Photochemical and Thermal Isomerization of Azoaromatic Residues in the Side Chains and the Backbone of Polymers in Bulk[1,2]

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ABSTRACT: Copolymers were prepared of methyl methacrylate, ethyl methacrylate, and styrene with small numbers of azobenzene or azonaphthalene residues in their side chains. The rate of photochemical trans–cis isomerization was found to be substantially slower in the glassy state than in solution. The photostationary state was similar in bulk and in dilute solution and almost independent of temperature if the bulk specimens were irradiated above T_g and cooled to lower temperatures under irradiation. Specimens irradiated below T_g yielded a substantially lower conversion in the photochemical process. The thermal cis–trans isomerization observed in the dark after attainment of the photostationary state followed, in rubbery bulk specimens, first-order kinetics, with rate constants similar to those found in dilute solution. In glassy specimens a portion of the azoaromatic groups reacted anomalously fast. This anomaly was reduced when irradiating in the glassy state for long periods and it was completely eliminated when irradiating in the rubbery state and cooling through T_g under irradiation before measuring the rate of the dark reaction. Two polyamides and a polyester containing azobenzene residues in the chain backbone were also studied. The photochemical isomerization of these polymers in bulk is inhibited much more drastically than in glassy polymers carrying azoaromatic groups in their side chains. On the other hand, the thermal cis–trans isomerization of an azobenzene residue in the backbone of a nylon 66 type polymer proceeded in bulk at only a slightly lower rate than in dilute solution of an analogous polyamide.

Previous studies in this laboratory[3,4] were concerned with the question of whether the rate of hindered rotation around a given type of covalent bond is different in the backbone of long-chain molecules and in their low molecular weight analogs. These studies used nmr spectroscopy to characterize the rate of rotation around the amide bonds in piperazine polyamides[3] and uv spectroscopy to follow cis–trans isomerization in copolyamides containing a small number of azodibenzoic acid or azodianiline residues in a nylon 66 type chain.[4] In both studies, the rates of the processes observed in dilute solutions of the polymers were indistinguishable from those obtained with their low molecular weight analogs. In addition, it was demonstrated in the second investigation that the rate of cis–trans isomerization in the chain backbone remains unchanged at polymer concentrations which correspond to a substantial interpenetration of the molecular chains.

We have now extended this investigation to a study of polymers in bulk. Polymers containing small numbers of azoaromatic residues in the side chains or in the chain backbone, as listed below, were employed. Observations were made concerning both the photochemical trans–cis isomerization and the thermal cis–trans conversion taking place in the dark. The behavior of the polymers in bulk was compared to that in dilute solution, and special attention was directed to changes in behavior related to the transition from the rubbery to the glassy state.

Experimental Section

Monomers. *p*-(*N*-Methacrylyl)aminoazobenzene (mp 150–152°) was prepared from recrystallized *p*-aminoazobenzene (Metro Scientific Inc., mp 125–127°) by reaction with methacrylyl chloride which was added dropwise to a pyridine solution at 30°. The product had an absorption maximum in dioxane at 353 nm with ϵ 20,700. To prepare 4-(*N*-methacrylyl)amino-1,1′-azonaphthalene, 1-naphthylamine was diazotized and coupled with 1-naphthylamine in alkaline solution to yield 4-amino-1,1′-azonaphthalene (mp 172–177°, lit.[5] 174°). This was then made to react with methacrylyl chloride in pyridine solution. Azodianiline was obtained from Eastman Organic Chemicals and *p,p*′-azodibenzoyl chloride was prepared as described previously.[4]

Polymers. Copolymers ABA-MMA, ABA-EMA, ABA-STY, and ANA-MMA were prepared from monomer mixtures containing 1 mol % of the component containing the azoaromatic group. Polymerization was carried out in dioxane solution containing azodiisobutyronitrile initiator which was heated for 2 hr to 82–85° under a nitrogen atmosphere. The N-nylon was prepared by analogy to the procedure of Morgan and Kwolek[6] by adding dropwise to a solution of 0.075 mol of terephthaloyl chloride and 25 mmol of phthaloyl chloride in 100 ml of chloroform a solution containing 39 mmol of *trans*-2,5-dimethylpiperazine (Aldrich Chemicals) and 0.1 mmol of 4,4′-azodianiline in 100 ml of chloroform. The polymer was precipitated in hexane and washed with water and anhydrous ether. The A-nylon was the material used in a previous investigation.[4] The polyester AZO-EST was made by the method of Eareckson.[7] To a solution containing 12 mmol of bisphenol A and 25 mmol of sodium hydroxide in 150 ml of water, 15 ml of a 10% aqueous solution of lauryl sulfate was added. A solution containing 0.25 mmol of *p,p*′-azobenzoyl chloride in methylene chloride was added with rapid stirring, followed, after 2 min, by a methylene chloride solution containing 12.4 mmol of an equimolar mixture of terephthaloyl and isophthaloyl chloride. After 5 min, the emulsion was poured into acetone and the polymer was filtered off and dried. Poly(methyl methacrylate) (PMMA) was received from the American Cyanamid Co. Poly(ethyl methacrylate) (PEMA) (Polysciences Inc.) and polystyrene (Dow Chemical Co.) were purified by dissolution and precipitation. A copolyamide designated nylon 66/56 was prepared from adipyl chloride and an equimolar mixture of hexamethylenediamine and pentamethylenediamine by the interfacial polycondensation proce-

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(2) Abstracted from a Ph.D. thesis to be submitted by C. S. P. to the Graduate School of the Polytechnic Institute of Brooklyn in June 1972.

