Rates of Conformational Transitions in Solutions of Randomly Coiled Polymers. I. Nuclear Magnetic Resonance Study of Transitions in the Backbone of Polyamides[1]

Yoram Miron, Bruce R. McGarvey, and Herbert Morawetz

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York 11201

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ABSTRACT: Nmr spectra were recorded for polyamides derived from piperazine or N,N′-dimethylethylenediamine and aliphatic aromatic dicarboxylic acids in aqueous phenol (containing 92.5 wt % phenol) over a range of temperatures. Similar measurements were carried out on acetylpiperidine and on acetyl or benzoyl derivatives of piperazine and N,N′-dimethylethylenediamine used as analogs of the polymers. Hindered rotation around the amide bond was evidenced by the splitting of NCH_2 and NCH_3 bands at low temperatures and coalescence of the split peaks on heating. The free energy of activation for hindered rotation was obtained from the coalescence temperature and the true chemical shift of the split peaks. The enthalpy of activation was computed from the temperature dependence of the half-width of the coalesced peak. No significant difference was found for these activation parameters in the polymers and their analogs and the implication of this finding on the mechanism of conformational transitions in long-chain polymers is discussed. The nmr spectrum of poly(succinylpiperazine) gives evidence of a preferred helical conformation. This feature is less pronounced in the adipyl and absent in the sebacyl polyamide. Differences in the interactions of NCH_3 groups and phenyl residues in poly(terephthaloyl-N,N′-dimethylethylenediamine) and its analog are attributed to restricted rotation of the phenyl rings in the polymer.

Long-chain polymer molecules can exist in solution in a large number of conformations and a substantial part of the physical chemistry of polymers has been concerned for many years with the experimental characterization and the theoretical interpretation of the extension of such chains under a particular set of conditions. By contrast, surprisingly little is known about the rate of interconversion of the various accessible conformations. This problem has been studied intensively only for the special case of the helix–coil transitions of polypeptides and polynucleotides, for which both experimental data[2] and theoretical treatments[2a,b,3] are available, and for the case of helix–helix transition in poly(L-proline).[2e,f]

In considering the rates of transitions between two randomly coiled conformations of a long-chain molecule, we should like to compare the velocities with which hindered rotation around a given type of covalent bond can take place in a small molecule and in the backbone of a polymer molecule. In analogy to the postulated crankshaft-like motion in polymer melts,[4] it was assumed that the rotation around a single covalent bond in the polymer backbone would be most improbable, since it would require motion of a long section of the chain through the viscous solvent medium, so that at least two such rotations would be correlated to restrict the motion to a relatively short section of the chain. This would, of course, render the activation parameters for conformational transitions in polymer backbones substantially higher than those for similar transitions in small molecules and it was the purpose of the present study to evaluate the magnitude of this effect.

Nuclear magnetic resonance spectroscopy provides a most convenient tool for a study of hindered rotation around a covalent bond. This principle may be exemplified on N,N-dimethylformamide[5] where the linkage between the carbonyl carbon and the nitrogen has partial double bond character. As a result, rotation around this C–N bond is relatively slow and the magnetic nonequivalence of the hydrogens in the methyl groups *cis* and *trans* to the carbonyl oxygen leads, at ambient temperatures, to two absorption bands in the nmr spectrum. At higher temperatures, where the rate of rotation around the C–N bond becomes faster than the chemical shift difference of the two methyl groups, the magnetic field of the two groups is effec-

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[1] Abstracted from a Ph.D. thesis to be submitted by Y. Miron to the Graduate School of the Polytechnic Institute of Brooklyn. Financial support of this study by Research Grant GM-05811 of the National Institutes of Health is gratefully acknowledged.

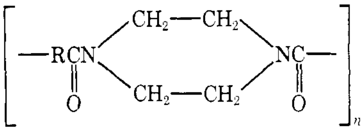
[2] (a) E. B. Freese and E. Freese, *Biochemistry*, **2**, 707 (1963); (b) D. M. Crothers, *J. Mol. Biol.*, **9**, 712 (1966); (c) P. F. Davidson, *ibid.*, **22**, 97 (1966), *Biopolymers*, **5**, 715 (1967); (d) H. C. Spatz and R. L. Baldwin, *J. Mol. Biol.*, **11**, 213 (1965); (e) A. R. Downie and A. A. Randall, *Trans. Faraday Soc.*, **55**, 2132 (1959); (f) I. Z. Steinberg, W. F. Harrington, A. Berger, M. Sela, and E. Katchalski, *J. Amer. Chem. Soc.*, **82**, 5263 (1960).

[3] C. Levinthal and H. R. Crane, *Proc. Nat. Acad. Sci. U.S.*, **42**, 436 (1956); W. Kuhn, *J. Mol. Biol.*, **3**, 473 (1961); H. C. Longuet-Higgins and B. H. Zimm, *ibid.*, **2**, 1 (1960); M. Fixman, *ibid.*, **6**, 39 (1963); G. Schwarz, *ibid.*, **11**, 64 (1965); M. E. Craig and D. M. Crothers, *Biopolymers*, **6**, 385 (1968), and papers cited therein.

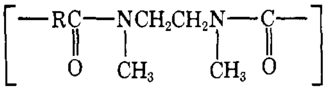
[4] T. Schatzki, *J. Polym. Sci.*, **57**, 496 (1962); *Amer. Chem. Soc., Div. Polym. Chem., Preprints*, **6**, 646 (1965); *J. Polym. Sci., Part C*, **14**, 139 (1966); B. Wunderlich, *J. Chem. Phys.*, **37**, 2429 (1962); R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303 (1963).

