Table I

	$\mu \times 10^{14}$, esu	$\beta^2 = (\mu/kT)^2E^2$	E_{calcd} (80% Orientation), V/cm
Takashima[44]	3.2	0.605	5,500
	1.5	0.133	11,600
Jennings and Plummer[41]	7.5	3.33	2,300

field of 2–12 kV/cm, *notwithstanding the total neglect of the contribution of the polarizability anisotropy* to the orienting torque. The discrepancy between the values of approximately 28,000 V/cm obtained from extrapolation of the measured dichroism and the values in Table I is new evidence for the inherent flexibility of the native calf thymus DNA helix.[45] It should be noted by way of caution that in the strict sense the electric field strength considered here should not be the applied field but the effective one in the vicinity of the molecule concerned.[46]

Electric Dichroism *vs.* Birefringence inside the 260-nm Band of DNA. A method for determining the phase difference or optical retardation by measuring the intensity of light transmitted through crossed polarizers introduces a serious error when the measurement is carried out inside a dichroic absorption band as clearly demonstrated in this work for the first time (Figure 13). To make the necessary corrections, the effect of linear dichroism must be taken into account. As can be seen from the figure, the anomalous dispersion of the linear birefringence calculated from the observed data with the aid of eq 16, which ignores the effect of the dichroism, is grossly altered in shape and in the positions of trough and peak (the magnitude remains unchanged). Thus, the electric birefringonce dispersion data inside an absorption band determined with any apparatus similar to the present one must be used with caution for quantitative considerations, unless a complete set of the corresponding parallel and perpendicular dichroism data is obtained under exactly the same conditions for necessary corrections. From these results, previous work on the anomalous birefringence dispersion of the dye-polymer complexes should be considered only from a qualitative point of view.[47-49] An infrared Kerr effect study[10] also ignored the contribution from dichroism, but the degree of orientation achieved with the small molecule in this study probably was insufficient to have a pronounced effect.

Although dispersion of the electric birefringence, as such, is a sensitive method of determining the relative orientation of a chromophore, the data corrected for dichroism is inevitably less accurate. This reduces the potential usefulness of the birefringence technique unless some methods, which do not require such corrections, are developed. However, a very weak birefringence can still be observed with the use of a phase-retardation plate under conditions where the dichroism signal is too weak to be detected. Therefore, the birefringence method may be the method of choice for molecules with small dipole moments and polarizability anisotropy such as globular proteins or oligomeric polymers. Some efforts are now being made to measure the true anomalous birefringence dispersion inside an absorption band without having recourse to electric dichroism measurements.

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(45) This has long-been indicated by hydrodynamic and light-scattering measurements. See, *e.g.*, the review by V. N. Tsvetkov in "Newer Methods of Polymer Characterization," B. Ké, Ed., Interscience, New York, N. Y., 1964.

(46) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier Publishing Co., Amsterdam, 1952, p 174.

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Studies of Polymers by Nuclear Magnetic Resonance at Magic Angle Rotation. III. Poly(γ-benzyl L-glutamate) in Solution†

D. Doskočilová and B. Schneider*

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

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ABSTRACT: Nmr spectra of solutions of poly(γ-benzyl L-glutamate) in $CDCl_3$ have been measured with magic angle rotation (MAR) at frequencies of 300–5000 Hz. In a solution of liquid crystal type, high-resolution spectra of the polymer in the α-helical form have been obtained. Bands of various proton groups in the side chain appear in the spectrum gradually with increasing spinning speed, but narrowing of the bands of protons on the helix backbone could not be achieved. In the narrowed lines, the rotationally invariant residual line widths are a function of frequency and form of rapid anisotropic motions of the respective groups.

In our preceding papers[1-3] it has been shown that, by rotation of the sample about an axis inclined at the so-called magic angle $\theta = 54.7°$ with respect to the direction of the static magnetic field H_0, and at a frequency comparable to the line width of the static sample ($\omega_r \gtrsim \delta\omega_{st}$), a significant line narrowing can be obtained in proton nmr spectra of some solids and heterogeneous systems normally broadened by static dipolar interactions. In heterogeneous solid–liquid systems, regular high-resolution spectra of the liquid phase can be obtained.[1,3] In the spectra of solid polymers magic angle rotation (MAR) usually leads to considerable line narrowing,[1] but the "high-resolution limit" has not been reached, because the residual line width is limited by the frequency of internal motion.[2]

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† Part II: D. Doskočilová and B. Schneider, *Macromolecules*, 5, 125 (1972).

