Measurements

Each sample of dyed polymer was thermostatted in a glass cell overnight in the dark and subsequently exposed for 15 min to the light of a 100 W tungsten lamp, a time long enough to reach a photostationary state without photofading. After irradiation, the cell was quickly introduced into the thermostatted cell compartment of a Cary 118 spectrophotometer and the thermal return to the *trans* configuration was kinetically followed by monitoring the absorbance changes at a proper  $\lambda_{max}$  according to a standard procedure.<sup>2-4</sup> The isomerization kinetics were found to be strictly first order.

Some kinetic runs, carried out in solvents different from pure fluid polymers, were found to be very fast. In these cases, a Nortech (Salisbury, England) model FPX1 flash photolysis apparatus was used. The transient signals were recorded by means of a Tektronix mode 5115 oscilloscope and a Polaroid camera.

## RESULTS

Seven polyethylenoxides (PEO) of different molecular weight ( $\bar{M}$ ) in the range 400–18,000 were considered. They were dyed with 3'-nitro-4-diethyl-

TABLE I  
 Values of Zero-Shear Viscosity ( $\eta_0$ ) vs. Temperature and Activation Energies of Viscous Flow ( $E_{\text{vis}}$ ) of Various Polyethylenoxides of Different Molecular Weight Dyed with  $2 \times 10^{-5}M$  NDAB

$T$ (°C)	$\eta_0$ (Pas)						$E_{\text{vis}}$ (kcal/mol)
	35	45	55	60	65	70	
$\bar{M} = 400$	0.073	0.051	0.036	0.030	0.027		$6.91 \pm 0.15$
1,000	0.162 <sup>a</sup>	0.124	0.089	0.072	0.064		$7.02 \pm 0.22$
2,000		0.226 <sup>b</sup>	0.190	0.162	0.140		$6.82 \pm 0.53$
4,000				0.502	0.432	0.372	$6.74 \pm 0.24$
6,000				1.098	0.942	0.811	$6.81 \pm 0.15$
10,000					6.328	5.419	$7.04 \pm 0.48$
18,000					45.285	39.056	$6.73 \pm 0.54$

<sup>a</sup>At 37°C.

<sup>b</sup>At 50°C.

aminoazobenzene (NDAB) in bulk. The zero-shear viscosities ( $\eta_0$ ) of the colored polymers were measured in the temperature range 35–70°C and the corresponding activation energies of viscous flow ( $E_{\text{vis}}$ ) were calculated (Table I).

After the irradiation of dyed samples with a tungsten lamp and the consequent photochemical *trans-cis* isomerization of the dye, the thermal return to the *trans* configuration of NDAB was kinetically followed. The first-order rate constants ( $k$ ) of the thermal *cis-trans* isomerization as functions of temperature and the corresponding activation parameters, evaluated according to Eyring equation, are reported in Table II. The thermal process was studied at a temperature much higher than the glass transition temperature of the polymer ( $T_g = -59^\circ\text{C}$ ).<sup>12</sup>

The trends of  $\ln \eta_0$  and  $\ln k$  at 65°C vs.  $\ln \bar{M}$  are shown in Figure 1.

The values of  $E_{\text{max}}$ , chosen as a polarity index of the medium and obtained from the relevant absorption maxima of NDAB in the various polymer samples, are reported in Figure 2 vs.  $\bar{M}$ , while the trend of  $\ln k$  at 65°C vs.

TABLE II  
 Rate Constants vs. Temperature and Activation Parameters for the Thermal *cis-trans* Isomerization of NDAB in PEOs of Different Molecular Weight

$T$ (°C)	$10^2 \times k$ (s <sup>-1</sup> )						$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (e.u.)
	35	45	55	60	65	70		
$\bar{M} = 400$	0.98	1.43	2.65	3.42	4.69		$10.3 \pm 0.7$	$-34.6 \pm 2.2$
1,000	0.56 <sup>a</sup>	0.82	1.38	2.01	3.08		$11.8 \pm 1.0$	$-31.0 \pm 3.1$
2,000		0.60 <sup>b</sup>	0.88	1.29	2.20		$17.8 \pm 1.3$	$-13.7 \pm 3.8$
4,000				1.12	1.79	2.59	$18.5 \pm 1.0$	$-12.2 \pm 3.0$
6,000				1.07	1.70	2.53	$18.9 \pm 0.8$	$-11.0 \pm 2.5$
10,000					1.58	2.50		
18,000					1.49	2.48		

<sup>a</sup>At 37°C.

