Rates of Conformational Transitions in Solutions of Randomly Coiled Polymers. III. The *cis–trans* Isomerization of Azobenzene Residues in the Backbone of Polyamides[1,2]

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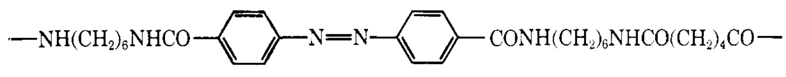
ABSTRACT: Copolyamides were prepared in which azodibenzoic acid or azodianiline were incorporated into Nylon 66. The azobenzene residues were irradiated to produce *trans–cis* isomerization and the dark *cis–trans* isomerization was followed spectroscopically. In dilute solution, isomerization rates of the polymers were very similar to those observed in low molecular weight analogs, suggesting that incorporation into the backbone of a high molecular weight chain polymer does not hinder the isomerization process. There was no evidence of the isomerization being slowed down at polymer concentrations corresponding to extensive chain entanglements. In the copolyamide containing azodibenzoic acid residues, the *cis–trans* isomerization did not follow first-order kinetics, but part of the azo groups isomerized much faster than the low molecular weight analog. This anomaly could be due to the oxidation of some of the azo groups to azoxy during the polycondensation and this interpretation is consistent with the kinetic data but does not fit the spectroscopic evidence.

In a previous communication from this laboratory, the question was raised whether hindered rotation around a given type of bond takes place at a different rate when the bond is part of the backbone of a long chain polymer and when it is part of an analogous compound of low molecular weight. This problem was investigated initially on polyamides and their low molecular weight analogs using nmr spectroscopy to calculate the rate of hindered rotation around the amide bonds.[3] However, this technique is limited to systems of low viscosity in which highly resolved nmr spectra can be obtained. It is, therefore, unsuited to a study of the extent to which changes in the conformations of polymer chains might be slowed down at higher polymer concentrations when the chain molecules are heavily intertwined.

To clarify this problem, we have prepared copolyamides of type **1** and **2** in which a small number of azobenzene residues were built into a Nylon-66-type chain. Azobenzene groups exist normally in the *trans* form, but are subject to photoisomerization to the *cis* form. The reverse reaction takes place in the dark and may be followed by spectroscopy in the visible or ultraviolet region.[4] This method is obviously not restricted to media of low viscosity and allows, therefore, studies to be carried out over a wide range of polymer concentrations.



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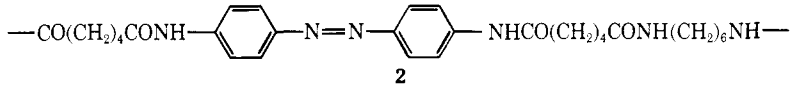

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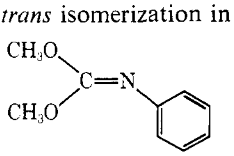
Conventionally, a distinction is made between rotations around single bonds which are referred to as conformational transitions, while *cis–trans* transitions in compounds containing double bonds are spoken of as isomerizations. This distinction has its historical origin in the relative ease with which *cis* and *trans* compounds can be physically isolated, while such isolation is generally not feasible with rotational isomers of singly bonded compounds. However, this distinction is merely a reflection of the relative height of the energy barrier to be overcome in the process under consideration. Actually, we cannot generalize that *cis–trans* isomerizations are necessarily slower than conformational transitions in single-bonded compounds. For instance, the *cis–trans* isomerization in compound **3** is characterized[5] by a free energy of activation $\Delta G^{\ddagger}$ =



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(2) Abstracted from a Ph.D. Thesis submitted by David Tabak to the Graduate School of the Polytechnic Institute of Brooklyn, June 1970.

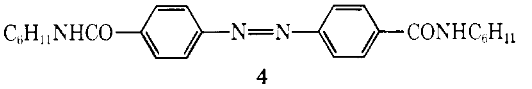
(3) Y. Miron, B. R. McGarvey, and H. Morawetz, *Macromolecules*, **2**, 154 (1969).

(4) (a) G. S. Hartley, *J. Chem. Soc.*, 633 (1938); (b) J. Halpern, G. W. Brady, and C. A. Winkler, *Can. J. Res., Sect. B*, **28**, 140 (1950); (c) D. Schulte-Frohlinde, *Justus Liebigs Ann. Chem.*, **612**, 138 (1958); (d) D. Kaplan, *Diss. Abstr.*, **20**, 3074 (1960); (e) E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967).

(5) F. Vogtle, A. Mannschreck, and H. A. Staab, *Justus Liebigs Ann. Chem.*, **708**, 51 (1967).

14.3 kcal/mol, which is actually much lower than, *e.g.*, $\Delta G^{\ddagger} = 21.0$ kcal/mol for the rotation around the amide bond in dimethylformamide.[6] At any rate, the distinction between the two types of processes is of no fundamental importance in the problem with which we are concerned.

In the present investigation we have compared the *cis–trans* isomerization rates of the azobenzene groups in the copolyamides **1** and **2** with the corresponding processes in the analogs **4** and **5**. Since the polymer was studied in formic acid solution and the isomerization rate is known to be sensitive to the acidity of the medium,[4a,7] we took special care to define the nature of the acid catalysis in the reaction of the two low molecular weight analogs.