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It is well known that even in solutions of macromolecules, the width of nmr lines is always larger than in solutions of the corresponding low molecular weight compounds; this can be expressed alternatively by stating[4] that in solutions of macromolecules $T_2 < T_1$, whereas in solutions of low molecular weight compounds in the high-resolution limit, $T_2 = T_1$. Due to the inequality $T_2 < T_1$, it can be assumed that MAR could also lead to the narrowing of nmr signals of macromolecules in solution. We have now attempted to find under which conditions such a narrowing can take place, how the residual line widths are limited in this case, and what information about the structure of macromolecules in solution can be obtained from MAR nmr spectra.

Poly(γ-benzyl L-glutamate), $(\text{BzlGlu})_n$, has been selected as a model molecule; in this polymer, the conformation of the polymer backbone (α helix–random coil) can be regulated by varying the concentration of trifluoroacetic acid (F_3CCO_2H) in chloroform; moreover, the degree of orientation of the helices can be regulated by varying the concentration of the polymer in the solvent. In this way it is possible to regulate in a broad range the mobility and the anisotropy of motion of various proton groups. Nmr spectra of $(\text{BzlGlu})_n$ solutions have been studied by many authors in great detail.[5-7] In solutions with 30% F_3CCO_2H and 70% $CDCl_3$, where $(\text{BzlGlu})_n$ is present in the form of a random coil, even samples with a very high molecular weight give well-resolved high-resolution spectra, whereas solutions of $(\text{BzlGlu})_n$ in $CDCl_3$ give lines so broad that they are hard to detect by standard high-resolution techniques, especially in high molecular weight samples. $(\text{BzlGlu})_n$ in $CDCl_3$ solution has been studied also by MAR by Cohn, *et al.*,[8] but only at low spinning speeds (max. 800 Hz). A certain line narrowing was observed only in the aromatic proton band, and an interpretation of the observed phenomena has not been presented. We have assumed that the high spinning speeds (up to 5000 Hz) achieved in our apparatus would permit a more detailed analysis of this system.

Experimental Section

$(\text{BzlGlu})_n$ was a polymer of DP = 500 kindly supplied to us by Professor M. Bradbury of Portsmouth Polytechnic. The 10% solution of this polymer in $CDCl_3$ was clear, the 20% solution was highly viscous and exhibited optical anisotropy.

Nmr spectra were measured on the high-resolution spectrometer PS-100 (Jeol) at 100 MHz, and on the spectrometer JNM-3-60 (Jeol) at 60 MHz, equipped both for high resolution and for broad-line measurements. The latter is also equipped for the measurement of MAR nmr spectra, as described in our previous communications.[1,9] The solutions of $(\text{BzlGlu})_n$ were measured either in hollow Teflon turbines (up to 2000 Hz), or in a hollow glass turbine with Teflon plugs (up to 5000 Hz). Some static broad-line spectra were measured in a thin-walled Teflon cell, in order to increase sensitivity. For chemical shift calibration, a capillary with hexamethyldisiloxane (HMDS) external standard was in some cases inserted into the turbines.

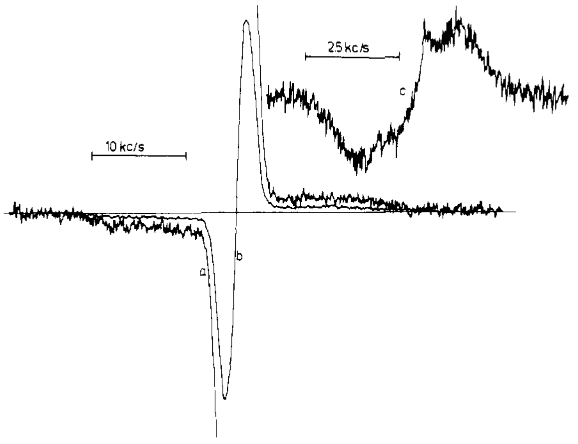

Figure 1. Standard static broad-line nmr spectra of $(\text{BzlGlu})_n$, 20% in $CDCl_3$, $\omega_0/2\pi$ = 60 MHz, 20°.