<sup>b</sup>At 50°C.

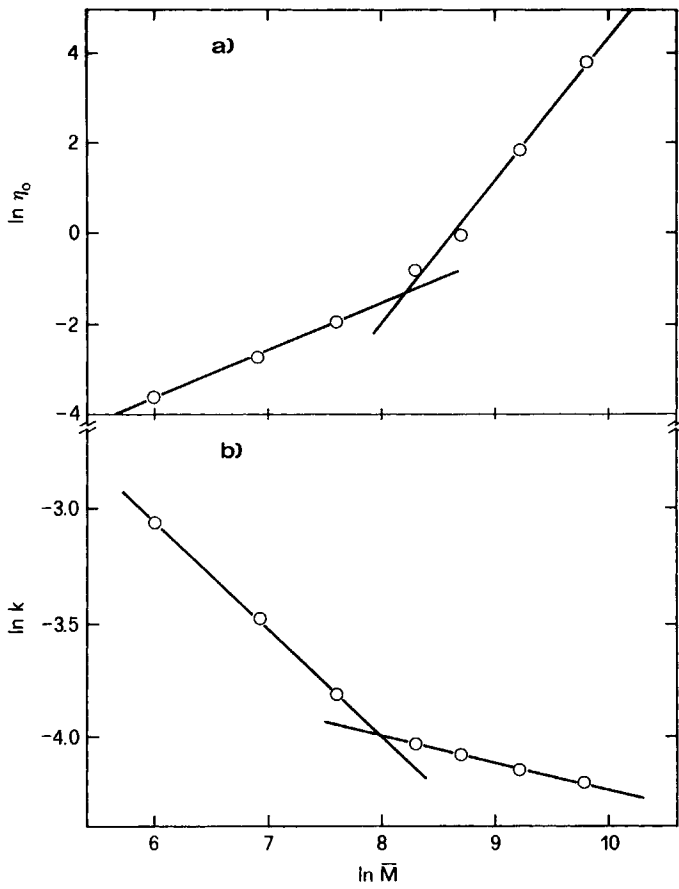


Fig. 1. Zero-shear viscosity ( $\eta_0$ ) of PEOs and (b) rate constants ( $k$ ) of the isomerization of NDAB in PEOs as functions of the polymer molecular weight ( $\eta_0/\text{Pas}$ ;  $k/\text{s}^{-1}$ ;  $T = 65^\circ\text{C}$ ).

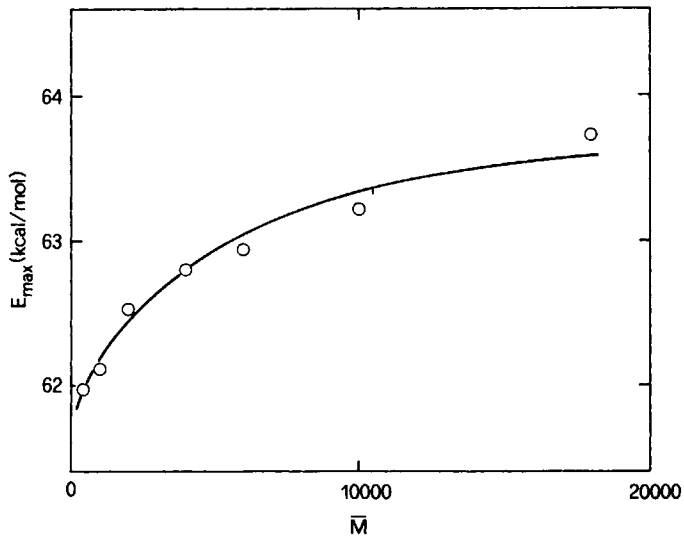


Fig. 2. Values of  $E_{\max}$  ( $\pi$ ,  $\pi^*$ ) as a function of the polymer molecular weight.