[5] (a) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956); (b) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962); (c) R. C. Neuman, Jr., and L. B. Young, *ibid.*, **69**, 2570 (1965); (d) C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci.*, **35** (2), 788 (1965).

tively averaged and the two bands coalesce to a single peak. Gutowsky and his collaborators have developed the theory from which the temperature dependence of the shape of the absorption band can be used to calculate the activation parameters for the hindered rotation.[5a,6,7] We have used similar methods to compare hindered rotation around the amide bonds in polyamides derived from piperazine and N,N′-dimethylethylenediamine, respectively (represented schematically by I and II), with the behavior of analogous low molecular weight model compounds.



I



$$\left[-\underset{\underset{\displaystyle O}{\|}}{RC}-\underset{\underset{\displaystyle CH_3}{|}}{N}CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{N}-\underset{\underset{\displaystyle O}{\|}}{C}-\right]$$

II

Experimental Section

Model Compounds. N-Acetylpiperidine (AP) was prepared by treating 0.2 mol of piperidine (City Chemical Co.) with 0.1 mol of acetic anhydride. The product was distilled collecting the fraction boiling at 125° at 35 torr. To remove piperidine acetate a hexane solution was extracted with water until the nmr spectrum in 92.5 wt % aqueous phenol at ambient temperature showed a single peak in the $-COCH_3$ region. Piperazine and N,N′-dimethylethylenediamine (Aldrich Chemical Co.) were acetylated by acetic anhydride. They were benzoylated by benzoyl chloride under Schotten–Baumann conditions. N,N′-Diacetylpiperazine (DAP) was recrystallized from benzene [mp 139.5–140° (lit.[8] mp 138.5°)], N,N′-dibenzoylpiperazine (DBP) was recrystallized from methanol [mp 192, 193° (lit.[9] mp 194°)], N,N′-diacetyl-N,N′-dimethylethylenediamine (ADE) was recrystallized twice from hexane [mp 94.5–95° (lit.[10] mp 90–92°)], and N,N′-dibenzoyl-N,N′-dimethylethylenediamine (BDE) was recrystallized from aqueous methanol [mp 177.5–178° (lit.[11] mp 177–178°)].

Polymers. A low molecular weight poly(succinylpiperazine) (PSuP) was prepared by interfacial polycondensation by adding 0.025 mol of succinyl dichloride in 200 ml of CCl_4 to 0.0275 mol of piperazine in an aqueous solution of 0.05 mol of sodium carbonate. The polymer emulsion was coagulated with dimethylformamide, filtered, washed with methanol, boiled with methanol, filtered after addition of ether, washed with ether, dried, redispersed in water, precipitated by cold methanol, filtered and dried. The average degree of polymerization ($\bar{P}$) determined by end group titration with 0.2 N HCl was 10, the intrinsic viscosity ($[\eta]$, deciliters per gram) was 0.11 in 90% formic acid ($[\eta]_{FA}$) and 0.16 in 1:1 $(CHCl_2)_2$–phenol ($[\eta]_{T-P}$). Poly(succinylpiperazine) of higher $\bar{P}$ ($[\eta]_{FA}$ 0.14, $[\eta]_{T-P}$ 0.77) was obtained by adding slowly 0.02 mol of piperazine to 0.01 mol of succinyl chloride in 20 ml of CH_2Cl_2. The precipitate was washed with CH_2Cl_2, boiled with water, filtered and washed with water. Poly(adipylpiperazine) (PAP) ($[\eta]_{FA}$ 0.48), poly(sebacylpiperazine) (PSeP) ($[\eta]_{FA}$ 0.88), poly(terephthaloylpiperazine (PTP) ($[\eta]_{T-P}$ 0.43), poly(sebacyl-N,N′-dimethylethylenediamine) (PSeDE) (mp 75–75°, $[\eta]_{FA}$ 0.15) and poly(terephthaloyl-N,N′-dimethylethylenediamine) (PTDE) [mp 295° (lit.[12] mp 380°), $[\eta]_{T-P}$ 0.31] were all prepared by interfacial polycondensation.

Analysis of Phenol–Water Solvents. Phenol–water mixtures were analyzed by bromination with 0.1 N Br_2 and back-titrated with 0.1 N $Na_2S_2O_3$. Unless otherwise specified, the medium contained 92.5 wt % phenol.

Nuclear Magnetic Resonance Spectra. The nmr spectra were obtained with a Varian 60 MHz spectrometer with a variable-temperature probe. In the absence of an external source of heat, the "ambient temperature" of the sample was 38–40°. Audiofrequency modulation was used to calibrate the spectra by the side-band method. The temperature dial was calibrated by the separation of ethylene glycol peaks above 40° or methanol peaks below 40°.[13] For each spectrum above the coalescence temperature the Y gradient and curvature were optimized. The sweep rate was 0.5 cps/sec. The homogeneity of the field was calibrated with a water sample. Chemical shifts are specified with reference to tetramethylsilane (TMS).

Analysis of Nmr Data

In order to select the method which will be used in determining the rates of hindered rotation from the nmr data, we must take account of two factors of the systems to be studied. (1) The absorption bands of polymers are relatively broad, because of the viscosity of polymer solutions, low mobility of the polymer segments, dipole–dipole interactions and spin–spin coupling. (2) The polyamides, which are the subjects of this investigation, are only soluble in hydrogen-bonding solvents. Since the extent of hydrogen bonding will be temperature dependent, a strong temperature dependence of the chemical shifts is to be expected.

