The Hindered Internal Rotation of Amide Groups of Polyacrylamide of Low Molecular Weights

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Polyacrylamides of low molecular weights (average degrees of polymerization($\overline{DP}$): 7.2, 18.3, 21.3, and 45.4) were prepared by radical polymerization, and their PMR spectra were observed over the temperature range of 30—90 °C. From the temperature dependence of the PMR spectra, the values of the energy barrier to the internal rotation about C–N bonds were determined by means of a total line-shape analysis. The energy barriers for the polymers above $\overline{DP}$: 18.3 were 10.6 kcal/mol, while those for the polymer of $\overline{DP}$: 7.2 were 9.2 kcal/mol. These results were interpreted in terms of the local environment around the amide groups. The intramolecular hydrogen bonding was also investigated.

In a previous investigation,[1] we observed an anomalous broadening for the absorption of *ortho* protons of poly(*p*-chlorostyrene) of very low molecular weights (average degrees of polymerization($\overline{DP}$)<15). This phenomenon was elucidated by assuming the "permissible conformation" which is permitted only in very short chains, and was termed the "polymeric effect on molecular structure" of polymers in solutions. The present investigation will be concerned with the "polymeric effect on intramolecular motion" of polymers in solutions.

Recent studies by various authors[2-6] have shown that the NMR spin-lattice relaxation times (T_1) of polymers in solutions change appreciably with the chain length in the region of short chains, and that T_1 becomes less sensitive to the chain length as the chains become longer ($\overline{DP}$: 10—30). Similar phenomena were also observed in ESR studies of spin-labeled polymers.[7,8] These observations have been interpreted in terms of the "polymeric effect on relaxation process"[4] (in other words, the "polymeric effect on molecular motion" of polymer chains). However, the rigorous analysis of NMR T_1 or ESR line widths is not always easy; that is, the precise separation of motional modes is impossible at the present stage. Therefore, the observations were understood rather qualitatively in either case, and a discussion focused on a local motion in the molecular motions of polymer chains was desired.

If the rate constants or the energy barriers on the specific local motion of polymer chains are estimated precisely as functions of the molecular weights, the polymeric effect on molecular motion could be understood in more detail.

Polyacrylamide is one of the most favorable samples for such a purpose. The amide protons of polyacrylamide represent the characteristic patterns of PMR signals reflecting the internal rotation about C–N bonds in amide groups. They make it possible to evaluate precisely the rate constants or the energy barriers on the specific local motion by analyzing the spectra of amide protons.

The PMR spectra of amide protons of polyacrylamide of a high molecular weight were analyzed by Bovey and Tiers[9] by means of peak separation method.* In the present investigation, the PMR spectra for the polymers of low molecular weights($\overline{DP}$: 7.2—45.4) were analyzed by means of more exact procedures (the total line-shape analysis). The local environment around the amide groups was discussed on the basis of the obtained rotational barriers.

The intramolecular hydrogen bonding was also investigated in a conventional manner.

Experimental

The samples of polyacrylamide were prepared by the procedure of Bovey and Tiers.[9] In order to control the molecular weights, the amount of the chain-transfer agent (sodium mercaptoacetate) was changed over the range from 0.5 g to 3 g per 10 g of the monomer. The polymers were precipitated in a large amount of ethanol in order to free them from any residual monomer, and were then dried *in vacuo*. The number-average molecular weights of these polymers were determined by using "KUNAUAR's vapor-pressure osmometer" in aqueous solutions at 37 °C. The number-average degrees of polymerization ($\overline{DP}$) of the polymer samples were 7.2, 18.3, 21.3, and 45.4 (they will be denoted as 7-, 18-, 21-, and 45-polymer).

The infrared spectra of these polymer samples were nearly identical. They consist of the absorption bands which were assigned by Savitskaya and Kholodova.[11]

The polymer solutions for PMR spectral measurements were prepared by dissolving 0.08 g of the polymer in 1.0 ml of water, previously adjusted to the proper pH, in small vials. One per cent of 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) was added to each solution to serve as the internal reference. The pH of the solutions was adjusted according to the directions of Bovey and Tiers.[9]

The polymer solutions were then transferred to 5 mm o.d. NMR tubes, which were sealed after the atmosphere had been replaced with nitrogen gas. The PMR spectra were observed by using a Japan Electric Laboratory "JNM PS-100 spectrometer" operated at 100 MHz. In the spectra, the peak-position values of each absorption were termed δ values to the methyl peak of DSS as the reference.