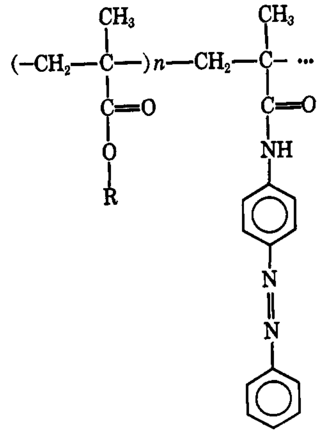
(3) Y. Miron, B. R. McGarvey, and H. Morawetz, *Macromolecules*, **2**, 154 (1969).

(4) D. Tabak and H. Morawetz, *ibid.*, **3**, 403 (1970).

(5) A. Michaelis and G. Erdmann, *Ber.*, **28**, 2198 (1895).

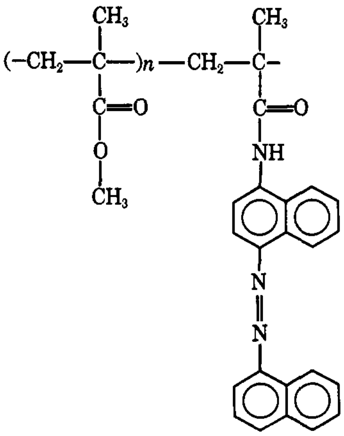
(6) P. W. Morgan and S. L. Kwolek, *J. Polym. Sci., Part A*, **2**, 181 (1964).

(7) W. M. Eareckson, *ibid.*, **40**, 399 (1959).

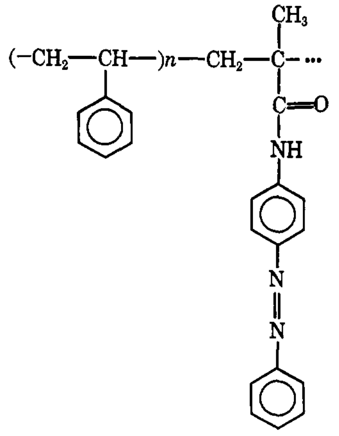


ABA-MMA, R = CH_3

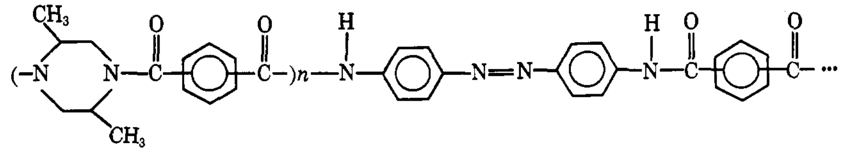
ABA-EMA, R = C_2H_5



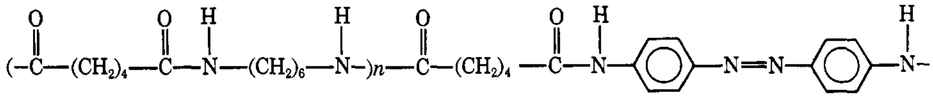
ANA-MMA



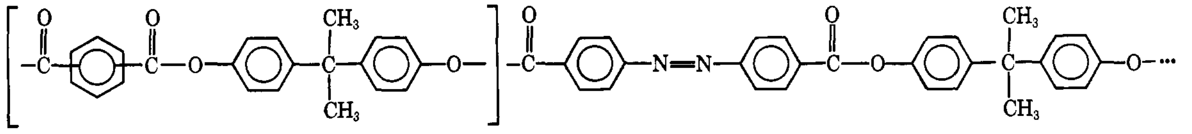
ABA-STY



N-nylon



A-nylon



AZO-EST

TABLE I
CHARACTERISTICS OF POLYMERS EMPLOYED

Designation	λ_{max} of azo residue, nm	Azo residues per repeat unit	$[\eta]_{25}$, dl/g	Ln (η_{rel}/c), dl/g
ABA-MMA	353	0.009	0.16	
ABA-EMA	353	0.010	0.12	
ABA-STY	353	0.005	0.15	
ANA-MMA	420	0.003	0.26	
A-Nylon	360	0.010	0.42	
N-Nylon	375	0.006		0.33[a]
AZO-EST	335	0.014		0.84[b]
PMMA			0.28	
PEMA			0.37	
Polystyrene			1.12	
Nylon 66/56				0.91[c]

[a] In chloroform at 25°, c = 0.28 g/dl. [b] In chloroform at 25°, c = 0.30 g/dl. [c] In trifluoroethanol at 31°, c = 0.27 g/dl.

dure described by Morgan and Kwolek for nylon 66.[8] Characteristics of all these polymers and copolymers are listed in Table I. The compositions of the copolymers quoted in this table were obtained by comparison of the optical density of copolymer and monomer solutions at the absorption maximum of the azoaromatic group.