These considerations led us to the procedure in which the half-width of the coalesced peak (*i.e.*, the band width at half of its maximum intensity) is used for the calculation of the rate of exchange of magnetically nonequivalent protons.[14] This method has several advantages as compared to those based on parameters obtained below the coalescence temperature, T_c. In particular, band broadening resulting from high solution viscosity, low chain mobility and spin–spin coupling of the poorly resolved spectrum is minimized and a relatively wide temperature range is available for study. (This is particularly important when using water–phenol mixtures as the solvent medium, since freezing of the solution narrows the temperature range below T_c over which measurements can be made.)

The procedure used consisted of the following steps.

1. Spectra were obtained at 2° intervals, optimizing the Y gradient and curvature on the most intense peak of the spectrum, so as to minimize its width. The half-width W of this peak was then measured with an accuracy of 0.1 cps.

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(6) H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *Ric. Sci.*, **21**, 279 (1953).

(7) H. S. Gutowsky and A. Saika, *ibid.*, **21**, 1688 (1953).

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(11) L. Bauer, *J. Amer. Chem. Soc.*, **78**, 1945 (1956).

(12) V. E. Shashoua and W. M. Eareckson, *J. Polym. Sci.*, **40**, 343 (1959).

(13) Model A-60 Analytical NMR Spectrometer System Manual, Varian Associates, Palo Alto, Calif.

(14) M. Takeda and E. O. Stejkal, *J. Amer. Chem. Soc.*, **82**, 25 (1960).

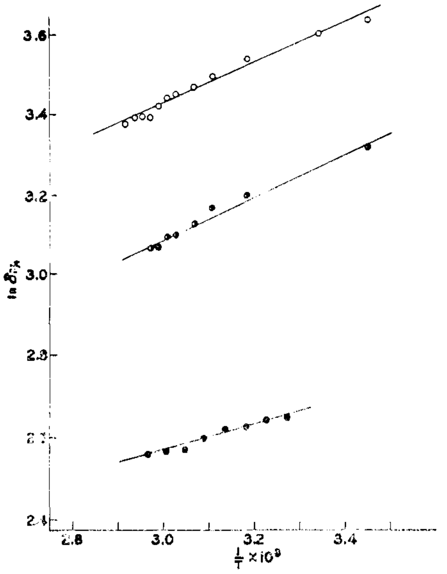

Figure 1. Temperature dependence of $\delta\nu_M$ for methylene hydrogen in piperazine ring: ○, DAP; ◑, PAP; ●, PSP.

2. The coalescence temperature, T_c, was determined as the lowest temperature at which the two absorption peaks merged into a single peak and the peak separations $\delta\nu$ were measured at $T < T_c$.

3. At temperatures well below T_c, the effect of chemical exchange on the apparent chemical shift $\delta\nu$ is negligible and we may approximate it to the true chemical shift $\delta\nu_M$. The true chemical shift at coalescence, $\delta\nu_{MC}$, was estimated by using the linear extrapolation of ln $\delta\nu_M$ against $1/T$ suggested by Gutowsky, *et al.*[15]

4. At T_c, the rate constant k for hindered rotation is

$$k_c = (\sqrt{2}\pi/2)\delta\nu_{MC} \qquad (1)$$

and the corresponding free energy of activation was obtained from

$$\Delta F^{\pm} = RT_c[\ln(RT_c/Nh) - \ln(\sqrt{2}\pi/2)\delta\nu_{MC}] \qquad (2)$$

where N is Avogadro's number and h is Planck's constant.

5. The half-width of the absorption peak W_m measured at the highest experimentally accessible temperature T_m was employed to estimate the half-width W_0 corresponding to the absence of exchange broadening, using[13]

$$k/\delta\nu_M = (\pi/2)\delta\nu_M/(W - W_0) \qquad (3)$$

and the assumed linear dependence of ln ν_M on $1/T$ to yield

$$\ln(W_m - W_0) = \ln(\delta\nu_M/\sqrt{2}) + (T_c^{-1} - T_m^{-1})\{-E_a - [d\ln\nu_M/d(1/T)]\} \qquad (4)$$

where E_a = activation energy for hindered rotation.

6. In first approximation, it was assumed arbitrarily that $\Delta S^{\pm} = 0$, so that $E_a \approx \Delta F^{\pm} + 0.7$ kcal/mol. The temperature dependence of $\delta\nu_M/k$ was then obtained from an Arrhenius plot, using eq 1 and estimating the slope of a plot of ln ν_M against $1/RT$ as 1 kcal/mol. The ratio $\delta\nu/\delta\nu_M$ was then obtained from[4a]

$$2k/\pi\delta\nu_M = [1 - (\delta\nu/\delta\nu_M)^2]^{1/2} \qquad (5)$$

and $\delta\nu$ being known, $\delta\nu_M$ was determined. These values were smoothed by fitting a straight line to a plot of ln $\delta\nu_M$ against $1/T$. Typical such plots are shown in Figure 1.

7. Values of $(k/\pi\delta\nu_M)$ were computed using the Takeda–Stejskal relation[13]

$$2k/\pi\delta\nu_M = [\mathcal{W}_0 + \mathcal{W}(1 + 2\mathcal{W}^2 - \mathcal{W}^4)^{1/2}] \times (\mathcal{W}^2 - \mathcal{W}_0^2)^{-1}$$

$$\mathcal{W}_0 = W_0/\delta\nu_M \qquad (6)$$

$$\mathcal{W} = W/\delta\nu_M$$

using an IBM-360 computer. The input included the slope and intercept of a plot of ln ν_M' against $1/T$, the calculated values of W_0 and $W = f(T)$ for $T > T_c$. The computer first determined $k/\pi\delta\nu_M$ and then fitted by a least-square analysis the best linear plot of ln $(k/\pi\delta\nu_M)$ against $1/T$ to determine E_a. Typical plots of this type are shown in Figure 2.