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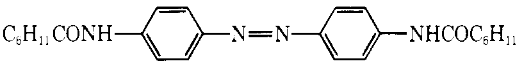

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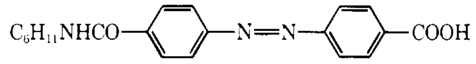
It should be noted that *cis–trans* isomerization rates in the backbone of polymer chains have been studied previously by a number of investigators. With polybutadiene[8] and polyisoprene[9] the thermal reaction is too slow to be observed in the temperature range in which the polymer is chemically stable, and the various studies were concerned with isomerization induced by ionizing radiation,[8a] photoisomerization,[8b] or isomerization catalyzed by a variety of catalysts. Photoisomerization was also studied in maleic acid polyesters.[10] Rather surprisingly, only a few of these studies compared the reaction rate in the polymer backbone with that in a low molecular weight analog. Ermakova, *et al.*,[8d] report a single kinetic point for butene-2 to substantiate the statement that the NO_2-catalyzed isomerization proceeds at a similar rate in polybutadiene and the analog. Cunneen, *et al.*,[9b] present more extensive data for a comparison of the SO_2-catalyzed isomerization of polyisoprene and 3-methylpent-2-ene. Golub and his collaborators reported similar comparisons of the rate of the radiation-induced isomerization of polybutadiene[8g] and polyisoprene[9e] with their low molecular weight analogs. The present work appears to be the most detailed examination of the question whether *cis–trans* isomerization around a double bond is impeded by incorporation of that bond into a polymer chain backbone in a simple thermal process.

Experimental Section

Model Compounds. *p,p'*-Azodibenzoic acid was prepared by reducing *p*-nitrobenzoic acid in aqueous alkaline solution with glucose to the hydrazo derivative, which was then oxidized by atmospheric oxygen.[11] The carboxylic acid was converted to the acid chloride by treatment with thionyl chloride and converted to compound **4** (mp 272–274°) by reaction with excess *n*-hexylamine in xylene solution. Azodianiline (Eastman Organic Chemicals) was recrystallized and reacted with *n*-heptanoyl chloride to yield compound **5** (mp 269–271°). To prepare compound **6** (mp 289–291°) *p*-nitrobenzoyl chloride was allowed to react with *n*-hexylamine, reduced to the amine derivative which was coupled with *p*-nitrosobenzoic acid in glacial acetic acid solution.



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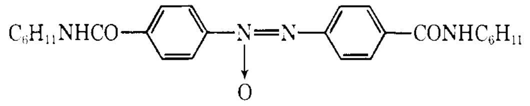
Compound **7** (mp 267–268°) was prepared from *p,p'*-azoxybenzoic acid (Columbia Organic Chemicals).



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Polymers. The copolyamides were prepared by interfacial polymerization. For copolyamide **1** the procedure of Morgan and Kwolek[12] was followed. Since azodianiline has a very low water solubility, copolyamide **2** was made by the procedure of Morgan, *et al.*,[13] in which the polycondensation is carried out in an emulsion system. The polymer was analyzed for the content of azobenzene residues by comparison of the absorption spectra with those of model compounds **4** and **5**. The molecular weights of the copolyamides were estimated from the intrinsic viscosity in formic acid containing 10 vol % water and 0.1 *M* sodium formate using the relation established for Nylon 66.[14] Copolyamides with a high content of azo residues were insoluble in this medium. We obtained qualitative information about their molecular weights by comparison of their solution viscosity in formic acid containing 4.7 *M* water and 0.7 *M* perchloric acid with the solution viscosity of Nylon 66 of known molecular weight in the same solvent medium. Table I lists the polymers employed in this study.

Solvent Media. Formic acid (Baker and Adamson 98–100%) was redistilled under reduced pressure. Formic acid solutions containing various concentrations of water, perchloric acid, or sodium formate were used as solvent media for the copolyamides and their analogs. A large part of the investigation was carried out in "95% formic acid" (*i.e.*, a solution containing 5 wt % of water) which had a density of 1.201 at 30°. The acidity of these media was characterized by the H_0 function.[15] The reference bases used and the H_0

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(6) M. Rabinowitz and A. Pines, *J. Amer. Chem. Soc.*, **91**, 1585 (1969).

(7) (a) D. Schulte-Frohlinde, *Justus Liebigs Ann. Chem.*, **612**, 131 (1958); (b) R. Lovrien and J. C. Waddington, *J. Amer. Chem. Soc.*, **86**, 2315 (1964); (c) G. Wettermark, M. E. Langmuir, and D. G. Anderson, *ibid.*, **87**, 476 (1965).

(8) (a) M. A. Golub, *J. Polym. Sci.*, **25**, 373 (1957); *J. Amer. Chem. Soc.*, **80**, 1794 (1958); **81**, 54 (1959); **82**, 5093 (1960); *J. Phys. Chem.*, **69**, 2639 (1965); (b) M. A. Golub and C. L. Stephens, *J. Polym. Sci., Part C*, **16**, 765 (1967); (c) W. A. Bishop, *ibid.*, **55**, 827 (1961); (d) I. I. Ermakova, B. A. Dolgoplosk, and E. N. Kropacheva, *Dokl. Akad. Nauk SSSR*, **141**, 1363 (1961); (e) M. Berger and D. J. Buckley, *J. Polym. Sci., Part A*, **1**, 2945 (1963); (f) F. Hrabak, *ibid., Part A-1*, **6**, 3259 (1968); (g) M. A. Golub, C. L. Stephens, and J. L. Brash, *J. Chem. Phys.*, **45**, 1503 (1966).

(9) (a) M. A. Golub, *J. Polym. Sci.*, **36**, 523 (1959); (b) J. I. Cunneen, G. M. C. Higgins, and W. F. Watson, *ibid.*, **40**, 1 (1959); (c) M. A. Golub and C. L. Stephens, *ibid., Part A-1*, **6**, 763 (1968); (d) I. I. Boldyreva, B. A. Dolgoplosk, E. N. Kropacheva, and K. V. Nel'son, *Dokl. Akad. Nauk SSSR*, **131**, 830 (1960); (e) M. A. Golub in "Radiation Research," G. Silini, Ed., North Holland Publishing Co., Amsterdam, 1967, pp 339–351.

