Rates of Conformational Transitions in Solutions of Randomly Coiled Polymers. II. Nuclear Magnetic Resonance Study of Hindered Rotation around Amide Bonds in Side Chains[1]

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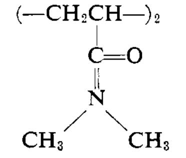
ABSTRACT: Poly(N,N-dimethylacrylamide) and an acrylic acid copolymer containing 10 mol % N,N-dimethylacrylamide were studied by nmr spectroscopy in D_2O solution. The $N(CH_3)_2$ portion of the spectrum, in both the homopolymer and the copolymer, consists of a doublet which coalesces at 96 ± 2° and a singlet which shows no evidence of separating down to 13.5°. The data are best interpreted by assuming that for some of the dimethylamide groups in the atactic polymer the chemical shift difference of NCH_3 groups *cis* and *trans* to the carbonyl oxygen is too small to be resolved under our experimental conditions. Poly(N-acetylaziridine) was studied in aqueous phenol solution containing 92.5 wt % phenol. The nmr spectrum at ambient temperature contained a doublet for the CH_3CO group with a coalescence temperature of 79 ± 2°. This doublet may be interpreted as resulting from differences in the relative conformations of neighboring amide groups in the polymer chain.

Hindered rotation around the amide bond in symmetrically disubstituted amides may be studied conveniently by nmr spectroscopy.[2] In such compounds, *e.g.*, N,N-dimethylformamide, the C–N bond has partial double bond character and rotation around this bond is, at ambient temperatures, slow compared to the difference between the chemical shifts of the nitrogen-linked methyl groups *cis* and *trans* to the carboxyl oxygen. This leads to a splitting of the $N(CH_3)_2$ absorption peak. As the temperature is raised, the doublet coalesces at a characteristic "coalescence temperature" T_c and the rate constant k_c for hindered rotation at that temperature may be obtained from[2a]

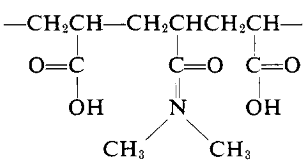
$$k_c = (\sqrt{2}\pi/2)\delta\nu_c{}^0 \qquad (1)$$

where $\delta\nu_c{}^0$ is the true chemical shift difference at T_c.

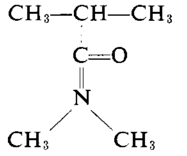
In the preceding investigation we employed this principle for a study of hindered rotations around the amide bonds in the backbone of polyamides.[3] The present paper deals with rotations around amide bonds in polymer side chains. Two problems of this type were investigated. First, rotation around the amide bond in a homopolymer and an acrylic acid copolymer of N,N-dimethylacrylamide was compared with the behavior of N,N-dimethylisobutyramide used as a low molecular weight analog. In this case it was of interest to find whether interactions of the polymer side chains with each other or with the polymer backbone lead to modifications in the rate of hindered rotation. Second, the nmr spectrum of poly(N-acetylaziridine) was studied over a range of temperatures. In this case, rotation around the amide bond does not alter the immediate neighborhood of the acetyl CH_3 group.



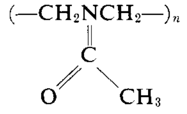
poly(N,N-dimethylacrylamide)



poly(N,N-dimethylacrylamide coacrylic acid)



N,N-dimethylisobutyramide



poly(N-acetylaziridine)

Nevertheless, we found the absorption due to this group to be characterized by a doublet under conditions where rotation around the C–N bond would be expected to be slow. This result led us to consider the possible causes for such splitting.

Experimental Section

Materials. N,N-Dimethylisobutyramide was prepared from dimethylamine and isobutyryl chloride under Schotten–Baumann conditions. The product was extracted with ether, washed with dilute HCl, water, dilute NaOH, water and

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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) 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. Newman, Jr., and L. B. Young, *ibid.*, **69**, 2570 (1965); (d) C. W. Fryer, F. Conti, and C. Franconi, *Ric. Sci.*, **35** (2), 788 (1965).

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

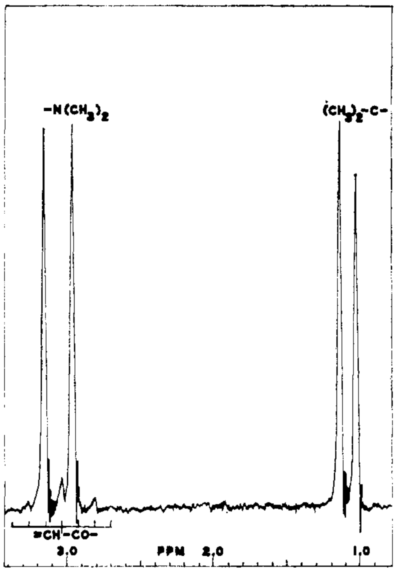

Figure 1. Nmr spectrum of N,N-dimethylisobutyramide in water at ambient temperatures.