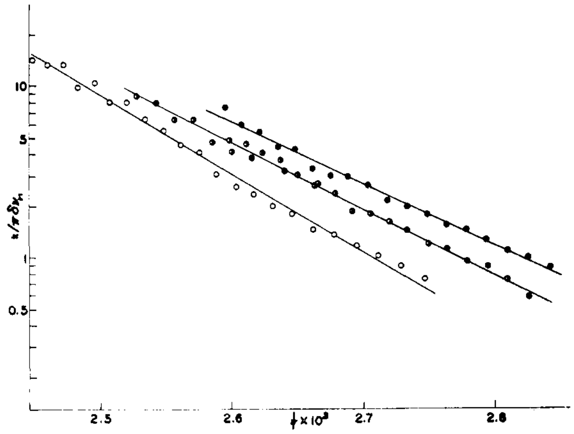

Figure 2. Temperature dependence of $k/\pi\delta\nu_M$: ○, DAP; ◑, PAP; ●, PTDE.

8. The value of W_0 is, in general, temperature dependent. For small molecules, diffusing and rotating rapidly, the spin–spin relaxation time T_2 equals the spin–lattice relaxation time T_1 and $W_0 = 1/\pi T_2$ is proportional to the ratio of viscosity and temperature.[16] For hydrogen-bonded systems, this quantity tends to decrease with temperature, as more and more of the hydrogen bonds are being dissociated. For diacetylpiperazine in 92.5% aqueous phenol the fraction of hydrogen-bonded complexes and the heat of dissociation of the complex were estimated from the temperature dependence of the chemical shift. This led to an estimate of 1.5 kcal/mol as the contribution from hydrogen bonding to the average activation energy of viscous

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[15] H. S. Gutowsky, J. Jones, and T. H. Siddall, *J. Amer. Chem. Soc.*, **89**, 4300 (1967).

[16] J. A. Pople, W. G. Schneider, and H. J. Bernstein "High Resolution Nuclear Magnetic Resonance," McGraw Hill Book Co., Inc., New York, N. Y., 1959, pp 201–207.

flow in the range 40–135°. This value compares to 1.8 kcal/mol obtained from the slope of a plot of ln (W_0T) against $1/RT$.

For polymeric solutes the estimate of W_0 at low temperatures is difficult, since line broadening is largely the result of spin–spin coupling and low resolution of the spectrum. Also, there is no trend, even at high temperatures, for T_1 to approach T_2[17] and the temperature dependence of W_0 has no relation to the temperature dependence of macroscopic viscosity.[18] Values of W obtained sufficiently far above T_c to make exchange broadening negligible were corrected for residual broadening by eq 4 and ln (W_0T) was computed as a function of $1/RT$. The plot was curved but had an average slope of 1.45 kcal/mol. Using the temperature-dependent W_0 values in eq 6 lowered E_a by 0.9 kcal/mol. All the E_a values were, therefore, lowered by 1 kcal/mol to account for the temperature dependence of W_0.

With diamide and polyamide derivatives of N,N′-dimethylethylenediamine, rotation around the C–N bond leads to isomers with the N-methyl *cis* or *trans* to the carbonyl oxygen, characterized by probabilities p_A and p_B, where $p_A \neq p_B$. In that case, we should use in place of eq 3 the more general relation, eq 7, and the

$$k/\delta\nu_M = 2\pi p_A p_B \delta\nu_M/(W - W_0) \qquad (7)$$

temperature dependence of $k/\delta\nu_M$ contains now also the variation of p_Ap_B with temperature. It can be shown that this contribution may be eliminated by subtracting from the apparent E_a value the correction $\Delta H(p_A - p_B)$, where ΔH is the enthalpy for the conversion B → A. For disubstituted amides of the type used in this study, ΔH may be assumed small and, since $p_A - p_B < 1$, the correction was neglected.

Results and Discussion

General Features of the Nmr Spectra of Model Compounds. N-Acetylpiperidine and diacetylpiperazine were used as model compounds for polyamides derived from piperazine and aliphatic dicarboxylic acids and N,N′-diacetyl-N,N′-dimethylenediamine served similarly as a model for polyamides derived from N,N′-dimethylethylenediamine. The benzoyl derivatives of piperazine and of N,N′-dimethylethylenediamine were used as models for polyamides derived from terephthalic or isophthalic acid. The model compounds were studied in the same solvent media as the polymers; of these, aqueous phenol is of particular interest, since it tends to magnify the chemical shift between rotational isomers. This effect is due to diamagnetic shielding by the aromatic nuclei, which has been used previously to resolve protons placed in slightly different environments on a polymer chain.[19] In our case the effect would be expected to be magnified because of hydrogen bonding of the phenol to the carbonyl oxygen of the amide, providing substantially greater shielding to protons placed *cis* to the carbonyl group. Figures 3–7 show the nmr spectra of the model compounds in phenol–water at ambient temperature and at 117°.

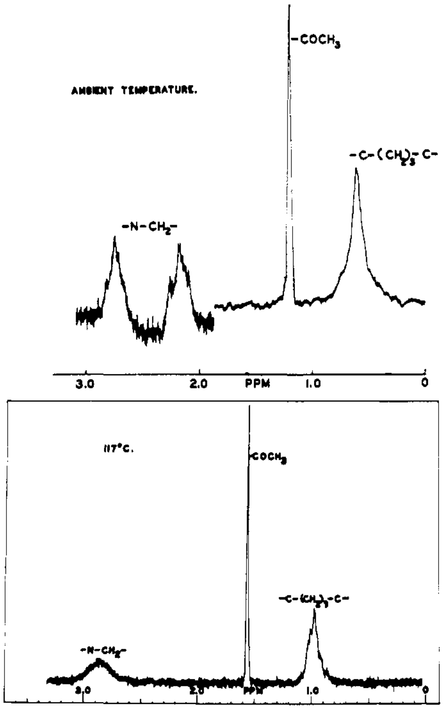

Figure 3. Nmr spectrum of AP. In the ambient temperature spectrum the amplitude of the —N—CH$_2$— peaks was doubled.