(10) J. Voigt, *Z. Phys. Chem.* (Leipzig), **209**, 255 (1958).

(11) M. L. Tomlinson, *J. Chem. Soc.*, 756 (1946).

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

(13) R. G. Beaman, P. W. Morgan, C. R. Koller, E. L. Wittbecker, and E. E. Magat, *ibid.*, **40**, 333 (1959).

(14) H. G. Elias and R. Schumacher, *Makromol. Chem.*, **76**, 23 (1964).

(15) L. P. Hammett, *Chem. Rev.*, **16**, 67 (1935).

TABLE I
POLYMER CHARACTERIZATION

Polymer designation[a]	Polymerzn temp, °C	Azo residues per repeat unit	$[\eta]_{25}$,[c] dl/g	$\bar{M}_v \times 10^{-4}$	$(\eta_{sp}/c)_{25}$,[d] dl/g
P 2-01	25–30	0.010	0.42	1.64	
P 2-04	25–30	0.045	0.167	0.41	
P 1-02H	25–30	0.023	0.66	3.24	
P 1-02L	0–6	0.021	0.854	4.7	
Nylon 66[b]			0.787	4.2	1.14
P 1-18H	25–30	0.18			0.8
P 1-18L	0–6	0.18			1.23

[a] The first number in the polymer designation characterizes it as copolyamide **1** or **2**. [b] Sample no. 11169 furnished by du Pont de Nemours. [c] In formic acid containing 10 vol % of water and 0.1 *M* sodium formate. [d] In formic acid containing 4.7 *M* water and 0.7 *M* perchloric acid.

TABLE II
FORMIC ACID SOLUTIONS USED AS SOLVENT MEDIA (TEMP 29.7°)

	Additive, *M*				Calibration standard	
Solvent no.	$HClO_4$	H_2O	HCOONa	H_0	Base[b]	pK_{base}
I	9.42	22.20				
II	5.89	16.30		−5.90	**4**	−5.3[c]
III	3.53	10.40		−4.86	2,4-DNA	−4.42[d]
IV	2.35	8.05		−4.39		
V	1.18	5.70		−3.77		
VI	0.353	4.04		−2.99	AB	−1.71[c]
VII	0.235	3.81		−2.74		
VIII	0.118	3.57		−2.52		
IX		3.34[a]		−1.11	*o*-NA	−0.29[e]
X		6.95[a]		−0.74		
XI		8.64[a]		−0.55		
XII		17.40[a]		+0.08		
XIII		3.34	0.147	+0.01	**5**	−0.62[c]
XIV		3.34	0.294	+0.26		
XV		3.34	0.735	+0.54	*p*-NA	+0.99[e]
XVI		3.34	1.47	+0.80		
XVII		3.34	2.94	+1.17		

[a] The water content was determined from the density of the solutions at 30°: International Critical Tables, Vol. 3, Mc-Graw Hill, New York, N. Y., 1928, p 122. [b] 2,4-DNA = 2,4-dinitroaniline; AB = azobenzene; *o*-NA = *o*-nitroaniline; *p*-NA = *p*-nitroaniline. [c] This work. [d] E. Hogfeldt and J. Bigeleisen, *J. Amer. Chem. Soc.*, **82**, 15 (1960). [e] R. Stewart and T. Mathews, *Can. J. Chem.*, **38**, 602 (1960).

values obtained are listed in Table II. For systems containing only formic acid and water, our values were in good agreement with those obtained by Stewart and Mathews.[16] The H_0 values were determined at 29.7° and their variation with temperature, which is known to be small, was neglected.[16,17]

Kinetic Measurements. Solutions prepared in the dark were placed in square 1-cm quartz cells. The cells were held in a thermostated copper block and placed in a specially designed Cary 14 spectrophotometer which allowed the samples to be alternately irradiated and analyzed in two directions perpendicular to one another. A 450-W xenon Osram lamp was employed for the irradiation with the beam focused on the sample cell. The light was filtered using Bausch and Lomb interference filters 33-78-34 and 33-78-36 (transmission maximum at 346 and 360 nm, half-width 35 and 23 nm, respectively) and a Corning filter 7-39 (transmission maximum 360 nm, half-width 47 nm). With the use of these three filters, the light intensity at the sample cell was 1.07, 6.67, and 13 mW/cm², respectively. These intensities were determined with the Black-Ray ultraviolet intensity meter (Ultraviolet Products, Inc., San Gabriel, Calif.). The temperature inside the cell was determined with a thermocouple. Samples were irradiated for 5–20 min, adequate to reach the photostationary state except for experiments with compound **4** in solutions of high acidity where the irradiation time was reduced to 3 min to minimize an irreversible side reaction. Following irradiation, the sample cell was shaken and the dark reaction was followed by recording automatically the change of absorbance at a suitable wavelength. The dark reaction was allowed to proceed for ten half-lives before recording a spectral absorption corresponding to the completion of the *cis–trans* isomerization.

Results

Behavior of Low Molecular Weight Analogs. When an azobenzene derivative is irradiated at an appropriate wavelength, the compound which may be considered to exist at equilibrium exclusively in the *trans* form is converted to the *cis* isomer. This reaction does not go to completion, since the reverse reaction takes place both by a thermal and a photochemical mechanism. At relatively low temperatures and at high irradiation intensities, the thermal *cis* → *trans* isomerization is negligible compared to the photochemical process and

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(16) See Table II, footnote *e*.
(17) C. D. Johnson, A. R. Katritzky, and S. A. Shapiro, *J. Amer. Chem. Soc.*, **91**, 6654 (1969).