Film Casting. To obtain film specimens with an optical density in the range of 0.3–1.0 for the absorption band of the azoaromatic group at a film thickness of about 0.03 mm, the methacrylate and styrene copolymers were diluted with the corresponding homopolymer. Methylene chloride solutions containing 20% solids (and di-*n*-octyl phthalate plasticizer if the preparation of plasticized films was desired) were cast on glass plates using a doctor blade. After most of the solvent had evaporated in air, the film was peeled off and dried overnight at 40° in a vacuum oven. Removal of traces of solvent was checked by ir spectroscopy. Solutions of N-nylon (in 88/12 chloroform–methanol) and of AZO-EST (in chloroform) were cast on quartz plates and evaporated to a thin adhering film on the plates used for the spectroscopic study of the isomerization reaction.

Kinetic Studies. A Cary 14 spectrophotometer was modified so that samples could be alternately irradiated by a 450-W xenon Osram lamp and analyzed in two directions perpendicular to one another. Bausch and Lomb interference filters 33-78-36, 33-78-42, and 33-78-39 (transmission maxima at 360, 420, and 390 nm, half-widths 49, 7, and 71 nm, respectively) were used in conjunction with a Corning filter 7-39 (transmission maximum at 360 nm, half-width 47 nm). The light intensity, controlled by neutral density filters, ranged from 180 to 1200 $\mu W/cm^2$ as measured with a Black-Ray ultraviolet intensity meter (Ultraviolet Products Inc.). Test solutions were placed in 1-cm^2 thermostated cells with quartz windows. Film specimens were held between two quartz plates inserted into a slit in a Teflon-insulated brass block. The slit was oriented at 45° to the irradiation, and the spectrophotometer beams and windows were cut through the brass block and the insulation for the two beams. The temperature of the assembly was varied by electrical heating or by circulation of coolant and

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(8) P. W. Morgan and S. L. Kwolek, *J. Polym. Sci.*, **62**, 48 (1962).

TABLE II
PHOTOISOMERIZATION OF AZOAROMATIC RESIDUES IN ABA-MMA AND ANA-MMA

Nature of specimen	Temp, °C	D_0[a]	$10^6 I_0$, W/cm²	y_∞	$10^2 A$, sec⁻¹	$\phi_t\epsilon_t$, arbitrary units
			ABA-MMA			
Dilute solution[b]	0	0.71	180 ± 10	0.76	1.18	5.0
Dilute solution[b]	0	2.35	180 ± 10	0.76	1.07	4.5
Dilute solution[b]	25	2.12	280 ± 10	0.76	1.64	4.4
Dilute solution[b]	25	2.43	500 ± 20	0.76	3.81	5.8
Concentrated solution[c]	0	2.51	500 ± 20	0.74	3.35	5.0
Plasticized film[d]	0	1.63	500 ± 20	0.55	1.33	1.5
Unplasticized film	0	1.19	500 ± 20	0.53	1.20	1.3
Unplasticized film	0	2.27	500 ± 20	0.53	0.92	1.0
Unplasticized film	25	1.23	500 ± 20	0.52	1.17	1.2
Unplasticized film	25	2.18	500 ± 20	0.52	0.96	1.0
			ANA-MMA			
Dilute solution[b]	−20	1.00	200 ± 10	0.55	5.56	15.3
Dilute solution[b]	0	1.02	200 ± 10	0.55	4.28	11.8
Plasticized film[d]	0	1.10	200 ± 10	0.18	1.40	1.3
Unplasticized film	−20	0.98	200 ± 10	0.125	1.37	1.1
Unplasticized film	0	0.97	200 ± 10	0.125	1.37	0.85

[a] Initial optical density at the maximum of the absorption band of the azoaromatic group. [b] Solution in butyl acetate. [c] Solution of copolymer containing 0.15 g of PMMA/ml. [d] Film containing 30% DOP.

was kept within 0.5° at the lower temperatures and within 1.0° at the highest temperatures used in this study. For photochemical trans–cis isomerization, the samples were irradiated close to the absorption maximum of the trans isomer and the progress of the reaction was followed by quick reading of the optical density after each interval of irradiation. When the photostationary state was reached, irradiation was discontinued and the thermal cis–trans isomerization was followed by recording automatically the optical density as a function of time. The reaction was usually taken to more than half conversion, but for some selected runs sufficient time was allowed to confirm the complete reversibility of the photochemical process.

Results

Photochemical Isomerization. When compounds containing azoaromatic groups are exposed to irradiation of an appropriate wavelength, both trans–cis and cis–trans isomerizations take place by a photochemical process. In addition, there takes place a thermal cis–trans isomerization, since the trans form corresponds to an energy lower by an estimated 10 kcal/mol.[9] In analyzing the overall kinetics of the reaction, we followed Zimmerman, *et al.*,[10] who assumed irradiation by monochromatic light, validity of Beer's law, quantum yields independent of irradiation intensity, and conditions under which the thermal reaction is slow compared to the photochemical process. With incident and transmitted light intensity I_0 and I, a quantum efficiency ϕ_t for the trans–cis conversion, a molar extinction coefficient ϵ_t of the trans isomer, and a fraction of y_∞ of the cis isomer in the photostationary state, they obtained

$$F(\delta) = \int \frac{D}{1 - \exp(-D)} \frac{d\delta}{\delta} = -At + \text{constant}$$

$$A = I_0\phi_t\epsilon_t/y_\infty \qquad (1)$$

where $\ln (I_0/I) = D$ at time t, $\ln (I_0/I) = D_\infty$ at $t = \infty$, and $\delta = D_\infty - D$. The integral may be approximated, for moderate values of D, by[11]

$$F(\delta) = \left[1 + \frac{D_\infty}{2} + \frac{D_\infty{}^2}{12}\right] \ln|\delta| - \left[\frac{1}{2}\frac{D_\infty}{6}\right] + \frac{\delta^2}{24} \qquad (2)$$