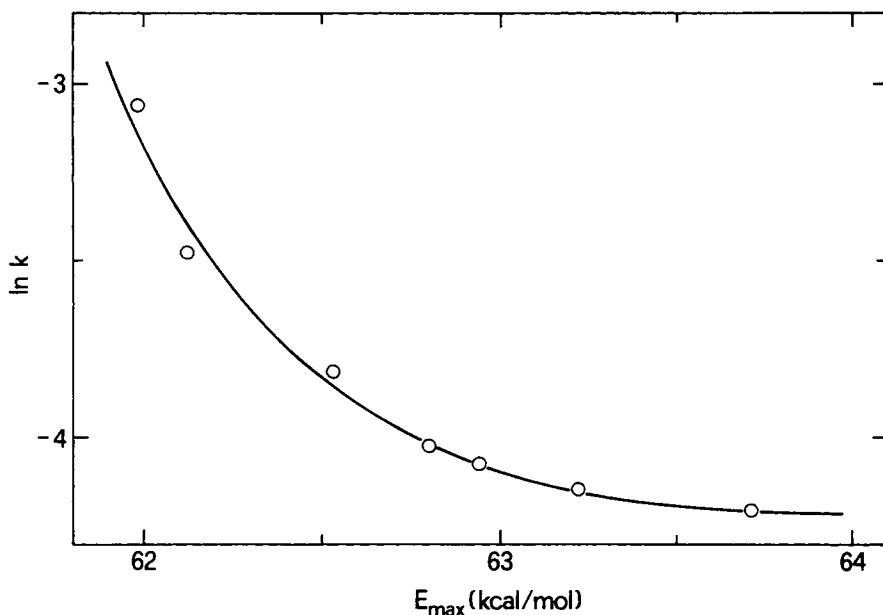


Fig. 3. Kinetic data at 65°C vs. polarity of the medium expressed by the values of  $E_{\max}$  ( $\pi$ ,  $\pi^*$ ).

$E_{\max}$  is drawn in Figure 3. In both cases no linear relationships have been obtained.

Some kinetic runs were carried out in ethylene glycol, carbon tetrachloride (and their mixtures with PEO 400), diethylene glycol, and diethylene glycol dimethyl ether, in order to check the sensitivity of the reaction to the solvent polarity in a more detailed manner. The kinetic coefficients of the isomerization of NDAB in ethylene glycol, carbon tetrachloride and their mixtures with PEO 400 are collected in Table III together with the corresponding values of  $E_{\max}$ .

### DISCUSSION

The zero-shear viscosity of the dyed molten polymers here considered increases with increasing molecular weight in the whole range of temperature

TABLE III  
Rate Constants at 25°C of the Thermal *cis-trans* Isomerization  
and Values of  $E_{\max}$  ( $\pi$ ,  $\pi^*$ ) for NDAB in Various Solvents

Solvent <sup>a</sup>	$10^4 \times k_{25}$ (s <sup>-1</sup> )	$E_{\max}$ (kcal/mol)
EG	$> 10^{7b}$	61.2
EG + PEO 400 10:90	911	61.7
EG + PEO 400 5:95	394	61.8
PEO 400	61.5	61.9
CCl <sub>4</sub> + PEO 400 20:80	29.1	62.2
CCl <sub>4</sub> + PEO 400 40:60	8.93	62.9
CCl <sub>4</sub>	1.28	66.0

<sup>a</sup> EG = Ethylene glycol; mixture composition in v/v.

<sup>b</sup> Estimated by flash photolysis.

explored 35-70°C (Table I). By plotting  $\ln \eta_0$  at 65°C vs.  $\ln \bar{M}$ , two linear trends with different slopes were obtained (Fig. 1). The resulting intersection point gives a value of the critical molecular weight of the polymer  $M_{cr} = 3600$  in a fair agreement with the literature value (3400).<sup>12</sup> For  $\bar{M} > M_{cr}$ , the slope is higher and its value 3.2 is well comparable with the coefficient 3.4 of the equation derived by Bueche on the basis of the influence of chain entanglements on polymer flow.<sup>13</sup> For  $\bar{M} < M_{cr}$ , where entanglements are not important to flow behavior, we obtained a slope value 1.0 close to the one usually measured.<sup>12</sup>

The thermal *cis-trans* isomerization of NDAB dispersed in the various PEOs showed strictly first-order kinetics. This was expected as the reaction was carried out in the molten polymer at temperatures much higher than its  $T_g$  value (-59°C) and it is in line with the results usually observed in fluid media when studying such an isomerization on analogous compounds.