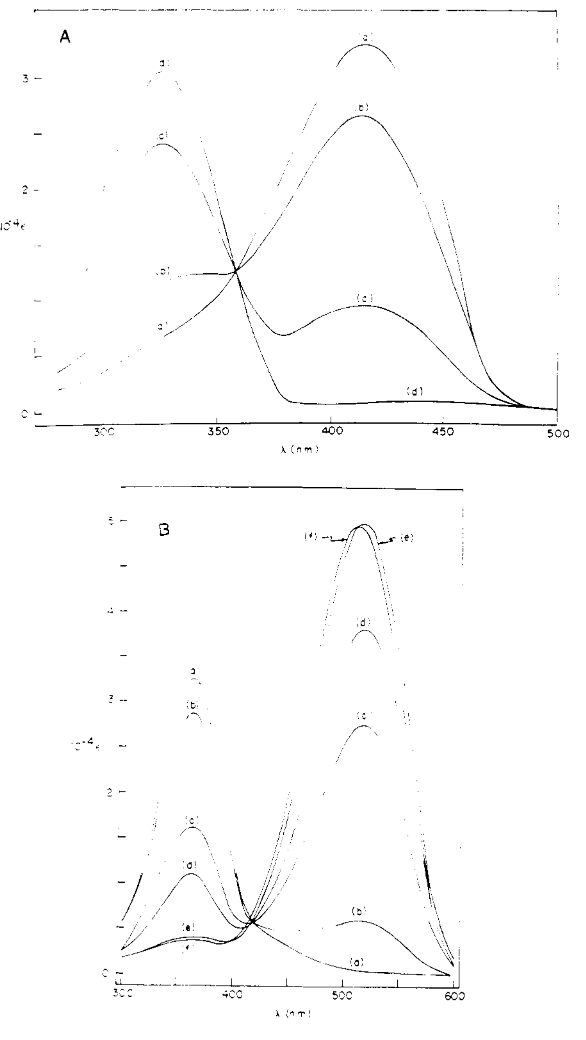


Figure 1. A, spectra of compound **4** at different solvent acidities: (a) in formic acid containing 9.42 *M* perchloric acid and 22.20 *M* water, (b) $H_0 = -5.90$, (c) $H_0 = -4.86$; (d) $H_0 = -1.11$ (temp 43.5°); B, spectra of compound **5** at different solvent acidities: (a) $H_0 = +1.17$, (b) $H_0 = +0.26$, (c) $H_0 = -1.11$, (d) $H_0 = 0.00$, (e) $H_0 = -2.52$, (f) $H_0 = -2.99$ (temp 29.7°).

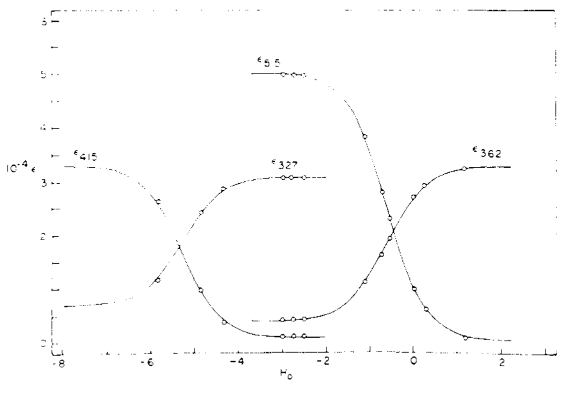
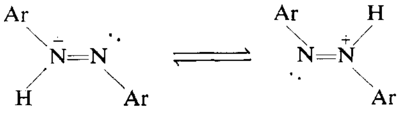


Figure 2. Effect of solvent acidity on molar extinction coefficients at the absorption maxima of compound **4** (ϵ_{415} and ϵ_{327}) and compound **5** (ϵ_{515} and ϵ_{362}).

the *cis*/*trans* ratio approaches a photostationary state.[18]

The situation is complicated by the fact that both the *trans* and *cis* isomers are engaged in acid–base equilibria, since in the models **4** and **5** both the azo groups and the amide groups can be protonated. The degree of protonation of the *trans* compounds may be obtained, in principle, from spectroscopic data. Protonation of *trans*-azobenzene is believed[19] to lead to structure **8** and it is accompanied by pronounced spectral changes [*e.g.*, the two prominent absorption peaks, which are characterized in the basic form of unsubstituted azobenzene by λ_{max} 428 (ϵ_{max} 1000), λ'_{max} 322 (ϵ'_{max} 20,500) become in the protonated form λ_{max} 420 (ϵ_{max} 27,100), λ'_{max} 236 (ϵ'_{max} 4000[19])]. Smaller spectral changes are characteristic of the protonation of the carbonyl oxygen[20] in amide groups of compounds such as acetanilide[21] (analogous to **5**) and N-methylbenzamide[22] (analogous to **4**). However, the amide absorption occurs at relatively low wavelengths at which our solvent medium is opaque and we were not in a position to study spectroscopically the amide protonation equilibria.



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The spectra of the *trans* isomers of **4** and **5** in media of varying acidity are shown in Figure 1. The isosbestic points are well defined, so that the absorption may be attributed to two species, containing the basic and the protonated azo groups.

In Figure 2 the molar extinction coefficients at the wavelength of the characteristic absorption maxima are plotted against H_0. The experimental points lie close to the theoretical curves expected for single protonation equilibria with $pK_{trans} = -5.3$ for compound **4** and $pK_{trans} = -0.62$ for compound **5**. (The only indication of an incipient protonation of the amide groups is a slight shift in the location of the long-wavelength absorption maximum of **5**, from 515 to 510 nm.)