Results

The broad-line nmr spectrum of a static sample of a 20% solution of $(\text{BzlGlu})_n$ in $CDCl_3$ is shown in Figure 1. The most prominent feature of this spectrum is a band with a peak-to-peak width of 2.5 kHz (Figure 1b) which at small amplitudes of the low-frequency modulation exhibits an asymmetric shape indicating the presence of components with a smaller line width and different chemical shifts (Figure 1c). At very high amplitudes of the modulation frequency, a broad component becomes evident, with a line width about 15–20 kHz (Figure 1a). This broad line, only slightly narrowed (about 15 kHz), can be detected even in the 10% solution. Neither the shape nor the relative intensity of this broad component can be accurately determined, because of the simultaneous presence of several overlapping narrow lines of different shapes. From rough intensity estimates, it could correspond to protons in α-CH and NH groups on the helix backbone.

In standard high-resolution measurements with slow rotation about a perpendicular axis, the 20% solution in $CDCl_3$ exhibits a single slightly asymmetric line, with a width at half-height equal to 700 Hz (Figure 2a). By increasing the temperature to 60°, the shape of this band hardly changes, and its width decreases slightly (to about 600 Hz). By decreasing the concentration of the polymer to 10% in $CDCl_3$ (Figure 2b), a prominent band of the phenyl protons at 7.2 ppm (width about 60 Hz) and a much less prominent band of the benzyl protons at 5.0 ppm, emerge from the band envelope. By increasing the temperature (Figure 2c), all the bands exhibit some narrowing, the phenyl band to 30 Hz, the benzyl band to 100 Hz at 60°; a slight indication of a very broad band around 2 ppm also becomes apparent. The spectrum of the 5% solution in $CDCl_3$ measured at 20° is very similar to the spectrum of the 10% solution measured at 60°. Lowering of concentration thus has a similar influence to an increase of temperature.

For comparison with the described spectra of $(\text{BzlGlu})_n$ in the α-helix form, the high-resolution nmr spectrum of the same sample in a solution containing 30% F_3CCO_2H and 70% $CDCl_3$, where $(\text{BzlGlu})_n$ is present as a random coil, is shown in Figure 3. The assignment of bands in Figure 2 follows from the assignment in Figure 3. The relatively narrow band around 2 ppm (Figure 2), with a slightly temperature-dependent chemical shift, probably corresponds to a small amount of some impurity in $CDCl_3$ (Figure 2d) and becomes apparent thanks to the extremely high modulation amplitude necessary for the detection

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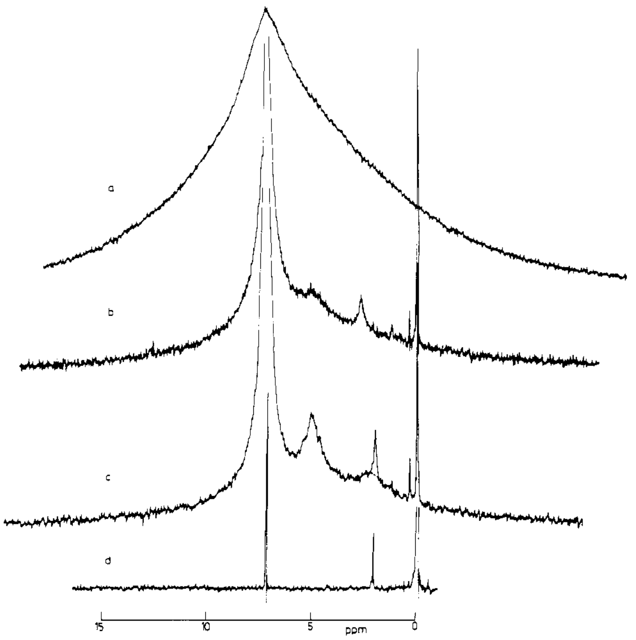

Figure 2. Standard high-resolution nmr spectra of $(BzlGlu)_n$ in $CDCl_3$ with internal HMDS, $\omega_0/2\pi$ = 100 MHz. (a) 20% in $CDCl_3$, 20°; (b) 10% in $CDCl_3$, 20°; (c) 10% in $CDCl_3$, 60°; (d) $CDCl_3$ with HMDS.