The slope of a plot of $F(\delta)$ against time yields, therefore, the quantity A, and Ay_∞/I_0 gives $\phi_t\epsilon_t$ if I_0 is expressed in einsteins cm^{-2} sec^{-1}. In applying the above theory, we assumed that I_0/I of the nonmonochromatic light from our irradiation source was approximated sufficiently by the ratio of incident and transmitted light at λ_{max} of the trans form of the azoaromatic group as followed by the spectrophotometer. The y_∞ values were estimated assuming that, at λ_{max} of the trans form, the contribution of cis azoaromatic groups to the optical density may be neglected.[10,12]

Our results for the photoisomerization of the azoaromatic residues in the side chains of ABA-MMA and ANA-MMA are listed in Table II.

Since we did not use monochromatic light for the irradiation, no attempt was made to obtain absolute values for $\phi_t\epsilon_t$. Nevertheless, the results show (a) that A is insensitive to D_0 and approximately proportional to I_0 as postulated in the analysis of Zimmerman, *et al.*; (b) that the photochemical efficiency of an isomerization reaction in the side chains of polymer molecules is not affected by increasing the polymer concentration to a point where the molecular chains are heavily intertwined; but (c) that the photochemical efficiency drops sharply for the polymers in bulk and for the plasticized polymers. This effect is much more pronounced for the ANA-MMA than for the ABA-MMA copolymer, presumably because of the larger bulk of the isomerizing azonaphthalene residues.

The results listed in Table II show also that the composition of the photostationary state is independent of the concentration of polymer solutions but is quite different in the bulk polymers. Plasticization with 30% DOP at 0° had no effect on y_∞, and it was suspected that this was so because both the plasticized and the unplasticized polymers were in the glassy state. This interpretation was supported by observations on copolymer ABA-EMA. Poly(ethyl methacrylate) has

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(9) R. Y. Corruccini and E. C. Gilbert, *J. Amer. Chem. Soc.*, **61**, 2925 (1939).

(10) G. Zimmerman, L. Chow, and U. Paik, *ibid.*, **80**, 3528 (1958).

(11) J. Blanc, *J. Phys. Chem.*, **74**, 4037 (1970).

(12) M. Frenkel, R. Wolowsky, and E. Fischer, *J. Chem. Soc.*, 3441 (1955).

Table III
Photostationary State of Polymers with Azobenzene Residues in the Chain Backbone

Polymer	Nature of Specimen	Temp, °C	y_∞
A-Nylon	Bulk, nylon 66/56 matrix	55–74	0.055
N-Nylon	Dilute $CHCl_3$ soln.	56.5	0.60
N-Nylon	Bulk	34–59	0.12
AZO-EST	Dilute $CHCl_3$ soln.	41	0.45
AZO-EST	Plasticized film, 50% DOP	50–70	0.12
AZO-EST	Bulk	43	0.025

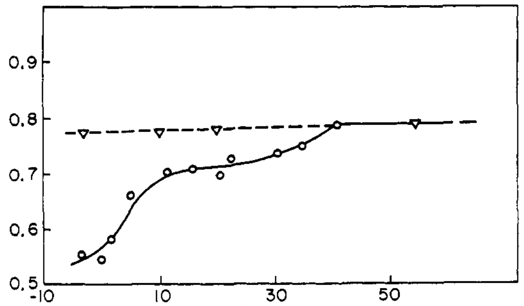

Figure 1. Temperature dependence of the photostationary state of ABA-MMA in bulk: (○) photochemical and dark reaction at the same temperature, (▽) sample irradiated at 55° and cooled under irradiation.

been reported to have $T_g = 65°$ [13] and it was found, in fact, that ABA-EMA in a PEMA matrix had y_∞ in the range of 0.57–0.59 when the temperature was increased from 24 to 60°, increasing sharply to $y_\infty = 0.72$ at 74°. This value, observed with the bulk polymer in the rubbery state was quite similar to $y_\infty = 0.76$ found in dilute solution at 25°.

A more extensive study of the effect of glass transition on the photostationary state was carried out with a plasticized ABA-MMA film. The glass transition temperature of PMMA has been reported as 105°.[13] The depression of T_g due to plasticization was estimated using the formula proposed by Kelley and Bueche[14] with $T_g = -70°$ for dioctyl phthalate.[15] This procedure yielded $T_g = 22°$ for plasticized PMMA containing 30% DOP, which we used as a matrix for ABA-MMA. The temperature dependence of the photostationary state of this sample when irradiated with light centered at 360 nm is shown in Figure 1. Two aspects of the results are striking. (a) When the temperature was kept constant during irradiation until the photostationary state was attained, y_∞ remained constant at temperatures above 41° but decreased sharply at lower temperatures. (b) If the sample was irradiated at 55° and cooled while the irradiation was continued, y_∞ retained almost a constant value down to −5°. Thus, the photostationary state depends, in this system, on the history of the specimen.