The degree of protonation of the *cis*-azobenzene derivatives will be reflected in the rate of *cis–trans* isomerization. Denoting by Z, ZH^+, ZH_2^{2+}, and ZH_3^{3+} the various species in equilibrium with each other in a medium of any given acidity, the observed rate constant k_{obsd} will depend on the fractions α of the various forms as

$$k_{obsd} = k_1\alpha_Z + k_2\alpha_{ZH^+} + k_3\alpha_{ZH_2^{2+}} + k_4\alpha_{ZH_3^{3+}} \quad (1)$$

If the p*K* values of the successive protonation equilibria are sufficiently removed from one another, then a plot of log k_{obsd} against the acidity function H_0 will exhibit a series of plateau regions within which the rate is independent of H_0, and will reach a limiting slope of −1 in the intermediate regions. The intersections of

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(18) E. Fischer, *J. Amer. Chem. Soc.*, **82,** 3249 (1960).

(19) M. A. Hoefnagel, A. Van Veen, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **88,** 562 (1969).

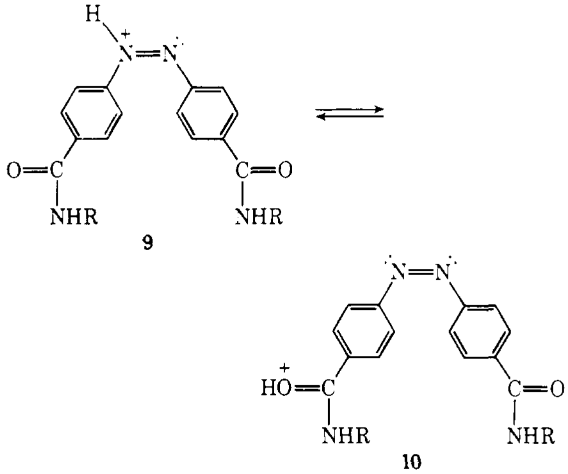
(20) (a) G. Fraenkel and C. Franconi, *J. Amer. Chem. Soc.*, **82,** 4478 (1960); (b) A. R. Katritzky and R. A. Y. Jones, *Chem. Ind.* (London), 722 (1961); (c) R. Stewart, L. J. Muenster, and J. T. Edward, *ibid.*, 1906 (1961).

(21) L. P. Hammett and A. J. Deyrup, *J. Amer. Chem. Soc.*, **54,** 4239 (1932).

(22) K. Yates and J. B. Stevens, *Can. J. Chem.*, **43,** 529 (1965).

these lines define the pK values characterizing the successive protonations.[7c]

The rates of the *cis–trans* isomerization of **4** and **5** were found to follow first-order kinetics under all experimental conditions investigated. Plots of log k_{obsd} against H_0 are shown in Figure 3. With compound **4** (curve A) the plot exhibited a linear range with a slope of −1 which appeared to approach two horizontal plateau regions. This curve defined $pK_{cis} = -3.5$. This may be compared with the spectroscopically determined $pK_{trans} = -5.3$, yielding $\Delta pK = pK_{cis} - pK_{trans} = +1.8$. A positive Δp$K$ has been reported previously for unsubstituted azobenzene[23] and would be expected, since the aromatic residues in the *cis* isomer are not coplanar[24] so that reduced resonance stabilization would tend to render the azo group more basic. However, since N-methylbenzamide has been reported to have $pK = -1.7$[22] we must consider ZH^+ to represent an equilibrium of species **9** and **10** with 1–2% of the protonation involving the amide groups. The addition of a second proton to ZH^+ is opposed by Coulombic forces and does, apparently, not take place to any appreciable extent for compound **4** within the H_0 range used in this study. This range was limited because of an increasing irreversibility of the photoisomerization of compound **4** in media of very high acidity, probably due to oxidative cyclization of the *cis* compound.[25]



In model compound **5**, the azo group is much more basic than in **4**, as would be expected, since the aromatic residues are now directly linked to the electron-donating -NHCOR instead of the electron-withdrawing -CONHR. As a result, the protonation of the azo groups takes place in much less acidic media than the protonation of the amide residues. The plot of log k_{obsd} against H_0 (Figure 3, curve B) suggests for ZH^+ a $pK = 1.65$ so that we obtain for compound **5** $\Delta pK = 2.27$. The addition of a second proton to ZH^+, which is characterized in the analogous acetanilide by $pK = -1.5$,[21] is less hindered by electrostatic interaction than in compound **4**, since the amide carbonyl is further removed from the azo group. It is, therefore, not surprising that we see the consequences of the second protonation in an increasing *cis–trans* isomerization rate at $H_0 < -1$. It should be noted, however, that our data do not allow us to assess the extent of amide protonation.

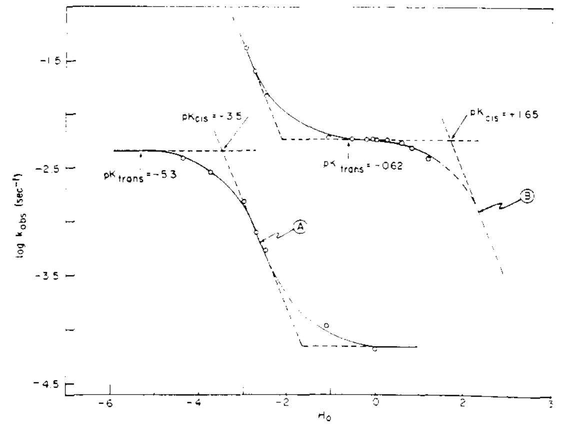


Figure 3. Variation of the observed rate constant for thermal *cis* → *trans* isomerization with solvent acidity: curve A, compound **4** at 43.5°; curve B, compound **5** at 29.7°.