As is shown in Table II, the kinetic coefficients increase regularly with temperature for a given polymer whereas, at a given temperature, they decrease with the increase of the polymer molecular weight. The trend of  $\ln k$  vs.  $\ln \bar{M}$  at constant temperature presents a discontinuity point comparable to that observed, in the opposite sense, when plotting  $\ln \eta_0$  vs.  $\ln \bar{M}$ . This is clearly evidenced in Figure 1(b) where the relevant data at 65°C are reported. In the first region of the graph correlating  $\ln k$  vs.  $\ln \bar{M}$ , the slope is about -0.5, while in the second region it becomes as low as -0.1. Taking into account the experimental errors that affect the kinetic measurements, the latter low value of slope suggests a substantial independence of rate from the polymer molecular weight. This is also supported by the  $k$  values at 70°C that remain essentially unaltered in going from  $\bar{M} = 4000$  to  $\bar{M} = 18,000$ , that is, in the whole second region.

The separation point between the two regions corresponds to a molecular weight value (2900) rather close to the aforementioned critical one.

The apparent relation between rate constant and molecular weight can be rationalized on the basis of several factors. First, the polarity of the medium has to be considered since it varies significantly along the series of the considered PEOs. The term  $E_{max}$  obtained from the absorption maxima of NDAB in the different polymer samples, can be used as a suitable parameter of the polarity of the medium (the higher  $E_{max}$ , the lower the polarity). Inspection of Figure 2 reveals that after an initial marked increase of  $E_{max}$  with the polymer molecular weight, there is a smooth trend of the curve evidencing very slight variations of polarity with  $\bar{M}$  over  $M_{cr}$ . Since high values of polarity lead to an enhancement of the isomerization rate (Table III), the behavior shown in Figure 2 parallels, from a qualitative point of view, that of Figure 1(b).

The polarity of the polymer samples under examination is, to a great extent, due to the presence of the terminal polar OH groups, whose number per unit weight linearly decreases with increase of the polymer molecular weight. A measure of the effect of these groups on the *cis-trans* isomerization of NDAB has been obtained by carrying out the reaction in diethylene glycol (a simple model of PEOs) and in diethylene glycol dimethyl ether. The isomerization in the glycol as such was found to be  $4 \times 10^5$  times faster than in the corresponding ether.

However, as is shown in Figure 3, there is not a linear relationship between the kinetics of the process (expressed by the  $\ln k$  values) and the polarity of the medium (expressed by the  $E_{\max}$  value). This lack of linearity in the homogeneous series of the polymers considered can be attributed either to the fact that  $E_{\max}$  is an insufficient parameter in characterizing the polarity of the medium or, more likely, to the fact that polarity might not be the sole factor determining the different kinetics of the reaction. Support of the latter hypothesis is given by the strict analogy between Figures 1(a) and 1(b), suggesting that the viscosity of the medium can also play a significant role in the reaction of isomerization.

The viscosity of a polymer fluid under  $M_{cr}$  depends on its free volume, the latter being a decreasing function of  $\bar{M}$  until  $\bar{M}$  approaches  $M_{cr}$ . Above this value of molecular weight, the polymer viscosity is determined more by the presence in the melt of considerable entanglements than by the free volume changes. The entanglements lead to a flow retardation of the large chains by intertwining with their neighbors, causing remarkable variations of viscosity. On the other hand, the value of the free volume remains unaltered, or scarcely modified, even by considerable change of  $\bar{M}$ .

Since the isomerization can be reasonably affected by significant free volume variations, a relationship between viscosity and reaction rate has to be expected under  $M_{cr}$ , whereas this is not the case in the range of molecular weights where the polymer structure governs the viscosity. All the above considerations are consistent with the experimental findings shown in Figure 1.

When a relation  $k/\text{viscosity}$  is attempted under  $M_{cr}$ , the following equation can be applied:<sup>11</sup>

$$\ln k = B - a \ln \eta$$

where  $B$  is not viscosity dependent and may vary with the temperature and  $a$  ( $< 1$ ) is the fraction of the free volume provided by the solvent for the rearrangement of the solute with respect to the critical free volume required for the motion of a solvent molecule. By applying the above equation the following values for  $B$  and  $a$  have been obtained:

	45°C	55°C	60°C	65°C
$B$	-6.1	-5.9	-5.4	-4.7
$a$	0.63	0.66	0.58	0.46

The values of  $a$  so obtained are acceptable from a physical point of view but seem to be somewhat perplexing since they should be considerably smaller than unity. In fact, the rearrangement of the solute involves only a limited relative motion of parts of the molecule.