In the case of polymers with azoaromatic groups incorporated into the backbone of the chain molecule, the photochemical isomerization, proceeding easily in dilute solution, is almost completely suppressed in bulk polymers (see Table III). Homopolymers analogous to N-nylon and AZO-EST (without the azobenzene residues) have extremely high T_g values (290[16] and 194°,[7] respectively). However, the inability of this group of copolymers to photoisomerize in bulk cannot be entirely a consequence of the glassy state, since even plasticization of AZO-EST with 50% DOP failed to produce more than a moderate increase in y_∞.

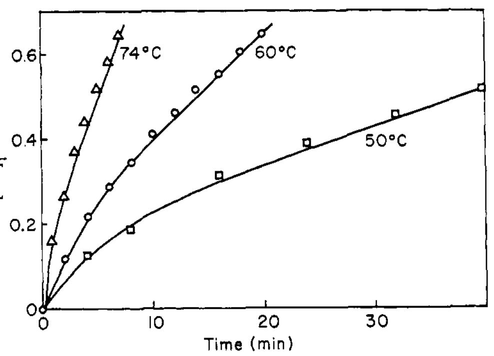

Figure 2. Thermal cis–trans isomerization of ABA-MMA in bulk after photochemical trans–cis isomerization at the same temperature.

Thermal Cis–Trans Isomerization. First-order plots of the thermal cis–trans isomerization of azobenzene residues in the side chains of ABA-MMA in a PMMA matrix were strongly curved, as shown in Figure 2. The kinetic plots could be fitted by a biphasic process in which about 14% of the groups isomerize much faster than the remainder, with the ratio of the rate constants for the "fast" and "slow" azobenzene residues falling from 12 at 50° to 8.6 at 74°. However, when the film was plasticized to convert it from the glassy to the rubbery state, the isomerization followed first-order kinetics and the rate constant was almost identical with that observed in dilute solution (Figure 3). Moreover, when comparing the results obtained with the plasticized and the unplasticized sample, we find that the "slow" azobenzene residues in the glassy state react at the normal rate observed in the rubbery sample and that it is the existence of the fast component which is anomalous. To clarify the nature of this anomaly, the following experiment was carried out. A film of ABA-MMA plasticized with 30% DOP was irradiated at 55° (in the rubbery state) until the photostationary state was attained and was cooled under constant irradiation to −2°. When the light was turned off, the dark reaction followed first-order kinetics, while a second run in which the photochemical reaction was carried out at −2° gave a strongly curved first-order plot for the thermal cis–trans isomerization (Figure 4).

Results obtained with ABA-EMA in a PEMA matrix (Figure 5) confirmed the relation between glass transition and deviation from first-order kinetics. The first-order plots were curved at temperatures up to 60° but linear when the temperature was further raised. Above the glass transition temperature of PEMA (65° [13]), the rate constants observed with the polymer in bulk were within experimental error of those found in dilute butyl acetate solutions. It was also found that the extent of the anomalous fast component of the dark reaction in the glassy state was reduced when extending the time of irradiation preceding the thermal process.

The glass–rubber transition is believed to represent a temperature at which segmental motions in the backbone of chain molecules are frozen out. Dielectric and mechanical relaxation methods reveal, however, other transitions at

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(13) S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).

(14) F. N. Kelley and F. Bueche, *J. Polym. Sci.*, **50**, 549 (1961).

(15) J. V. Koleske and L. H. Wartman, "Poly(vinyl chloride)," Gordon and Breach, New York, N. Y., 1969, p 58.

(16) M. Katz, *J. Polym. Sci.*, **40**, 337 (1959).

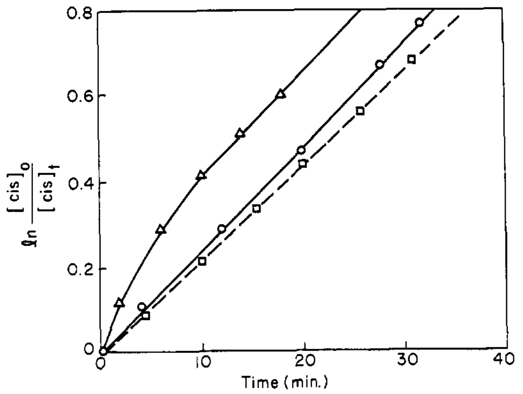

Figure 3. Thermal cis–trans isomerization of ABA-MMA at 60° after photochemical trans–cis isomerization at the same temperature: (△) bulk polymer, (○) polymer plasticized with 30% DOP, (□) dilute solution in butyl acetate.