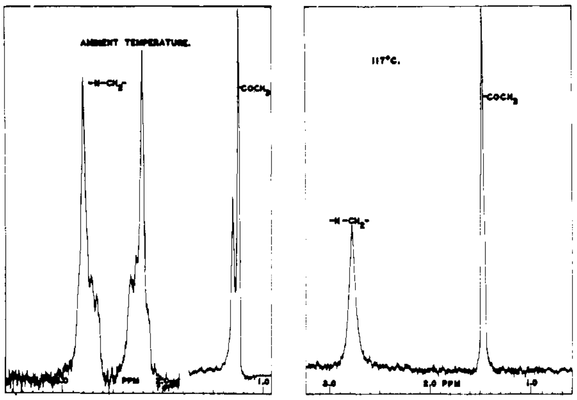

Figure 4. Nmr spectrum of DAP.

In considering acylated derivatives of piperazine, two types of hindered rotations may lead, in principle, to nmr line splitting, *i.e.*, inversion of the piperazine ring and rotation around the C–N bond of the amide group. Ring inversion is the much more rapid process, *e.g.*, the coalescence temperature T_c of dimethylpiperazine is −25°,[20] while T_c values for N,N-dialkylamides lie generally well above ambient temperature.[4] It may then be assumed that under the conditions of the present investigation (*i.e.*, $T \geqslant 40°$) the magnetic nonequivalence of axial and equatorial positions of hydrogens in the piperazine ring are effectively averaged and any splitting of the nmr bands due to chemical exchange reflects hindered rotation around the amide bond. This con-

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[17] W. P. Slichter and D. D. Davis, *Macromolecules*, **1**, 47 (1968).

[18] A. W. Nolle, *Phys. Rev.*, **98**, 1560 (1955); *Bull. Amer. Phys. Soc.*, **1**, 109 (1956).

[19] K. J. Liu, *J. Polym. Sci., Part A-2*, **5**, 1199, 1209 (1267); *Macromolecules*, **1**, 213 (1968); M. Magei and A. Nishioka, *J. Polym. Sci., Part A-1*, **6**, 1655 (1968).

[20] L. W. Reeves and K. O. Stroemme, *J. Chem. Phys.*, **34**, 1711 (1961).

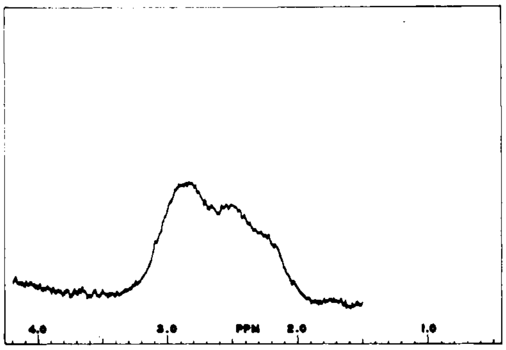


Figure 5. Nmr spectrum of NCH_2 signal in DBP at ambient temperature.

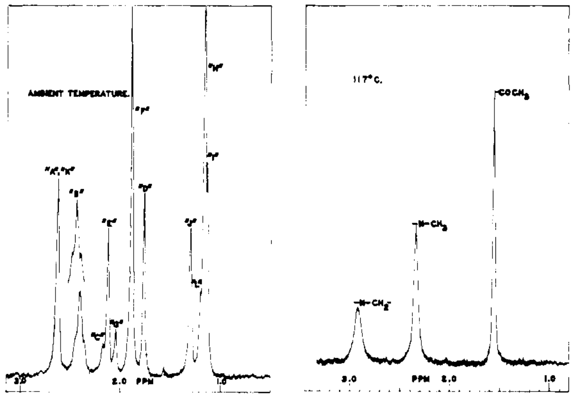


Figure 6. Nmr spectrum of ADE.

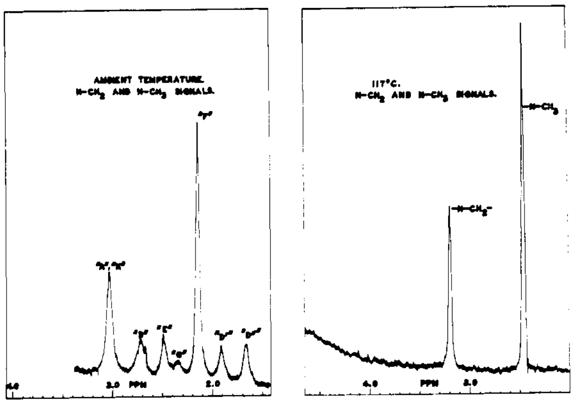
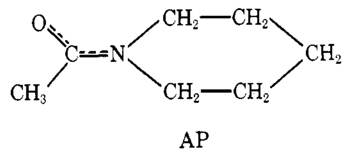
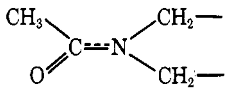


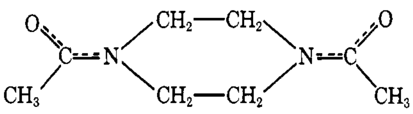
Figure 7. Nmr spectrum of BDE.