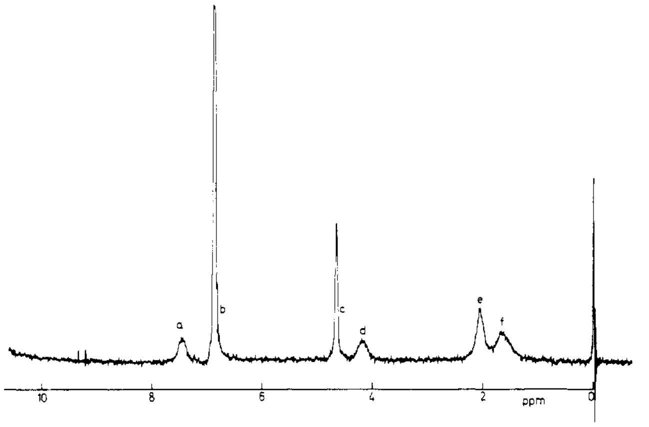

Figure 3. Standard high-resolution nmr spectra of $(BzlGlu)_n$ in 70% $CDCl_3$ + 30% F_3CCO_2H with internal HMDS, 20°, $\omega_0/2\pi$ = 100 MHz. Assignment of bands: (a) NH, (b) phenyl, (c) benzyl, (d) α-CH, (e) γ-CH_2, and (f) β-CH_2.

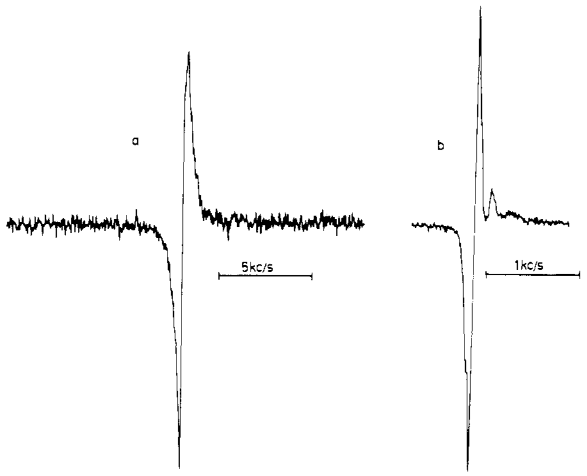

Figure 4. Broad-line nmr spectra of PBGL, 20% in $CDCl_3$, $\omega_0/2\pi$ = 60 MHz, 20°. (a) Sample rotated about axis perpendicular to H_0, ν_r = 3 kHz; (b) sample rotated at magic angle, ν_r = 4.5 kHz.

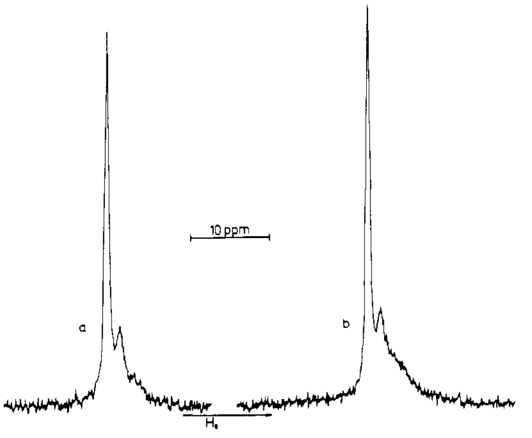

Figure 5. High-resolution nmr spectra of $(BzlGlu)_n$, 20% in $CDCl_3$, $\omega_0/2\pi$ = 60 MHz; sample rotated at magic angle. (a) ν_r = 2.5 kHz; (b) ν_r = 4.7 kHz.

of the very broad bands of the $(BzlGlu)_n$ helix in dilute solution.