Fischer has pointed out[26] that it is possible to calculate the spectrum of the pure *cis* isomer, if spectra of the *trans* form and of the photostationary states obtained on irradiation at two different wavelengths are available.

Figure 3 shows that in 95% formic acid ($H_0 = -1.11$) the *cis* form of **4** is almost completely deprotonated, while the *cis* form of **5** exists in the protonated form. These media were used, therefore, to determine the spectra of these two species. The basic form of the *cis* isomer of **5** was similarly studied in *n*-butyl alcohol solution. A quantitative determination of the spectrum of the *cis* isomer of protonated compound **4** is not possible because of the irreversible cyclization process referred to above. The various spectra of the *trans* and *cis* isomers are shown in Figures 4 and 5.

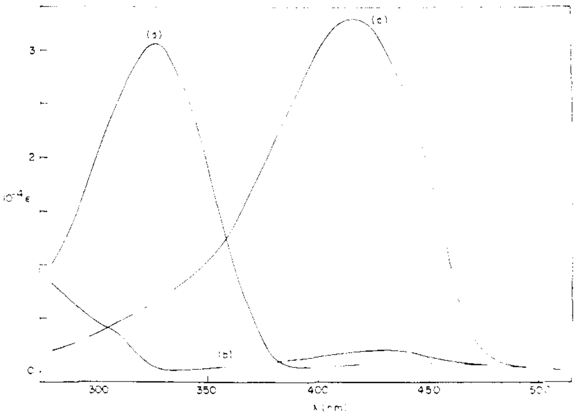


Figure 4. Compound **4**: (a) spectrum of the *trans* isomer in the basic form ($H_0 = -1.11$); (b) calculated spectrum of the *cis* isomer in the basic form ($H_0 = -1.11$); (c) spectrum of the *trans* isomer in the acid form (formic acid made 9.42 M in perchloric acid and 22.20 M in water) (temp 43.5°).

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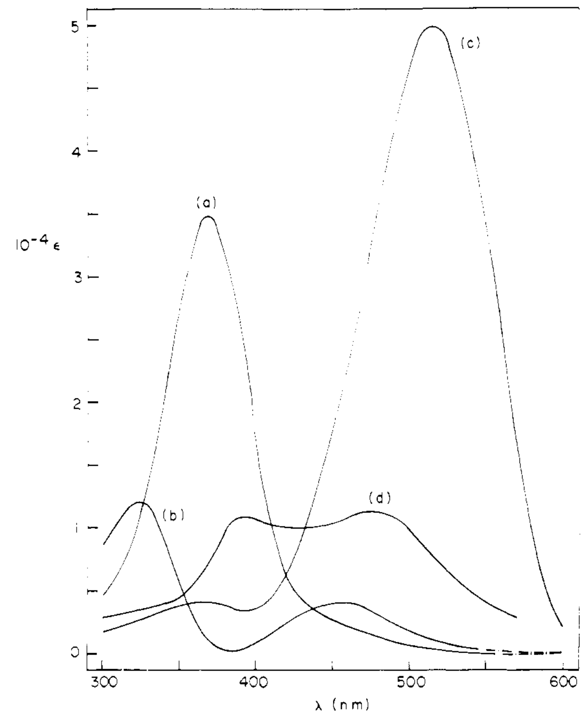

Figure 5. Compound **5**: (a) spectrum of the basic form o the *trans* isomer in *n*-BuOH (temp 29.7°); (b) calculated spectrum of the basic form of the *cis* isomer in *n*-BuOH (temp 29.7°); (c) spectrum of the acid form of the *trans* isomer (H_0 = 2.52, temp 29.7°); (d) calculated spectrum of the acid form of the *cis* isomer (H_0 = 1.11, temp 9.6°).

Behavior of Polymers. Most of the polymer studies were carried out in 95% formic acid ($H_0 = -1.11$). In this medium, the absorption spectrum of copolyamide **1** was identical with that of model **4**, corresponding to unprotonated azo groups. With copolyamide **2**, where the pK_{trans} is close to the H_0 of the medium, the spectral data reveal a considerably lower degree of protonation of the polymer than that of the model compound, *i.e.*, 0.61 as against 0.76. This is to be expected, since the mutual repulsion of the ionic charges attached to the macromolecular chain would render protonation of the azo group increasingly difficult with increasing charge density, so that the effective p*K* shifts gradually to higher values.[27] In the case under consideration, the azo residues are too distant from one another for significant Coulombic interaction and we must assume that the protonation of the azo groups is being hindered by a partial protonation of the amide residues. This partial protonation is revealed by the viscosity behavior of Nylon 66 in formic acid solution, which exhibits a pattern of behavior typical of polyelectrolytes, unless salts are added to increase the concentration of counterions.[28]

We may note that aliphatic amides are significantly more basic than amide groups directly linked to aromatic rings. For instance, propionamide and N-*n*-butylacetamide have been characterized by $pK = -0.8$ and $pK = -0.4$, respectively,[22] as against $pK = -1.53 \pm 0.08$ determined for acetanilide.[21] Only the protonation of the aromatic amide groups would be expected to interfere with the conversion of the azo residues of copolyamide **2** to their acidic form.

Table III

Kinetic Data on Compound **5** and Related Polymers (Temp 29.7°)

Solvent no.	Additive (0.15 g/ml)	$k_{obsd} \times 10^5$, sec^{-1} **5**	P 2-01	P 2-04
VI		4100		
VII		2600		
VIII		1450		
IX		580	500	470
	Nylon 66[a]		390	
	N-PPA[b]		415	
X		580		
XI		580		
XII		580		
XIII		580		
XIV		580		
XV		535		
XVI		470		
XVII		384		

[a] $\bar{M}_v$ = 42,000. [b] N-PPA = N-propylpropionamide.