clusion is supported by the behavior of the nmr spectrum of AP. The NCH_2 band is split at 40° and coalesces at 100°, while the $C(CH_2)_3C$ band appears as a singlet (broadened by spin-spin splitting of nonequivalent hydrogens in the 4 position with those in position 3 and 5) even at 40°. If splitting of the NCH_2 band were the result of ring inversion, the large difference in the chemical shifts of axial and equatorial protons (*e.g.*, $\Delta\tau = 0.27$ ppm for N,N-dimethylpiperazine[20] and $\Delta\tau = 0.48$ ppm for cyclohexane-d_{11}[21]) would also split the $C(CH_2)_3C$ band; on the other hand, these protons are too far from the amide group to be significantly affected by rotation around the C–N bond.[21a]

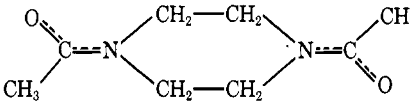


AP





cis DAP

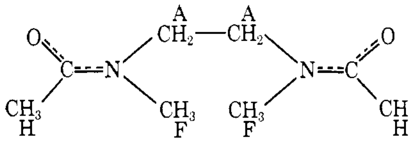


trans DAP

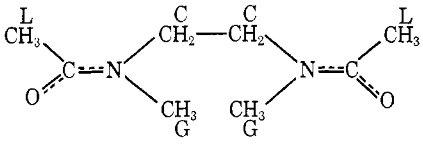
DAP has a somewhat more complicated spectrum in the NCH_2 region than AP, undoubtedly because of the existence of *cis* and *trans* isomers. The $COCH_3$ signal is composed, at low temperature, of two unequal peaks with the low-field component less intense. The 3.50-cps separation of the two $COCH_3$ peaks is independent of phenol concentration. The splitting of the $COCH_3$ band in DAP originates, presumably, from the *cis–trans* isomerism. The NCH_2 and $COCH_3$ doublets coalesce, as expected, under the same conditions of heating or a change of solvent (from phenol–water to 90% formic acid).

The low-temperature spectrum of the NCH_2 protons in DPB has a high field peak broader, less intense and showing an additional shoulder at high field. This may result from an interaction between equatorial protons of the piperazine ring in the methylenes *cis* to the phenyl ring and the *ortho* hydrogens of the phenyl residues.

The low-temperature spectrum of ADE is much more complicated, because *cis* and *trans* rotamers of unequal energy give rise to *cis–cis*, *cis–trans* and *trans–trans* forms.



cis–cis ADE



trans–trans ADE

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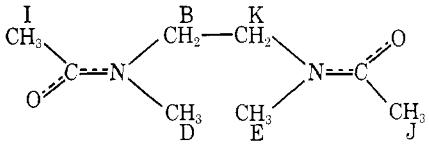
(21) F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *J. Chem. Phys.*, **41**, 2041 (1964).

(21a) NOTE ADDED IN PROOF. The spectrum of AP in water solution does not exhibit this splitting.



cis–trans ADE

These forms are shown with the assignments of the various peaks in the nmr spectrum based on the observation that NCH_3 *trans* to the carbonyl is energetically preferred.[22] At 117°, single peaks characterize the NCH_3, NCH_2 and $COCH_3$ protons. If chloroform is substituted for phenol–water as the solvent medium, the chemical shift difference between the *cis* and *trans* positions decreases significantly and only two peaks can be resolved for each group of protons. This effect, observed also with DAP, is in accord with the expected effect of the use of phenol as a solvent on the nmr spectra, as discussed above. The amine portion of the low-temperature spectrum of BDE is similar to that of ADE, except for a splitting of the D peak into two well-resolved peaks. This effect is similar to that observed with DBP and is presumably again due to an interaction of the NCH_3 protons with the protons of the aromatic nucleus. The better resolution of the two peaks in BDE may result from hindrance to the rotation of the phenyl ring. The fact that the F peak is not split in a similar manner leads us to assign this peak to the *trans–trans*, rather than the *cis–cis* species.

General Features of the Nmr Spectra of Polyamides. Spectra of poly(succinylpiperazine), poly(adipylpiperazine), poly(sebacylpiperazine), poly(sebacyl-N,N′-dimethylethylenediamines) and poly(terephthaloyl-N,N′-dimethylethylenediamine) at ambient temperature and at 117° in phenol–water are shown on Figures 8–12. As would be expected, the resolution of the polymer spectra is, particularly at low temperature, much poorer than that of the low molecular weight analogs. The most interesting feature is the asymmetry of the low-temperature NCH_2 spectrum of PSuP. The high-field peak is obviously broader, possibly because of a preferred conformation of the polymer chain. It is tentatively suggested that the effect could arise if the chain conformation places the carbonyl oxygens hydrogen bonded to the phenol solvent onthe outside of a helical section of the chain. The NCH_2 *trans* to the oxygen would then be inside the helix and their absorption peak would be broadened by dipole–dipole interaction with neighboring chain segments. The possibility that some solvent media may stabilize a helical conformation of PSuP was supported by the observation that the intrinsic viscosities of the two samples of this polymer differed very little in 90% formic acid ($[\eta]$ = 0.11 and 0.14), but differed by a large factor in phenol–$(CHCl_2)_2$ ($[\eta]$ = 0.16 and 0.77). We may also note the splitting of the $COCH_2$ peak, which could result either from causes similar to those leading to the $COCH_3$ splitting in the AP and DAP model compounds, or from a preferred conformation of the polymer chain. The asymmetry of the NCH_2 absorption is much less pronounced in PAP and is absent in PSeP.