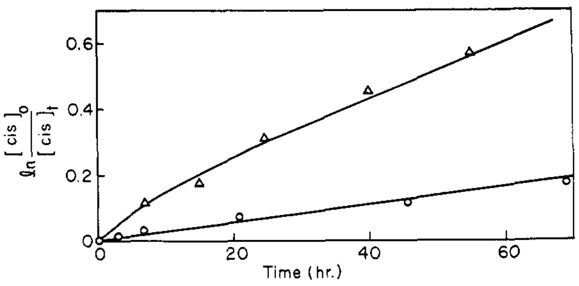

Figure 4. Thermal cis–trans isomerization of ABA-MMA plasticized with 30% DOP at −2°. Photochemical trans–cis isomerization at −2° (△) and at 55° with cooling under irradiation (○).

progressively lower temperatures (β, γ, δ transitions) at which side-chain motions are immobilized. With polystyrene a broad β transition has been reported in the 20–30° range,[17] and it was of interest to see whether the transition would affect the isomerization velocity of azobenzene residues appended to a polystyrene backbone. The first-order plots of the reaction of ABA-STY in a polystyrene matrix in the temperature range 2–60° were again curved, but could not be represented as a biphasic process. The kinetics were characterized by $t_{1/4}$ and $t_{1/2}$ corresponding to $(D - D_\infty)/(D_0 - D_\infty)$ of 0.75 and 0.50, respectively. The results are represented as an Arrhenius plot in Figure 6, and it can be seen that no break in the plot appears in the temperature range of the β transition. There is a tendency for $t_{1/2}/t_{1/4}$ to decrease with increasing temperature; *i.e.*, the reaction of azobenzene residues which isomerize at an anomalously high rate is characterized by a lower activation energy.

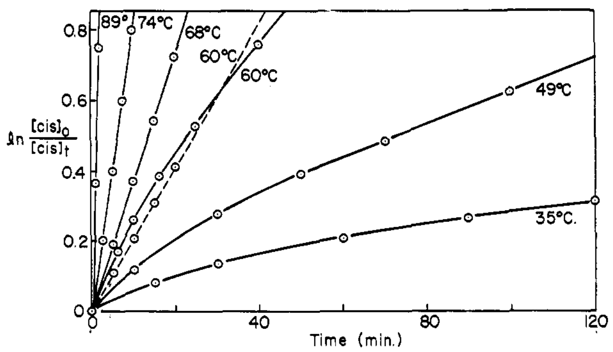

Figure 5. Thermal cis–trans isomerization of ABA-EMA after photochemical trans–cis isomerization at the same temperature.

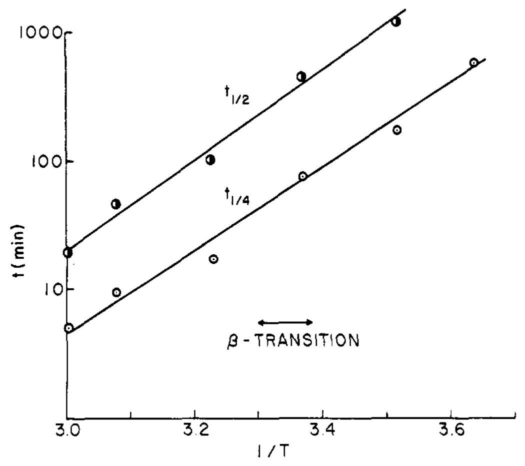

Figure 6. Arrhenius plot of the half-times and quarter-times of the thermal cis–trans isomerization of ABA-STY. The figure shows also the temperature range of the β transition in polystyrene.

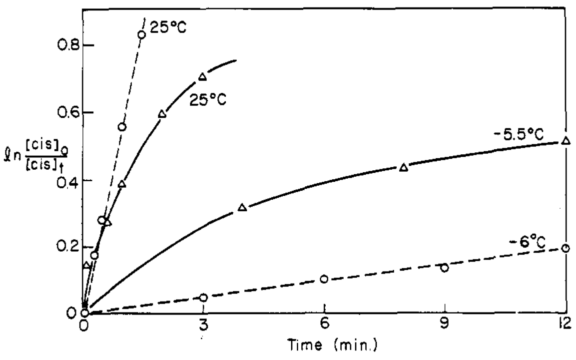

Figure 7. Thermal cis–trans isomerization of ANA-MMA after photochemical trans–cis isomerization at the same temperature: polymer in bulk (△), polymer in dilute butyl acetate solution (○).

The study of copolymers carrying azonaphthalene residues was of interest for two reasons. First, the thermal cis–trans isomerization of azonaphthalene is more than two orders of magnitude faster than the corresponding reaction of azobenzene,[12] and this facilitates an extension of experimental conditions to lower temperatures. Secondly, it was of interest to see whether the isomerization of the larger azonaphthalene residues would be affected more strongly in bulk polymers than the corresponding reaction of azobenzene groups. Some typical results obtained with ANA-MMA in solution and in bulk are shown in Figure 7. At −5.5° the "slow" azonaphthalene groups in the bulk polymer have a reaction rate similar to that observed in dilute solution. However, at 25° the situation appears to be reversed, so that the initial reaction rate is similar in solution and in bulk, while conversions are lower for the bulk specimen for longer reaction times.