The *cis–trans* isomerizations of solutions of copolyamide **2** followed strictly first-order kinetics under all experimental conditions. In comparing the behavior of the polymer with that of the corresponding model compound, we must take account of the difference in their degree of protonation as discussed above. This may be done, in principle, by comparing the isomerization rate of the polymer in 95% formic acid ($H_0 = -1.11$) to that of the model compound **5** in a medium with $H_0 = -0.82$ (here we are assuming that pK_{cis} and pK_{trans} are shifted equally by the charge density of the polymer chain). Actually, inspection of Figure 3 shows that in the range of $-1.11 < H_0 < 0$ the isomerization rate of model compound **5** is practically independent of the acidity of the medium, since the *cis* azobenzene residues have attained virtually complete protonation and the effect of amide protonation is not yet kinetically significant. It is, therefore, admissible to compare the isomerization rates of **2** and **5**, both in 95% formic acid solution.

The kinetic data obtained with copolyamide **2** and model **5** are listed in Table **III**. The following points may be made. (a) The isomerization rate of the polymer is only 15% lower than that of the analog. Incorporation into the polymer backbone appears, therefore, to have very little effect on the ease with which this reaction takes place. (b) The isomerization rate of the polymer is independent of the concentration of azobenzene residues in the chain. (c) Addition of 0.15 g of Nylon 66 per milliliter of solution affects the rate approximately in the same way as the addition of the same concentration of N-propylpropionamide, a low molecular weight nylon analog. It should be stressed that this nylon concentration lies well above the critical concentration c^* which is related to the intrinsic viscosity $[\eta]$ by $c^* = 2.5/[\eta]$ (g/ml).[29] In our case c^* =

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TABLE IV
COMPARISON OF KINETIC BEHAVIOR OF COPOLYAMIDE 1 AND RELATED MODEL COMPOUNDS

Compd designation	Solvent no.	Temp, °C	$k_1 \times 10^5$, sec^{-1}	$k_2 \times 10^5$, sec^{-1}	α
4	VI	43.5		153	
7	VI	43.5		700	
P 1-02H	VI	43.5	415	76.5	0.095
P 1-18H	VI	43.5	380	72	0.265
4	IX	43.5		10.7	
7	IX	43.5		100	
P 1-02H	IX	43.5	67	6.9	0.095
P 1-02L	IX	43.5	78	7.4	0.095
P 1-18H	IX	43.5	60	6.9	0.265
P 1-18L	IX	43.5	71	7.0	0.265
4	IX	57		23.4	
6	IX	57		31	
P 1-02H	IX	57	190	15	0.095
P 1-02L	IX	57	140	17	0.095
P 1-18H	IX	57	140	17	0.265
P 1-18L	IX	57	150	16	0.265

0.032 g/ml, so that the chains of the nylon must have been heavily intertwined with the copolyamide.

The *cis–trans* isomerization of copolyamide **1** did not follow first-order kinetics. Analysis of the kinetic data showed that the reaction could be generally represented as a biphasic process of the form

$$c/c_0 = \alpha \exp(-k_1t) + (1 - \alpha) \exp(-k_2t) \quad (2)$$

where c and c_0 are the concentrations of the azo groups in the *cis* form at time t and at the outset of the dark reaction. The data listed in Table IV show that the reaction has the following characteristics. (a) The rate constants k_1 and k_2 are very similar in the copolyamide in which about 2% and about 18% of the repeat units contained azobenzene residues. (b) The ratio of the high and low rate constant k_1/k_2 appeared to decrease with increasing acidity of the medium. (c) The fraction of the azobenzene residues isomerizing at the fast rate did not change with a change in the reaction temperature but was almost three times as large in the copolyamide with the high azo content. (d) The isomerization rate of model compound **4** under comparable conditions is very similar to k_2, *i.e.*, the rate constant characterizing the "slow" azo groups in the polymer.

Although the photoisomerization of copolyamide **1** is not strictly reversible in the more acidic media, because of the oxidative cyclization referred to above in our discussion of model **4**, this factor would not account for deviation from first-order kinetics in the dark reaction. It also seems improbable that the anomaly is in some manner connected with the polymeric nature of the reagent, since no similar phenomenon was observed with copolyamides of type **2**. We considered two possible interpretations for the existence of groups with a faster isomerization rate. If such groups occur at the chain ends where only one of the carboxyls of azodibenzoic acid has reacted, then the ratio of the isomerization rate constants for model compounds **6** and **4** should be approximately k_1/k_2. The data in Table IV show that **6** is only 30% faster than **4**. Another possible cause of the anomaly is the oxidation of a part of the azo groups to the corresponding azoxy derivative, since it has been reported that azoxybenzene undergoes *cis–trans* isomerization in nonprotonating media 50 times as fast as azobenzene.[30] To evaluate this possibility, we compared model **7** with model **4**. The data in Table IV show that in 95% formic acid and at 43.5° the azoxy derivative isomerized faster by a factor of 9.3. In a much more acidic medium containing 0.35 *M* perchloric acid, the ratio of the rate constants of the two model compounds decreased to 4.7, as would be expected since azoxybenzene is protonated with much greater difficulty than azobenzene.[31] We see then, that the assumption that the biphasic reaction of the polyamide **1** is due to partial oxidation of the azo groups is supported both by the magnitude of k_1/k_2 and by the decrease of this ratio in the more acidic medium. This interpretation is, however, inconsistent both with a theoretical consideration and with another type of experimental evidence. (1) The oxidation of azo to azoxy groups is favored by an increase in the basicity of the azo function[32] and it is, therefore, difficult to understand why oxidation should have occurred in the preparation of polymer **1**, with its less basic azo group, but not in polymer **2**. (2) The spectrum of model compound **4** in 95% formic acid has characteristic absorption peaks at 327 and 445 nm with extinction coefficients of 30,500 and 850, respectively. The azoxy compound does not absorb appreciably at 445 nm and has ϵ_{327} 20,800. We may, therefore, characterize the mole fraction of azobenzene residues oxidized to the corresponding azoxy derivative from $\epsilon_{445}/\epsilon_{327}$. This ratio was found to be 0.0279 both in copolyamide P1-18 and in model compound **4**, although an azoxy content corresponding to $\alpha = 0.265$ (where α is the fraction of groups isomerizing at the fast rate) would have led to a reduction of $\epsilon_{445}/\epsilon_{327}$ to 0.0224.