Results and Discussion

Hindered Internal Rotation of Amide Groups and Molecular Weight. Figure 1a shows the absorption of the amide protons (NH_2) of the 21-polymer in the aqueous solution of pH 4.5 at 40 °C. The absorption

* However, Allerhand *et al.*[10] estimated the errors introduced in various approximate methods; the errors involved in the peak-separation method reach 100% in some cases, and so approximations are undesirable.

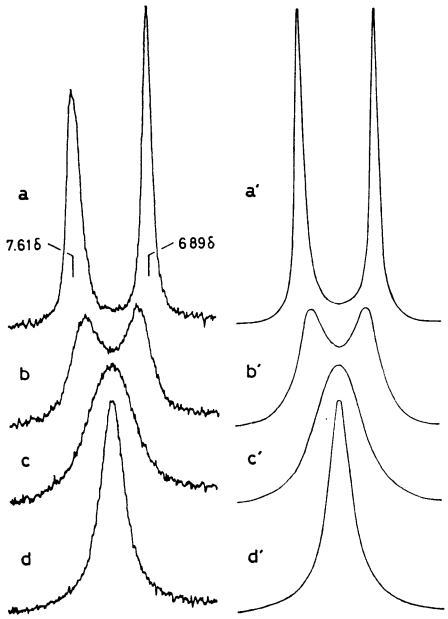
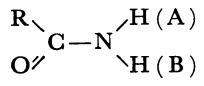


Fig. 1. Experimental PMR spectra (left) of amide protons of polyacrylamide ($\overline{DP}$: 21.3) in aqueous solutions of pH 4.5 (8 w/v%): (a) 40 °C; (b) 70 °C; (c) 80 °C; (d) 90 °C. The best-fit calculated spectra (right): the mean life time $\tau_{AB}(\tau_{BA})$ (a') 0.032 s; (b') 0.0090 s; (c') 0.0050 s; (d') 0.0030 s.

in the lower field is broader than that in the higher field; such spectra were also observed by Bovey and Tiers.[9] The broadening of the absorption may be attributed to the spin coupling with protons of the main chain.[12] In the line-shape analysis to be described below, the line-widths of the calculated spectra are arranged for the absorptions in the higher field. The absorption of water protons appeared to the right (4.62δ) of these amide peaks. Figures 1b, c, and d show the NH_2 absorptions at 70, 80, and 90 °C respectively.

The structure of amides is generally regarded as being approximately planar, and the two sites marked A and B are chemically nonequivalent. The C–N bond



R: $-CH_2CH-$ in the present study

has a partial double-bond character, and the rotation about the bond can be described as a rate process which interchanges the two protons between two environments. The rate process is characterized by rate constants in the range of 10^{-1} to 10^5 s^{-1}; such a rate process causes profound changes in the shapes of the PMR signals. On the other hand, when water is used as the solvent, the amide protons undergo a hydrogen-exchange reaction with the hydrogen of water. This rate process is also characterized by similar rate constants. Therefore, the spectra shown in Fig. 1 should be analyzed by assuming the three-site exchange system represented in Fig. 2.[13a] A total line-shape analysis[13b] can be used for the exact analysis of the spectra reflecting such an exchange system.

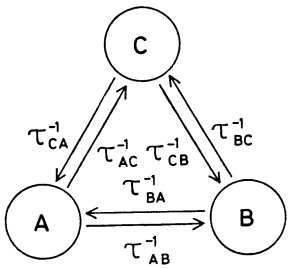


Fig. 2. Diagram for three-site exchange process. A: position A in amide group; B: position B in amide group; C: solvent(water). The arrows indicate the six possible transitions. τ_{ij}^{-1}(i, j=A, B, and C): the rate constants for jumps from site i to j.

Table 1. Parameters yielding the best-fit calculated curves

Temperature (°C)	$\overline{DP}$: 21.3 $\tau_{AB}(\tau_{BA})$ (s)	$\overline{DP}$: 7.2 $\tau_{AB}(\tau_{BA})$ (s)
30	0.060	0.050
40	0.032	0.026
50	0.022	0.016
60	0.016	0.012
70	0.0090	0.0080
80	0.0050	0.0050
90	0.0030	

$\tau_{AC}(\tau_{BC})$: 1.0×10^2 s, $\tau_{CA}(\tau_{CB})$: 9.8×10^3 s. Spin-spin relation times(T_2): 0.6 s for the proton at each site.