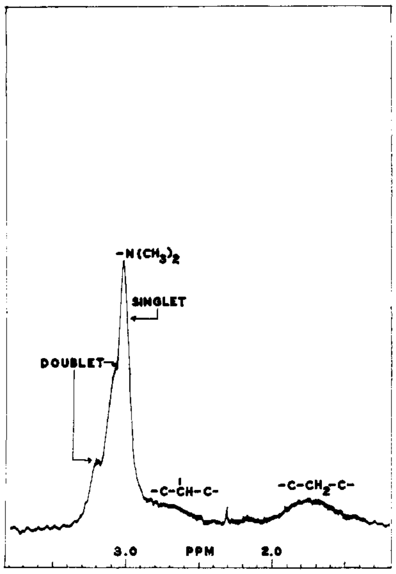

Figure 2. Nmr spectrum of poly(N,N-dimethylacrylamide) in D_2O at ambient temperature.

dried over $CaCl_2$, bp 50° (3 torr) [lit.[4] 175–176° (745 torr)]. Poly(N,N-dimethylacrylamide) was prepared from N,N-dimethylacrylamide (K & K Laboratories) purified by fractional distillation, collecting the fraction boiling at 93–95° (30 torr).

Anal. Calcd for C_5H_9NO monomer: C, 60.58; H, 9.15; N, 14.13; O, 16.14. Found: C, 60.24; H, 9.73; N, 14.08; O, 16.29.

A 20% monomer solution in toluene was polymerized at 75° using 0.2% benzoyl peroxide initiator. The polymer was precipitated in hexane, purified by reprecipitation and dried at 70°. Its intrinsic viscosity in methanol at 25° was 0.31 dl/g. A copolymer was prepared from 0.26 g (10 mol %) of N,N-dimethylacrylamide and 1.74 g (90 mol %) of acrylic acid in 9.25 g of carbon tetrachloride, using 0.02 g of benzoyl peroxide initiator and polymerizing for 48 hr at 75°. The precipitated polymer was filtered off and purified dissolving twice in methanol and reprecipitating with ether. Its intrinsic viscosity $[\eta]$ in 2 M NaOH at 25° was 1.14 dl/g. Poly(N-acetylaziridine) prepared by BF_3-catalyzed ring opening polymerization of 2-methyl-2-oxazoline[5,6] was obtained from Dr. Harold H. Roth of the Dow Chemical Co.

Procedures. The nmr spectra were recorded on a Varian 60-Mc spectrometer. The details of the procedures used is described in a previous report.[3]

Results and Discussion

N,N-Dimethylacrylamide Polymers. N,N-Dimethylisobutyramide was used as the analog of the monomeric residues in the homopolymers and the copolymer of N,N-dimethylacrylamide. Its spectrum in water solution at ambient temperature (~40°) is shown in Figure 1. The splitting of the $N(CH_3)_2$ peak ($\delta\nu = 12$ cps) is the result of the magnetic nonequivalence of the nitrogen-linked methyl groups *cis* and *trans* to the carbonyl oxygen. The two peaks coalesce at 74 ± 2° and the rate constant for hindered rotation around the amide bond at T_c obtained from eq 1 (with $\delta\nu = 12$ cps taken as a fair approximation of $\delta\nu_c{}^0$) corresponds to a free energy of activation of 18.3 ± 0.1 kcal/mol.

The spectrum of poly(N,N-dimethylacrylamide) in D_2O at ambient temperature is shown in Figure 2. The $N(CH_3)_2$ portion of the spectrum consists of a strong singlet, which does not separate even at temperatures as low as 13.5° and a weak doublet at lower field coalescing at 96 ± 2°. The hindered rotation around the amide bond characterized by the doublet corresponds to a free energy of activation of 19.3 ± 0.1 kcal/mol, higher by 1 kcal/mol when compared to N,N-dimethylisobutyramide. This result is similar to that obtained by Bovey and Tiers,[7] who found that attachment of amide bonds to the backbone of polyacrylamide and polymethacrylamide does not affect appreciably the rate of hindered rotation around the amide bonds. However, observation of the singlet which does not give any indication of incipient separation even at a temperature as low as 13.5° is so unexpected, that we felt compelled to check in a variety of ways on the purity of the monomer employed. Since the elemental analysis was in good agreement with theory and the nmr spectrum was in accord with that to be expected (with the expected doublet, but no singlet, in the $N(CH_3)_2$ region) the identity of the polymer could hardly be questioned. It would seem absurd to conclude that attachment of the $-CONCH_3$ group to a polymer could *speed up*, by a large factor, the rate of rotation around the amide bond. We believe, therefore, that the data are best interpreted by assuming that in the atactic polymer some of the stereoisomeric sequences place the $N(CH_3)_2$ groups in an environment in which the chemical shift difference between the methyl groups *cis* and *trans* to the carbonyl cannot be resolved under our experimental conditions.