Discussion

The results of the present study reinforce our earlier conclusion[3] that conformational transitions involving rotation around a bond in the backbone of a long chain molecule take place with no greater difficulty than a corresponding rotation in small molecules.[33] The implications of this result are even more far reaching in the present case, since the conversion from the *cis* to the *trans* azobenzene moiety involves, on the basis of crystallographic data on the two forms of azobenzene,[24a, 34] an increase in the distance between the two *para* carbons from 5.5 to 9.0 Å. The local expansion attending *cis–trans* isomerization of copolyamides **1** and

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(33) The use of the term "rotation" is not meant here to bear on the mechanism of the *cis–trans* isomerization in the azobenzene residues which is believed to involve a linear intermediate rather than rotation around the –N=N– bond (*cf.* J. Binenboym, A. Barcat, A. Lifschitz, and J. Shmir, *J. Amer. Chem. Soc.*, **88**, 5039 (1966); E. R. Talaty and J. C. Fargo, *Chem. Commun.*, 65 (1967); D. Gegiou, K. A. Muszkat, and E. Fischer, *J. Amer. Chem. Soc.*, **90**, 5907 (1968).

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2 is even larger, since the amide groups are rigidly attached to the azobenzene residue. The isomerization also changes from 62 to 0° the angle between the bonds connecting the $-CONHC_6H_4N{=}NC_6H_4NHCO-$ (or, the $-NHCOC_6H_4N{=}NC_6H_4CONH-$) groups to the rest of the chain molecule. We must then consider the question of how this restraint can be without a significant effect on the rate of the process.

The result may be rationalized in the following manner. The necessity to rearrange the conformation of a considerable portion of the polymer chain as the transition state in the *cis–trans* isomerization is being approached will, indeed, slow down the approach to the transition state, but it will reduce equally the rate at which the geometry of the strained azobenzene group returns to that characterizing its ground state. Thus, the equilibrium concentration of any intermediate state will not be altered as long as the energy of the azobenzene moiety, in any given geometric form, is unaffected by the incorporation of this group into the polymer chain. We should, therefore, not expect the isomerization rate to be reduced unless the time required for the change of the chain conformation to a form consistent with the transition state of the azo group is comparable with the relaxation time of the *cis–trans* isomerization in the absence of such added restraints. The requirement for extensive changes in the chain conformation is apparently not rate limiting for the *cis–trans* isomerization process even at polymer concentrations corresponding to extensive chain entanglements. We hope to explore in the future the isomerization behavior at still higher polymer concentrations and particularly the characteristics of such processes in bulk polymers, both above and below the glass transition point.

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The Conformation about the Nitrogen—α-Carbon Bond in Random-Coil Polypeptides

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ABSTRACT: The conformation about the N—C$^\alpha$ bond in random-coil polypeptides is studied by computing the average vicinal coupling $J_{N\alpha}$ of the peptide NH and C$^\alpha$ proton. Previously calculated conformational energies of random-coil polypeptides make possible the computation of the vicinal proton coupling by taking an average over the calculated conformations and assuming a reasonable Karplus-like dependence of $J_{N\alpha}$ on the dihedral angle φ'. The calculated coupling agrees within the probable experimental error with the values observed in solution for three different random-coil polypeptides.

Measurements such as light scattering,[1,2] viscosity,[1,2] and dielectric increments[3] yield information concerning the overall extension of a random-coil polypeptide chain in solution, as expressed by the mean square end-to-end distance $\langle r^2 \rangle$. By contrast, the measurement of the nuclear magnetic resonance spectra of random-coil polypeptides in solution gives information concerning the local conformation about the N—C$^\alpha$ bond through the magnitude of the vicinal coupling $J_{N\alpha}$ of the peptide NH and C$^\alpha$ proton (see Figure 1).

The assumption of a reasonable Karplus-like dependence[4] of $J_{N\alpha}$ on the dihedral angle φ' leads to the following relation

$$J_{N\alpha}(\text{Hz}) = \begin{array}{ll} 8.5\cos^2\varphi' & (0° \leq \varphi' \leq 90°) \\ 9.5\cos^2\varphi' & (90° \leq \varphi' \leq 180°) \end{array} \qquad (1)$$

where φ' is the customarily defined dihedral angle between N–H and C$^\alpha$–H$^\alpha$ and is directly related to the rotation angle[5a] φ about the N—C$^\alpha$ bond. A similar relation is given by Bystrov, *et al.*[6]

$$J_{N\alpha}(\text{Hz}) = 8.9\cos^2\varphi' - 0.9\cos\varphi' + 0.9\sin^2\varphi' \qquad (2)$$

From the conformational energy calculations of Brant and Flory[7] and Brant, Miller, and Flory[8] ap-

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