The derivative nmr spectrum of 20% $(BzlGlu)_n$ in $CDCl_3$ measured at rotation about an axis perpendicular to H_0 with a frequency ν_r = 3 kHz is shown in Figure 4a. This spectrum exhibits a single band with a peak-to-peak width 500 Hz, without any fine structure, corresponding to the line measured in the standard high-resolution regime at much smaller spinning speeds. On inclination of the spinning axis into the magic angle, the line narrows conspicuously already at very low spinning speeds ($\nu_r \sim$ 300 Hz) together with the appearance of the corresponding spinning side bands. At frequencies above 1000 Hz the second, and above 2500 Hz the third line become apparent, with improving resolution at increasing spinning speeds. At ν_r = 4.5 kHz (Figure 4b) the MAR derivative spectrum thus exhibits three well-resolved bands differing in width and chemical shift. The lines are so narrow that they deserve to be studied in the high-resolution regime (Figure 5). By line-shape analysis of the high-resolution spectrum it was found, that the band envelope can be completely decomposed into three lines of Lorentzian shape centered at 7.2, 5.0, and 2.2 ppm (from HMDS as external standard). At ν_r = 2.5 kHz (Figure 5a), the widths of these lines are 30, 90, and 250 Hz, respectively, and their integral intensities are in the ratio 5:2:2. At ν_r = 4.7 kHz (Figures 5b and 6) their widths are 30, 90, and 330 Hz and the intensity ratio changes to 5:2:4.

Based on the relative band intensities, and by comparison with the spectra of the $(BzlGlu)_n$ random coil (Figure 3), the lines at 7.2 and 5.0 ppm can be safely assigned to phenyl and benzyl protons, respectively. It is also evident that their line widths, 30 and 90 Hz, are rotationally invariant at spinning speeds above 1 kHz and correspond thus to the limiting residual line widths of these groups. At 2.2 ppm, the bands of γ- and β-CH_2 protons evidently overlap; one of the two is narrowed by MAR already at spinning speeds between 1 and 2.5 kHz, whereas the other is narrowed only at spinning speeds higher than 2.5 kHz, with a residual line width higher than that of the first band. If the width of the first band measured at 2.5 kHz is considered as rotationally invariant, then the width of the second band measured at 4.7 kHz would be 400 Hz. It is natural to assume that the narrower of these bands corresponds to γ-CH_2 and the broader to β-CH_2 protons.

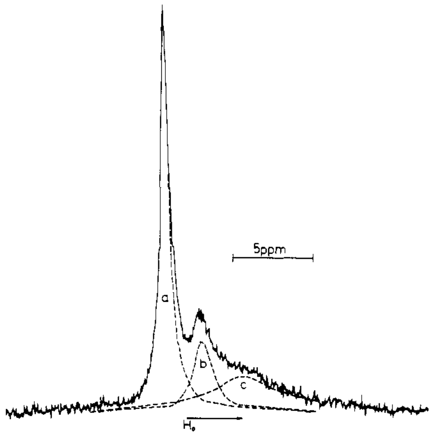

Figure 6. Nmr spectrum of (BzlGlu)$_n$, same as in Figure 5b, showing line separation. (a) Phenyl, (b) benzyl, and (c) β- and γ-CH$_2$.

From our experiments it cannot be decided, if the values 250 and 400 Hz represent true limiting residual line widths; for this even higher presently unattainable spinning speeds would be needed. The bands of the backbone α-CH and NH protons are not detectable in our spectra even at the highest spinning speeds.

In MAR spectra of the 10% solution of (BzlGlu)$_n$ in CDCl$_3$ only the phenyl band can be measured well. Its limiting residual line width is again 30 Hz, *i.e.*, equal to that in the preceding case, and evidently independent of concentration. The benzyl proton band, as well as all other bands, are lost in the noise. However, even this negative finding indicates that these bands in the 10% solution are not narrower than in the 20% solution. The spectrum of (BzlGlu)$_n$ in the system 30% F$_3$CCO$_2$H + 70% CDCl$_3$ does not change by magic angle rotation.

Discussion

General Considerations. The line-width function of two like nuclei of spin ½ is given by the expression[10]

$$\frac{1}{T^2} = \frac{9}{8}\gamma^4\hbar^2 r^{-6}\left[\frac{1}{4}J_0(0) + \frac{5}{2}J_1(\omega_0) + \frac{1}{4}J_2(2\omega_0)\right] \qquad (1)$$

where γ is the gyromagnetic ratio, ω_0 is the nuclear magnetic resonance frequency, r is the length of the internuclear vector, and $J_i(\omega)$ are Fourier intensities of functions of space coordinates at frequency ω. If the reorientation of the interacting spin system can be described as a random process characterized by an exponential correlation function with a single correlation time τ_c, then the $J_i(\omega)$ values are of the well-known shape

$$J_i(\omega) = K_i[2\tau_c/(1 + \omega^2\tau_c^2)]$$

where the K_i are statistical averages of functions of space coordinates which generally depend on the geometrical form of the motion.