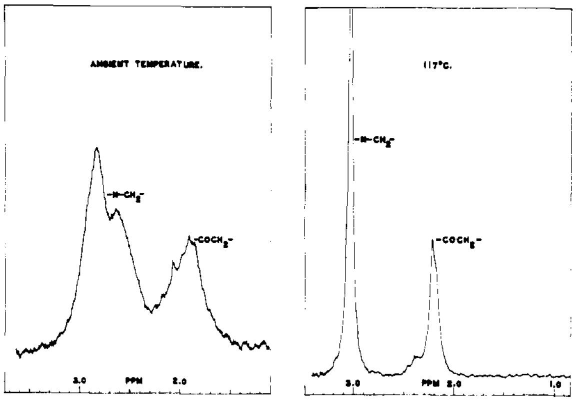


Figure 8. Nmr spectrum of PSuP.

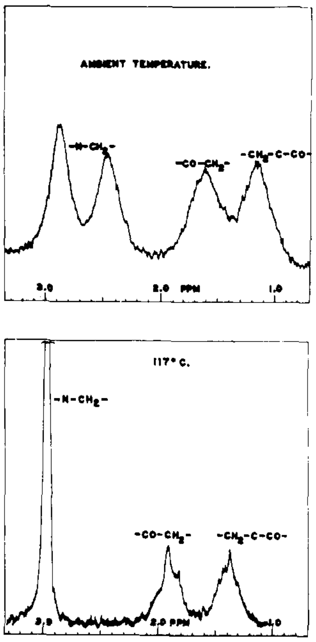


Figure 9. Nmr spectrum of PAP.

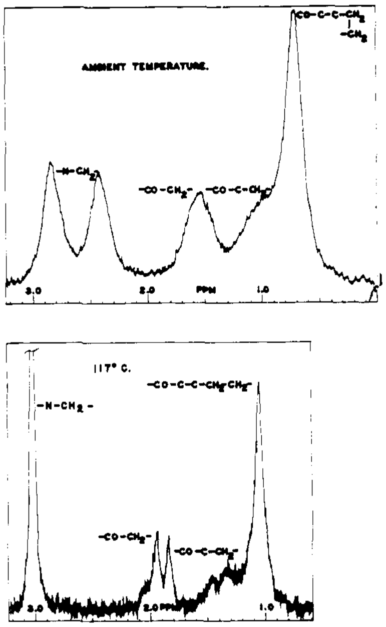


Figure 10. Nmr spectrum of PSeP.

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[22] F. A. Bovey, J. J. Ryan, and F. P. Hood, *Macromolecules*, 1, 305 (1968).

Table I

Compound	T_c, °C	$\delta\nu_{MC}$, cps	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol
N-Acetylpiperidine	100 ± 2	26.2	19.1 ± 0.2	21 ± 3
Diacetylpiperazine	91 ± 2	27.0	18.5 ± 0.2	20.3 ± 3
Poly(succinylpiperazine)	72 ± 2	12.5	18.0 ± 0.2	14.9 ± 3
Poly(adipylpiperazine)	79 ± 2	20.0	18.1 ± 0.2	17.0 ± 3
Poly(sebacylpiperazine)	79 ± 2	19.4	18.1 ± 0.2	18.8 ± 3
Dibenzoylpiperazine	43		16	
Poly(terephthaloylpiperazine)	29		15	

This may signify that the stabilization of a helical conformation in polyamides derived from piperazine depends critically on a close spacing of the piperazine rings.

The amine portion of the spectrum of PSeDE is similar to that in the ADE model compound except that some of the low intensity peaks are not visible in the less well resolved polymer spectrum. The chemical shift differences corresponding to *cis–trans* isomerism are smaller in the polymer, suggesting perhaps some hindrance to the association with the phenol in the solvent medium. This effect appears to be analogous to Liu's observation of differences in the chemical shifts characterizing chain segments relatively close to the ends of long-chain molecules.[19]

The spectra of PTDE and poly(isophthaloyl-N,N′-dimethylethylenediamine) are very similar to each other and to the spectrum of their low molecular weight analog BDE. The most significant difference is the fact that the D peak is not split in the polymers, reflecting differences in the steric restraint, determining the orientations of the phenyl residues relative to *cis* NCH_3 groups. This observation is analogous to differences in the nmr spectrum of the aromatic residues in polystyrene and its monomer analog cumene, which have also been ascribed to steric restraints in the polymer.[23]

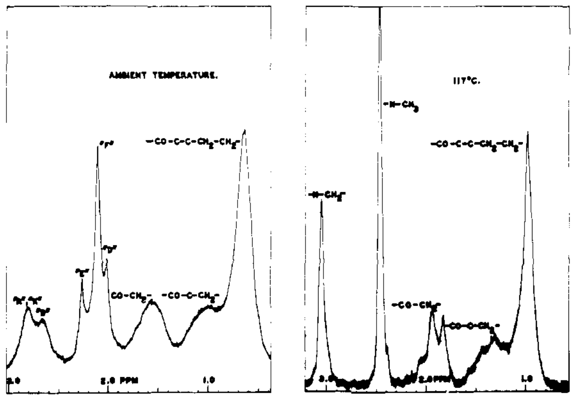


Figure 11. Nmr spectrum of PSeDE.

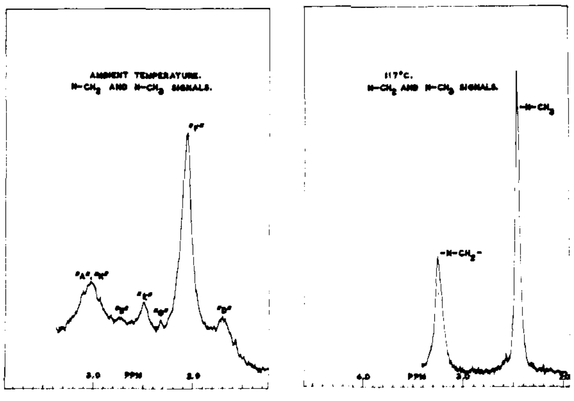
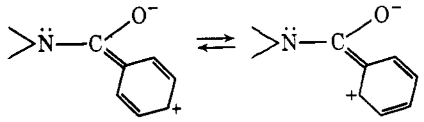


Figure 12. Nmr spectrum of PTDE.