The scope of studies of the thermal isomerization rate of azobenzene residues incorporated into the backbones of polymer chains was sharply limited by experimental difficulties. The crystallinity of A-nylon leads to light scattering (even though the less crystalline nylon 66/56 was selected as the matrix material), and this impairs the precision of the spectral data. Also, A-nylon is only soluble in strongly acidic media, and a comparison of isomerization rates of this polymer

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(17) K. H. Illers and E. Jenkel, *Rheol. Acta*, **1**, 322 (1958).

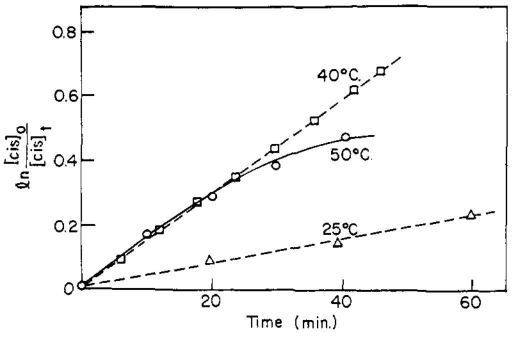

Figure 8. Thermal cis–trans isomerization in the chain backbone of polyamides: (—) A-nylon in a nylon 66/56 matrix, (- - -) N-nylon in chloroform.

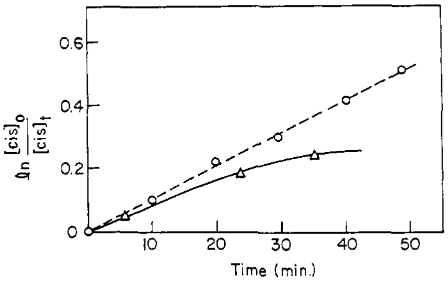

Figure 9. Thermal cis–trans isomerization in the chain backbone of AZO-EST: (—) film plasticized with 50% DOP at 51°, (- - -) dilute chloroform solution at 50°.

in bulk and in solution would be meaningless, since strong acids are powerful catalysts for the reaction.[4] It was because of this difficulty that we prepared N-nylon and AZO-EST, which appeared to be completely amorphous and were soluble in chloroform. Unfortunately, these materials photoisomerized to such a small extent in bulk that it was impossible to obtain reliable data on the rate of the corresponding dark reaction. However, a comparison of the behavior of A-nylon in bulk with that of N-nylon in chloroform solution is meaningful, since the nature of the chain into which the azodianiline moiety is incorporated does not affect the thermal isomerization rate in dilute solution.[4] The result of such a comparison (Figure 8) shows that the initial rate for the bulk specimen at 50° is comparable to the rate characterizing the dissolved polymer at 39.5°. Finally, a comparison of AZO-EST in a film plasticized with 50% DOP and in dilute solution (Figure 9) gave similar initial rates but smaller conversions in the concentrated system at longer reaction times.

Discussion

Molecular motions in bulk polymers have been studied by a number of techniques including dynamic-mechanical, dielectric, and nmr relaxation methods and analysis of the viscoelastic and dielectric dispersion spectra. In employing a spectroscopic method by which rotation around a well-defined bond is followed kinetically, we hoped to obtain additional insight into the mobility of side chains and the chain backbones of polymer molecules in the rubbery and the glassy state.

Phenomena Associated with the Glass Transition. With polymers carrying azoaromatic residues in their side chains, the transition from the rubbery to the glassy state produced two types of changes in the chemical behavior. (a) The photostationary state, when determined under isothermal conditions, was shifted to a much lower conversion from the trans to the cis isomer. (b) The thermal cis–trans isomerization, which followed first-order kinetics above T_g, now deviated from this simple behavior with a fraction of the azoaromatic residues isomerizing *faster* than in the rubbery state at the same temperature. It should be pointed out that such phenomena are apparently not dependent on the attachment of the reacting residue to the polymer backbone. Gardlund[18] and Gardlung and Laverty[19] studied benzospiranes which, after conversion to a colored isomer in a photochemical reaction, revert to the colorless compound by a thermal process. This reaction, although first order in solution, was found to be biphasic when these compounds were incorporated in poly(methyl methacrylate) at room temperature. First-order kinetics were found to be restored in a rubbery polymer matrix, *i.e.*, poly(butyl methacrylate) at 60°, but the rate was lower by an order of magnitude as compared with that in dilute solution.[19] Gardlund interpreted his observation by assuming that the colored species consists of a mixture of two isomers which are in equilibrium with one another in solvents of low viscosity, while their interconversion is very slow in the glassy state; the biphasic kinetics would then reflect the difference in the velocity of the bleaching reaction of these two compounds. Vandewijer and Smets[20] carried out a similar study in which, however, the photochromic 3,3′-dimethyl-6-nitrobenzthiazolinospirane groups were attached as side chains to various types of polymers. They found that the thermal bleaching reaction in dilute solution could be first order or biphasic, depending on the nature of the solvent medium. They also assumed that two colored species were involved and reasoned that attachment to a polymer backbone may, under some conditions, block their interconversion. Finally, Priest and Sifain[21] studied systems rather similar to ours. They incorporated 2,2′-azonaphthalene or 4-ethoxyazobenzene in a matrix of polystyrene, in bulk or in compositions plasticized with various proportions of *n*-butylbenzene. They found that the content of the cis isomers in the photostationary state decreased steadily with increasing viscosity of the medium and that the dark reaction deviated from first-order kinetics when the plasticizer content was too low to effect the glass–rubber transition. In conformity with our results, they also reported that a portion of the cis azo compounds reacted anomalously *fast* in the glassy state.