It was of interest to compare the behavior of the N,N-dimethylacrylamide homopolymer with the be-

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[4] N. Gavrilov, A. V. Koperina, and M. Klutcharova, *Bull. Soc. Chim. Fr. Mem.*, **12**, 773 (1945).

[5] W. Seeliger, E. Aufderhaar, W. Diepers, R. Feinauer, R. Naehring, W. Thier, and H. Hellmann, *Angew. Chem. Intern. Ed. Engl.*, **5**, 881 (1966).

[6] D. A. Tomalia and D. P. Sheetz, *J. Polym. Sci., Part A*, **4**, 2253 (1966).

[7] F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci., Part A*, **1**, 849 (1963).

havior of N,N-dimethylacrylamide residues in an acrylic acid copolymer. Since the copolymer was prepared from a monomer mixture containing 90 mol % acrylic acid, the N,N-dimethylacrylamide units may be assumed to be mostly isolated from one another. Figure 3 shows the nmr spectrum at ambient temperature in D_2O and in D_2O rendered basic by addition of 2.3 equiv of NaOH per equivalent of carboxyl. The $N(CH_3)_2$ groups are again characterized by a doublet and a singlet and both the coalescence temperature and the free energy of activation for rotation of the groups characterized by the doublet are the same as in the homopolymer. In contrast to the homopolymer, the $N(CH_3)_2$ doublet in the copolymer is well resolved from the singlet. The doublet is unsymmetrical in acidic solution but becomes symmetrical on addition of base, which also increases the singlet–doublet separation. It should be noted that the spectra were recorded at a rather high polymer concentration (5.2 g/100 ml) and that the basic solution contained 1.6 *N* Na^+. Under such conditions the polyions would not be highly expanded, but the mutual repulsion of neighboring anionic groups on the polymer backbone should affect, to some extent, both the distribution of chain conformations and the rate of conformational transitions.

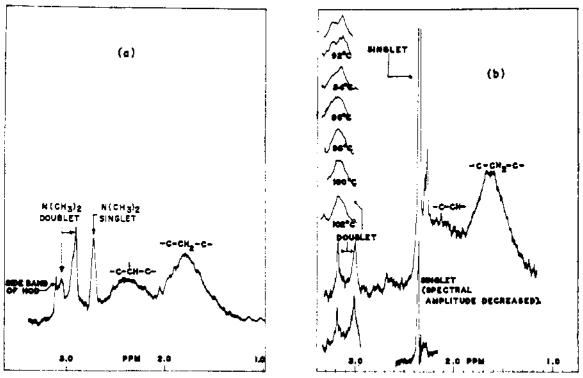
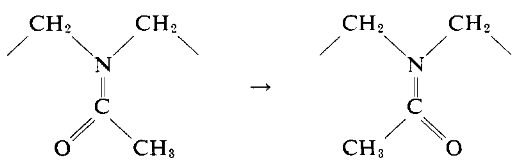
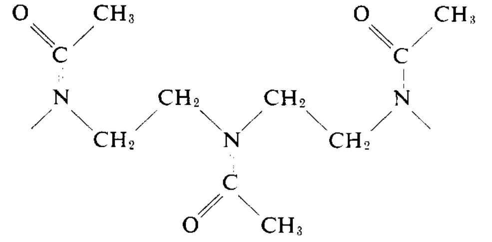


Figure 3. Nmr spectrum of copolymer of 90 mol % acrylic acid and 10 mol % N,N-dimethylacrylamide at ambient temperature: a, solution in D_2O; b, solution of D_2O with 2.3 equiv NaOH per equivalent of carboxyl. The coalescence pattern of the $N(CH_3)_2$ doublet is also shown.