Motion in polymeric molecules must usually be described by several motional modes, characterized by different correlation times τ_c, and differing also by their anisotropy in space. A simple system modelling this situation has been analyzed by Woessner.[11] For two spins reorienting anisotropically about an axis by random jumps between three equilibrium positions at an average rate $(3\tau_c)^{-1}$, with the axis performing isotropic motion with a correlation time τ_{c1}, he obtained for the $J_i(\omega)$ an expression of the form

$$J_i(\omega) = K_i\left[A\frac{2\tau_{c1}}{1 + \omega^2\tau_{c1}^2} + B\frac{2\tau_{c2}}{1 + \omega^2\tau_{c2}^2}\right] \qquad (2)$$

where $\tau_{c2} = [(1/\tau_{c1}) + (1/\tau_c)]^{-1}$, A and B are normalized functions of the angle between the inter-nuclear vector and the reorientation axis, and K_i are the conventional isotropic averages of space coordinate functions.

According to the treatment of Haeberlen and Waugh,[12] MAR (similarly to the multiple pulse sequence methods) at a spinning frequency $\omega_r \ll \omega_0$ affects the line-width function of a system with isotropic internal motion and a single correlation time by transforming the $J_0(0)$ term of eq 1 to

$$J_0(0)_r = \frac{2}{3}K_0\left[\frac{2\tau_c}{1 + \omega_r^2\tau_c^2} + \frac{\tau_c}{1 + 4\omega_r^2\tau_c^2}\right] \qquad (3)$$

For significant line narrowing by MAR to be observed, the condition $\omega_r\tau_c \gtrsim 1$ must be fulfilled. In a system with anisotropic internal motion and several characteristic times τ_c, like that analyzed by Woessner, MAR is expected to be effective if at least one of the motional modes considered (*e.g.*, the isotropic motion of the axis) is so slow as to fulfill the above condition ($\omega_r\tau_{c1} \gtrsim 1$), even if the other motion is rapid ($\omega_r\tau^c{}_2 \ll 1$). At sufficient spinning speeds ($\omega_r\tau_{c1} \gg 1$), the members with τ_{c1} should become negligible, and only the members with τ_{c2} would be retained in the expression for the line width (eq 1). The rotation invariant residual line width would then be limited by the correlation time τ_{c2} (approximated by the reorientation jump rate in this case), multiplied by the respective geometrical factors.

In case of a more complicated internal motion, with a greater number of motional modes and different correlation frequencies, the spectral intensity expressions would be expected to contain the corresponding number of similar terms in the square bracket of extended eq 2, with different τ_{ck}'s and different analytical form and numerical value of the geometrical factors A, B, C, . . ., etc. By MAR, the contributions of all members with τ_{ck} so long that $\omega_r\tau_{ck} \gg 1$ should again become negligible, and only the members corresponding to "rapid" motions, with $\omega_r\tau_{ck} \lesssim 1$ would be retained in the expression for the line width.

From the limiting residual line width it is therefore possible in principle to determine the correlation times τ_{ck} of these "rapid" motions, of course only if it is possible to calculate the corresponding geometrical factors. If the spectrum exhibits separate, chemically shifted lines of various proton groups, as in the described spectra of (BzlGlu)$_n$, it is possible to follow by this method the motional behavior of each group separately. In this connection it is very favorable that the relaxation mechanism of each group is proportional to r^{-6} so that it will be dominated by intragroup interactions.[13] Separate eq 1 and 2 must of course be used for each group.

Analysis of Experimental Results

From the spinning frequency at which a given line begins to narrow, and from the condition $\omega_r \gtrsim \delta\omega_{st}$, the width of a given line in the spectrum of a static sample can be estimated. The narrowed bands of various proton groups in the side chain of (BzlGlu)$_n$ appear in the MAR

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spectrum gradually with increasing spinning speed. Therefore, in the static spectrum of the 20% solution of $(BzlGlu)_n$ in $CDCl_3$, the line of the aromatic protons would be expected to be <300 Hz, that of benzyl protons 300–1000 Hz, of γ-CH_2 1–2.5 kHz, and that of β-CH_2 2.5–4.5 kHz wide. This line-width estimate is in good agreement with the overall shape of the static spectrum. From this it is evident that the static spectrum is a superposition of separate bands of different width, justifying the neglect of intergroup interactions, as compared to intragroup interactions, in the first approximation. In discussing the relaxation mechanism manifested by the shape of separate chemically shifted bands, only the intragroup dipolar interactions of the respective proton group need be considered.