We believe that the results of Priest and Sifain and the additional observations of the present study reflect the nonequilibrium nature of the glassy state in which the free volume is unequally distributed in space. A fraction of the volume is too rigid to allow the photochemical isomerization to proceed in either direction. An additional portion of the system will allow the photoisomerization to proceed, but the cis isomer will be trapped in a strained conformation, from which it can return more easily to the trans form than the relaxed cis species. We believe that the interpretation of some of the kinetic curves as the sum of two first-order processes is without significance, and that the anomalously fast cis azoaromatic residues are, in fact, characterized by a continuous distribution of relaxation times. When the cis isomer is produced in the rubbery state, it assumes its equilibrium conformation and this is retained on cooling through the T_g range. If the thermal reaction rate is not sensitive to the local free volume—for reasons to be discussed below—we obtain then first-order kinetics for the dark reaction.

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Comparison of the Thermal Reaction Rate in Bulk and in Dilute Solution. It is at first sight surprising that the thermal isomerization of side chains of polymers in the rubbery state should proceed as easily as in dilute solution, since changes in the geometry of such bulky groups must require extensive rearrangements in the conformation of neighboring chain molecules. However, the following argument seems to account for the observed behavior. The conversion from a cis to a trans azo group should not be thought of as taking place in a single step, but as a result of many small oscillations of the -N=N—C bond angle.[22] Although the increase of this angle should be slowed down by the requirement that neighboring chains assume a conformation allowing such a change, the reverse process should be impeded to the same extent. Thus, the fundamental postulate of the theory of absolute reaction rates, *i.e.*, that the transition state be in equilibrium with the ground state of the reagent, remains valid, and the restrictions on mobility due to the nature of the medium do not affect the reaction rate. We have here a unimolecular analog of the well-known fact that bimolecular reactions characterized by an appreciable activation energy have rates independent of the viscosity of the medium, since a decreased mobility slows down equally the mutual approach and separation of the reacting species. The above argument appears to hold approximately even for thermal isomerization in the backbone of a polymer chain of polymers in bulk. This rules out, for our case, mechanisms in which it is postulated that changes in the shape of a chain molecule occur by two correlated conformational transitions.[23] Such mechanisms may still apply in cases where conformational transitions involve very low energy barriers, but the spectroscopic method would then, unfortunately, not be applicable for a kinetic investigation.

[22] We are here assuming that the isomerization takes place by the inversion mechanism, in which the C—N=N—C grouping remains coplanar and is linear in the transition state as postulated, *e.g.*, by E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967), and by D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 12 (1968).

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Helix–Coil Stability Constants for the Naturally Occurring Amino Acids in Water. IV. Alanine Parameters from Random Poly(hydroxypropylglutamine-*co*-L-alanine)[1]

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ABSTRACT: The synthesis and characterization of water-soluble random copolymers containing L-alanine and N^5-(3-hydroxypropyl)-L-glutamine are described, and the thermally induced helix–coil transition of these copolymers in water has been studied. The incorporation of L-alanine was found to increase the helix content of the polymer. The Zimm–Bragg parameters σ and s for the helix–coil transition in poly(L-alanine) in water were deduced from an analysis of the melting curves of the copolymers in the manner described in earlier papers. The values obtained for the enthalpy, entropy, and transition temperature for the conversion of a coil to a helical residue in poly(L-alanine) in water were found to be in good agreement with those obtained earlier using sandwich-type block copolymers of L-alanine and D,L-lysine in the same solvent, thereby supporting the view that the conformational state of an amino acid residue (except possibly proline) in a polypeptide or protein is essentially independent of the chemical nature of its neighbors.

The use of the "host–guest" technique for the evaluation of the helix–coil stability constants of amino acids in water was illustrated in earlier papers of this series.[3-5] This technique involves the study of the perturbation of the helix–coil transition in a homopolymer of a host amino acid residue (with known transition parameters, σ and s, of the Zimm–Bragg theory[6]) by a guest residue (for which parameters are sought) distributed randomly in the copolymer of the two monomers. The validity of this method was established by the determination of the transition parameters of poly[N^5-(3-hydroxypropyl)-L-glutamine] and poly[N^5-(4-hydroxybutyl)-L-glutamine] (PHPG and PHBG, respectively) from both homopolymer and copolymer experimental data,[4] and the values of σ and s for glycine were obtained from an analysis of the melting curves for copolymers of glycine and N^5-(4-hydroxybutyl)-L-glutamine (HBG).[5] In the present paper, this approach is extended to L-alanine, using N^5-(3-hydroxypropyl)-L-glutamine (HPG) as the host residue in the copolymer. The choice of the host was made on the expectation, which was demonstrated by this work, that the melting curve of the homopolymer of the host residue, PHPG, would be progressively shifted toward higher temperatures within the available temperature range in water by the incorporation of L-alanine, since the latter is known to act as a helix former.[7-9]

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