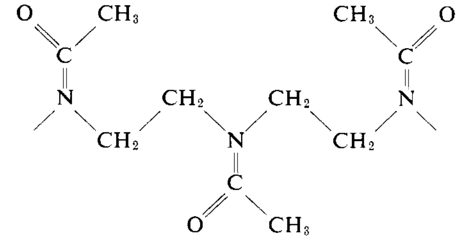
Poly(N-acetylaziridine). The ambient temperature spectrum of this polymer in aqueous phenol containing 92.5 wt % phenol (Figure 4) is composed of a broad NCH_2 peak which could not be resolved and a $COCH_3$ doublet separated by 7 cps coalescing at 79 ± 2°. If we consider in the transition



only the immediate neighborhood of the CH_3 group, rotation around the C–N bond would not be expected to change the environment of the methyl protons and the splitting of the methyl peak absorption could not be understood on that basis. However, if we consider the two nearest-neighbor amides of any given amide group in the chain, then it is clear that four distinguishable situations (with respect to the conformation of the amide groups) are possible.



a



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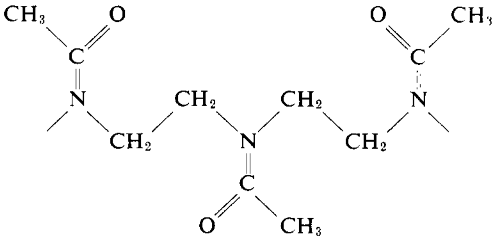
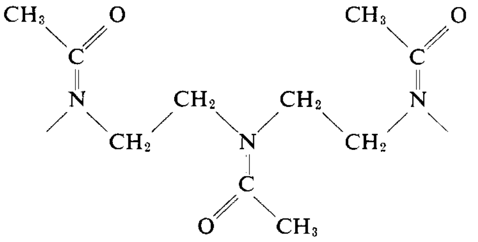


c



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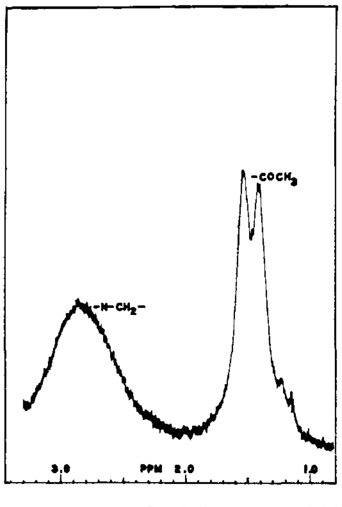
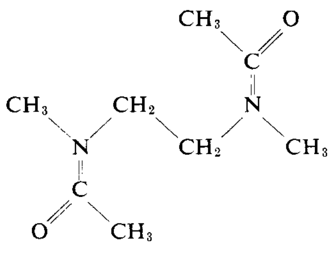
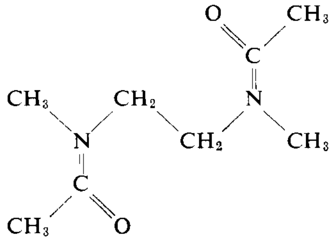


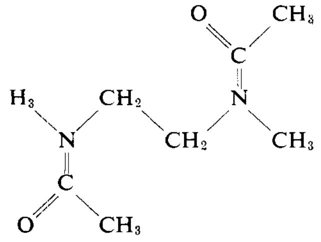
Figure 4. Nmr spectrum of poly(N-acetylaziridine) in aqueous phenol solution at ambient temperature.



cis–cis



trans–trans



cis–trans

Thus one might in principle account for the appearance of four absorption peaks. The fact that only two peaks are observed at the level of resolution used in this work may signify that hindered rotation of only one of the amide neighbors (presumably that in the direction along the chain toward which the methyl group of a given amide is pointing) results in an appreciable shift of the CH_3 absorption. Thus one of the observed peaks corresponds to structures a and c, while the other one corresponds to b and d. At higher resolution, the methyl absorption would presumably exhibit a pair of closely spaced doublets, with all peaks of similar intensity since sequences a, b, c and d would not be expected to differ appreciably in energy. The above interpretation seems plausible in view of the results obtained previously with N,N′-diacetyl-N,N′-dimethylethylenediamine.[3] This substance can exist in the *cis–cis*, *trans–trans* or *cis–trans* form and the nmr spectrum in 92.5% phenol–water contains a well-resolved quadruplet in the region of the $-COCH_3$ absorption. A similar conclusion has recently been reached in a study of the nmr spectrum of polysarcosine[8] where the N-methyl absorption appears as an octet due to interaction effects between nearest-neighbor rotamers. Our case is different in that there does not exist any intrinsic *cis–trans* isomerism of the isolated monomer residue, so that the number of distinguishable triplets is reduced from eight to four.

It is interesting to note that the type of splitting of an nmr absorption band such as we have found in poly(N-acetylaziridine) could arise, in principle, even in the case where the amide functions could not interact with one another, if the chain backbone can assume a preferred helical conformation. In that case, the two rotamers of the amide group may not be equivalent and splitting would then result if the helical structure persists locally for periods long compared to the mean time intervals between rotation around the amide bond.

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