The analysis is accomplished by fitting a calculated curve to an experimental curve. Figures 1a'—d' show the best-fit calculated curves for the NH_2 spectra of the 21-polymer. The parameters which yield the best-fit curves are listed in Table 1. The values of T_2 were determined in the following way: we calculated the theoretical spectra for various T_2 values and chose 0.6 s as the most reasonable value of T_2; the line-width of the calculated spectra for 0.6 s does not exceed that of the observed spectra. The parameters, $\tau_{AC}(\tau_{BC})$ and $\tau_{CA}(\tau_{CB})$, did not depend on the temperature; the values of these parameters remained constant. The spectra of other polymer samples ($\overline{DP}$: 7.2, 18.3, and 45.4) were also analyzed in the same way. For example, the parameters for the NH_2 spectra of the 7-polymer are also given in Table 1. In these parameters, the parameters which characterize the rotation about C–N bonds are the mean life-times $\tau_{AB}(\tau_{BA})$. The rotational barriers about the C–N bonds can be calculated by means of the Arrhenius plots of those mean life-times.[13b] The energy barriers for each polymer sample were determined, and they are collected in Table 2. The energy bar-

Table 2. Degrees of polymerization and energy barriers for internal rotation about the C–N bond in polyacrylamide

$\overline{DP}$	7.2	18.3	21.3	45.4
E_a(kcal/mol)	9.2	10.6	10.6	10.6

riers for the 18-, 21-, and 45-polymer were 10.6 kcal/mol, while those for the 7-polymer were smaller by 1.4 kcal/mol.

In NMR or ESR studies of polymers, the molecular motion of polymer chains has mainly been discussed on the basis of NMR T_1 or ESR line-width measurements. The effective correlation times, reduced from the T_1 or line-widths, can be divided into two terms: (a) an overall rotation with rate (τ_o^{-1}), and (b) a segmental motion with rate (τ_s^{-1}). The polymeric effect on molecular motion cited in the beginning section has been understood in terms of τ_o and τ_s.[3,5-8] However, such an analysis provides only limited insight into the details of molecular motion because such a motional model is undoubtedly oversimplified for realistic models of the molecular motion of polymer chains. In these investigations, a detailed discussion of the motion of the local mode was not presented. Analyses of the detailed motion of polymer chains (the rigorous analyses of correlation times) have been devised by various investigators;[14-17] however, they are not yet useful.

On the other hand, the reciprocals of the mean life-times (τ_{AB}, τ_{BA}) obtained in this experiment are the rate constants for the rotation about C–N bonds of amide groups. The energy barriers(E_a) reflect the amount of hindrance to this internal rotation. Therefore, $\tau_{AB}(\tau_{BA})$ or E_a is well suited for a detailed discussion of the local motion. Tables 1 and 2 obviously show that the internal rotation in the 7-polymer is less hindered than that in the polymers above $\overline{DP}$:18. This observation may be termed the polymeric effect on local motion.

In the previous work,[1] we assumed the "permissible conformation" in order to elucidate the PMR spectra of poly(*p*-chlorostyrene) of low molecular weights. This conformation is permitted only in short chains: in short chains side groups are able to escape from each other, whereas in long chains such a conformation is limited by steric restrictions. The phenomenon called the "polymeric effect on molecular structure" was understood as the limitation of the permissible conformation.

Meanwhile, the limitation of the permissible conformation would result in a decrease in the distance between side groups in a polymer chain. This intramolecular packing of side groups causes an increse in the interaction between side groups, and may interfere with the local motion of polymer chains.

The permissible conformation can be assumed not only for poly(*p*-chlorostyrene), but also for polyacrylamide chains. Therefore, on the basis of the experimental fact and the consideration described above, we can draw a reasonable interpretation for the molecular-weight dependence of the energy barriers to the internal rotation about C–N bonds.

Although the 7-polymer could occupy the permissible conformations, in the polymers above $\overline{DP}$: 18 such conformations are forbidden. The intramolecular packing of side groups resulting from the limitation of the conformation increases the intraction between side groups in a polymer chain. The increase in this interaction inhibits the internal rotation about the C–N bonds of amide groups. As a result, the energy barriers (E_a) increase from 9.2 to 10.6 kcal/mol as the degrees of polymerization increase from 7.2 to 18.3.

This change in the local environment arising from the limitation of the conformation corresponds to the phenomenon called the "polymeric effect on molecular motion" cited in the beginning section.

Recently, Nomura and Miyahara[18] observed the molecular-weight dependence of the local motion (the tumbling motion of phenyl groups of polystyrene). Their observation may also be termed the polymeric effect on local motion.