A question arises when considering the activation enthalpies of the isomerization (Table II) in comparison with the activation energy of viscous flow (Table I). A sound correspondence isomerization rate-viscosity should involve a similar energetic behavior in the two cases. On the contrary, values of  $\Delta H^\ddagger$  varying from 10 to 18 kcal/mol have been obtained under  $M_{cr}$ , while the activation energy  $E_{vis}$  was found to be almost constant and close to 6.9

kcal/mol. A constant value of  $E_{\text{vis}}$  was expected, since it is known that this term is independent of the polymer molecular weight.

The aforementioned excessive values of  $\alpha$  and the contradictory results in terms of activation energies suggest that, even if invoking viscosity results in a further understanding of some experimental facts, the trend shown in Figure 1(b) cannot be explained on the basis of the sole viscosity of the medium. As a result, polarity and viscosity likely converge together in determining the different kinetics of the isomerization rate of NDAB in the PEO samples here taken into account.

Interestingly, the behavior of NDAB in the region of high molecular weights is similar to that observed when studying analogous dyes in a solid amorphous polymer over  $T_g$  where negligible, if any, variations in rate with  $\bar{M}$  have been observed.

Eventually, it must be noted that the lowering of the isomerization rate when using higher molecular weights is essentially due to the higher activation enthalpies, while the increasing values of the entropic term tend to accelerate the reaction.

Adventitious catalytic action by traces of acidic impurities in the various polymer samples was checked by adding in some cases appropriate amounts of triethylamine to the solutions under investigation. Since the isomerization rate was found to be scarcely altered by this addition, and by considering that the polymer samples had comparable acidic characteristics, a significant influence of the acidity of the medium in determining the different reaction rates was ruled out.

## CONCLUSIONS

The kinetics of the thermal *cis-trans* isomerization of dye NDAB in the various PEO samples here considered was found to be a useful probe of the structural features of the polymer, being capable of evidencing the passage from a Newtonian to a non-Newtonian behavior of the medium as well as using viscosity measurements.

The dependence of the reaction rate on the polymer polarity appeared to be significant under  $M_{\text{cr}}$  and scarce above  $M_{\text{cr}}$ .

The different kinetic trends below and above the critical molecular weight were found to be relative also to the presence or absence of strong entanglements in the melt that induce marked structural modifications of the medium surrounding the dye. Under  $M_{\text{cr}}$ , where the viscosity of the polymer is essentially related to the free volume, the rate constant trend versus  $\bar{M}$  parallels that of the viscosity, while over  $M_{\text{cr}}$ , where the entanglement effects prevail, the kinetics remain substantially unaltered.

Financial support by Consiglio Nazionale delle Ricerche (C.N.R.) through Progetto Finalizzato del C.N.R. per la Chimica Fine e Secondaria is gratefully acknowledged. We thank L. Pradella for his contribution to the experimental work.

## References

1. N. Nishimura, T. Sueyoshi, H. Yamanaka, E. Imai, S. Yamamoto, and S. Hasegawa, *Bull. Chem. Soc. Jpn.*, **49**, 1381 (1976).
2. B. Marcandalli, E. Dubini-Paglia, and L. Pellicciari Di Liddo, *Gazzetta*, **111**, 187 (1981).



3. B. Marcandalli, L. Pellicciari Di Liddo, C. Di Fede, and I. R. Bellobono, *J. Chem. Soc. Perkin Trans. II*, 589 (1984).
4. E. Dubini-Paglia, P. L. Beltrame, B. Marcandalli, P. Carniti, A. Seves, and L. Vicini, *J. Appl. Polym. Sci.*, **31**, 1251 (1986).
5. P. L. Beltrame, E. Dubini-Paglia, P. Sadocco, and A. Seves, *J. Appl. Polym. Sci.*, **33**, 2965 (1987).
6. C. S. Paik, and H. Morawetz, *Macromolecules*, **5**, 171 (1972).
7. C. D. Eisenbach, *Makromol Chem.*, **179**, 2489 (1978).
8. K. S. Schanze, T. F. Mattox, and D. G. Whitten, *J. Org. Chem.*, **48**, 2808 (1983).
9. T. Asano, T. Okada, S. Shinkai, K. Shigematsu, Y. Kusano, and O. Manabe, *J. Am. Chem. Soc.*, **103**, 5161 (1981).
10. A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
11. D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Am. Chem. Soc.*, **90**, 12, (1968).
12. D. W. van Krevelen, *Properties of Polymers*, Elsevier, New York, 1976.
13. F. Bueche, *J. Chem. Phys.*, **20**, 1959 (1952).

Received August 7, 1987

Accepted September 29, 1987