Activation Parameters for Hindered Rotation in Polyamides and Model Compounds. Table I lists values of T_c, $\delta\nu_{MC}$, $\Delta F^{\ddagger}$, and $\Delta H^{\ddagger}$ obtained by the methods discussed above for the various polyamides derived from piperazine and aliphatic dicarboxylic acids, with T_c and $\Delta F^{\ddagger}$ data for dibenzoylpiperazine and poly(terephthaloylpiperazine). It may be seen that the $\Delta F^{\ddagger}$ values, which may be determined with very high precision, are almost identical for the polyamides and their analogs. (The lower $\Delta F^{\ddagger}$ values obtained from the aromatic acid derivatives may be explained by the electron-donating character of the phenyl ring, which stabilizes the structures shown below



and thus reduces the double-bond character of the amide bond.) A similar pattern emerges in comparing the free energies of activation for hindered rotation around the amide bond in the diacetyl derivative of N,N′-dimethylethylenediamine and in the polyamide obtained from sebacic acid and this diamine (Table II). In this case, it is possible to check the reliability of the data by calculating the activation parameters from the half-width of the NCH_2, NCH_3 and $COCH_3$ peaks and the concordance of the $\Delta F^{\ddagger}$ results obtained is most gratifying. The $\Delta H^{\ddagger}$ calculations are clearly subject to much greater error, but again, there is no evidence of a significant difference between the behavior of the polymers and their analogs.

The finding that there is no significant difference in the rates of hindered rotation around the amide bonds in the polymers and in small model compounds is quite contrary to the assumptions with which this investigation was initiated and requires some comment. It still seems to us inconceivable that rotation could take place around a single bond in the central portion of the chain backbone of a long polymer chain with all the other bonds remaining undisturbed, so that a

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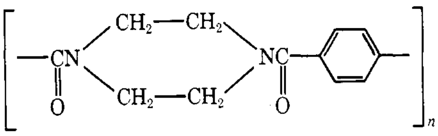
(23) F. A. Bovey, G. V. D. Tiers, and G. Filipovich, *J. Polym Sci.*, 38, 73 (1959).

TABLE II

	Absorption peak	T_c, °C	$\delta\nu_{MC}$, cps	$\Delta F^{\ddagger}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol
N,N′-Diacetyl-N,N′-dimethylethylenediamine	NCH_2	104.5 ± 2	10.8	19.9 ± 0.2	20.5 ± 3
	NCH_3	98.5 ± 2	10.4	19.6 ± 0.2	19.8 ± 3
	$COCH_3$	86.5 ± 2	10.0	19.1 ± 0.2	19.8 ± 3
Poly(sebacyl-N,N′-dimethylethylenediamine)	NCH_2	91 ± 2	9.0	19.3 ± 0.2	23.2 ± 3
	NCH_3	84 ± 2	7.5	19.0 ± 0.2	15.1 ± 3

major portion of the chain would have to be swung a considerable dstance through a viscous solvent medium. The question then arises as to how it is possible for the rotation around a given bond in the chain backbone to involve only the motion of a relatively restricted section of the chain, without rotation around another bond, which would raise the activation parameters for the process. Even in a material such as, *e.g.*, poly(adipylpiperazine), where the second rotation could involve a C–C bond with a relatively low energy barrier, the additional energy requirement for this rotation is in the range 3–4 kcal/mol[24] and an increase of $\Delta F^{\ddagger}$ by this amount would have easily been detected. The problem is still more severe with a polymer such as poly(terephthaloylpiperazine) (PTP), in which hindered rotation can take place only around the amide bond or by inversion of the piperazine ring, a process involving the relatively high activation energy of 13 kcal/mol.[20] Yet, even a comparison of the $\Delta F^{\ddagger}$ values of PTP and its DBP analog shows no significant difference.[25]



PTP

We believe that the dilemma can be resolved by assuming that the stress imposed by rotation around a given amide bond is relieved by the cumulative effect of many small distortions of the internal angles of rotation or valence bond angles. Since small distortions of this type require an energy proportional to the square of the distortion, the spreading of the disturbance over a number of bonds may reduce the energy requirement below the limit observable by our technique.[26]

Acknowledgment. We are happy to acknowledge most helpful discussions of this work with Professor Anita H. Lewin, Dr. R. Ullman, Professor S. Lifson, and Dr. James A. Ferretti. We are also grateful to Dr. I. Skeist for assisting us in many ways in the execution of this research.

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(24) M. V. Volkenstein, "Configurational Statistics of Polymer Chains," Interscience Publishers, New York, N. Y., 1963, p 70.

(25) A similar problem arises in the interpretation of kinetic data describing the helix-helix transition in poly(L-proline). The $\Delta H^{\ddagger}$ value has been variously estimated as 20.2 and 20.6[2f] or 22.9 kcal mol,[2e] close to the value to be expected in similar small molecules and the frequency number has also a value in the "normal" range.[2e]

(26) An alternative approach to the interpretation of the results of this study is based on the assumption that the activation energy required for the hindered rotation of a given bond in the chain backbone remains stored in the chain and can be utilized for the rotation around another bond. A detailed theoretical analysis of this mechanism is beyond the scope of this paper.