Whenever line narrowing by MAR is observed, at least some interactions must conform to the condition $\omega_r\tau_c > 1$. From the narrowing of the phenyl band already at ω_r approaching 10^3 sec^{-1}, it can be assumed that the slow mechanism causing the broadening of lines in the 20% solution of $(BzlGlu)_n$ in $CDCl_3$ must have a $\tau_c > 10^{-3}$ sec. We assume that this slow mechanism corresponds to isotropic reorientations of helix axes in the solution of liquid crystal type. By dilution, the constraints on the motion of the helix axes are loosened, and for this reason dilution leads to a similar result as MAR. When such a quality of spectrum has been obtained by dilution that it cannot be further narrowed by MAR, then it can be concluded that the reorientation of helix axes in the dilute solution is isotropic with a correlation frequency exceeding the highest macroscopic spinning frequency used in the experiment.

From the shape of the static spectrum of a 20% solution of $(BzlGlu)_n$ in $CDCl_3$ and from the process of its narrowing with increasing spinning speed, the static width of the band assigned with great probability to β-CH_2 protons is estimated to be 2.5–4.5 Hz. If, in addition to the very slow reorientation of helix axes, the rapid rotation of the β-CH_2 group about the C_α–C_β bond were the only relaxation mechanism of this group, then the resulting line width would have to be of the order of one-half of the width of the rigid lattice doublet,[14] *i.e.*, much larger than observed. This implies that the β-CH_2 group must participate in some other rapid motion, in addition to the rotation about the C_α–C_β bond. Such an additional rapid motion could be represented by rotation about the helix axis, with a correlation time $\tau_c < 1/\omega_r = 2 \times 10^{-4}$ sec.

For the narrowing of bands of α-CH and NH protons, with a static line width of 15–20 kHz, neither the attainable macroscopic spinning frequencies nor the correlation frequencies of isotropic helix reorientations in dilute solution are sufficient. The necessary frequencies can evidently only be reached when segmental motion of the polymer backbone sets in, as in the random-coil conformation.

The residual line widths corresponding to side-chain proton groups are limited by rapid motional mechanisms, especially by reorientations of the respective group about the sequence of axes represented by the system of chemical bonds in the side chain. It may be expected that the correlation time of these motions will decrease with increasing distance of the group from the main chain, in agreement with the observed decreasing limiting line width of the corresponding lines. Simultaneously, however, with the increasing complexity of the anisotropic motion of increasingly more distant groups, the geometrical factors *A*, *B*, etc., in the line-width expressions (eq 1 and 3) are expected, from Woessner's analysis, to gradually change. Therefore the correlation frequencies of motions of the separate proton groups of the side chain cannot be determined quantitatively without a detailed analysis of the motional mechanism and calculation of the geometrical factors Such a calculation for $(BzlGlu)_n$ and some simpler model systems will be the subject of a subsequent communication.

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Carbon-13 and Proton Nuclear Magnetic Resonance Observations of the Conformation of Poly(L-proline) in Aqueous Salt Solutions

Douglas E. Dorman, Dennis A. Torchia, and Frank A. Bovey*

Bell Laboratories, Murray Hill, New Jersey 07974. *Received October 11, 1972*

ABSTRACT: Proton nmr at 220 MHz and ^{13}C nmr at 25 and 15.08 MHz have been employed to confirm previous conclusions that the disordering of poly(L-proline) chains in concentrated aqueous salt solutions arises primarily from the formation of random sequences of cis and trans peptide bonds. The effects of KI and $CaCl_2$ are essentially similar. The β- and γ-carbon resonances of the proline ring appear to be the most reliable monitors of this isomerization process, giving distinct and well resolved peaks for the cis and trans conformations.

The disordering of poly(L-proline) chains in concentrated aqueous salt solutions has been interpreted as arising from either (a) an increase in the accessible range of the C_α—C═O angle ψ,[1-5] or (b) the formation of random sequences of cis and trans peptide bonds.[6-9] Kurtz and Harrington[10] have ascribed the loss of regular structure to a combination of increased excursions of ψ and small deviations of the peptide bond from planarity. Johnston and

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