Hydrogen Exchange and Intramolecular Hydrogen Bond. Polyacrylamide has NH groups and CO groups, which can form hydrogen bonds. For some polymer amides, intramolecular hydrogen bonds (NH···O=C) were observed.[19] If such intramolecular hydrogen bonds exist in polyacrylamide chains, a modification of the conclusion presented in the preceding section may be required. Therefore, in this section, the possibility of the existence of the intramolecular hydrogen bond in polyacrylamide will be discussed in a conventional manner(the investigation of the pH dependence of hydrogen exchange between amide groups and water).[20]

Figure 3 shows the NH_2 absorptions of the 45-polymer in solutions of various pH at 30 °C, and the best-fit calculated curves for these absorptions. The exchange rates, τ_{AC}^{-1}, which characterize the hydrogen-exchange reaction between amide groups and water are shown in Fig. 4 as a function of the pH. Figure 4 indicates that the hydrogen exchange is catalyzed by both H^+ and OH^- and that the rates of the reaction are minimum at near pH 4.5 and the rates (k_{min}) are 9×10^{-3} s^{-1}. The discussion of the intramolecular hydrogen bonds is carried out on the basis of this k_{min}.

Snyder and Klotz[19] investigated the k_{min} of poly(*N*-isopropylacrylamide) in the range of molecular

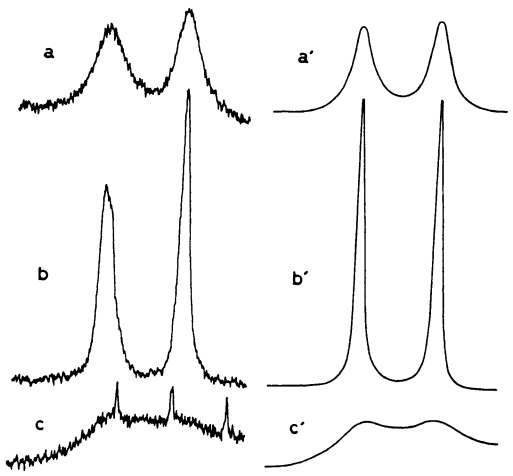


Fig. 3. Experimental PMR spectra (left) of amide protons of polyacrylamide ($\overline{DP}$: 45.4) in aqueous solutions of various pH (8 w/v%) at 30 °C: (a) pH 8.6; (b) pH 7.0; (c) pH 0.0. The spike peaks in (c) are side bands of absorptions of solvent. The best-fit calculated spectra (right): the mean life times τ_{AC} (τ_{BC}) (a') 0.020 s; (b') 0.90 s; (c') 0.0050 s.

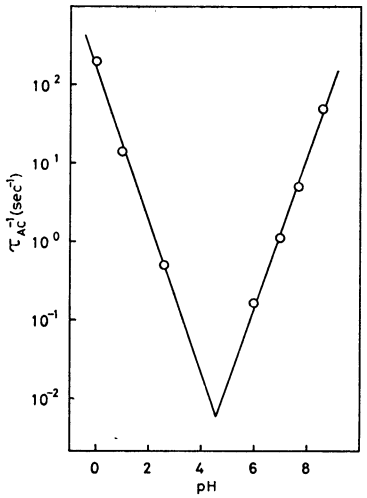


Fig. 4. Hydrogen exchange rates between amide groups and solvent (water) as a function of pH.

weights from 100 (monomer) to 2×10^5. They found that the k_{min} decreased abruptly from 1×10^{-2} to 8×10^{-5} s^{-1} when the amide was transferred from the monomer to the polymer of molecular weights 10^3 ($\overline{DP}\approx10$). The abrupt decrease in k_{min} was concluded to be due to the formation of intramolecular hydrogen bonds.

If the intramolecular hydrogen bonds are formed by NH and CO groups in polyacrylamide chains, the k_{min} must be of the order of 10^{-5}. However, the k_{min} values of the 45-polymer were quite large, and were of the same magnitude as the k_{min} values of small amides (poly(*N*-isopropylacrylamide)-monomer (k_{min}: 1×10^{-2} s^{-1})[19] or *N*-methylacetamide (k_{min}: 2×10^{-3} s^{-1}),[21] *etc.*). The k_{min} for the 21-polymer gave the same value as that for the 45-polymer.

These results mean that no intramolecular hydrogen bond exists in polyacrylamide chains, and indicate that the modification of the conclusion presented in the preceding section is not required.

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