^{1}H n.m.r. measurements on aqueous solutions of poly(methacrylic acid)

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^{1}H n.m.r. spectra of aqueous solutions of poly(methacrylic acid) have been measured at a Larmor frequency of 60 MHz. It is shown that the methyl linewidth can be analysed in terms of triad placements of methyl groups, having individual linewidths that are relaxation determined. The contribution of the magnetic dipolar interaction between water protons and methyl protons to the methyl proton linewidth is shown to be negligible. The influence of polymer tacticity, concentration and charge was studied as a function of temperature. The linewidth is found to be strongly dependent on the amount of polymer charge at charge densities up to 50%; the actual shape of this dependence varies with polymer tacticity and concentration. The variable temperature experiments yield energies of activation (3–4 kcal/mole) that are in agreement with results of pulsed n.m.r. experiments on the same system. Values of the self-diffusion constant of the polymer, obtained by n.m.r. pulsed gradient experiments, are given; no simple relationship between this constant and the methyl linewidth is found, while the polymer charge dependence of the self-diffusion constant is opposite to the charge dependence of the diffusion constant in a concentration gradient.

INTRODUCTION

The potentiometric titration curves of poly(methacrylic acid), PMA, differ markedly from the curves obtained by titration of the non-α-substituted poly(vinylic acid) [poly(acrylic acid), PAA][1–4]. The deviation encountered in PMA solutions, relative to PAA solutions, has been discussed in terms of a transition between sets of different conformations, a transition which is induced by increasing the degree of neutralization, α', in the range 0–0.4. Acquisition of microdynamical characteristics of these systems is the object of an n.m.r. investigation, part of which is reported here. The present paper reports some results of the application of nuclear magnetic reconance, *viz.* the determination of methyl proton linewidth and the macromolecular self-diffusion coefficient in D_2O solutions of PMA; part of the linewidth results were published previously[5]. In a recent paper values of the linewidth of the PMA methyl protons were published, but they were determined at lower temperature and at a high concentration only[6].

EXPERIMENTAL

Atactic PMA was synthesized and fractionated as described before[7]. The viscosity-averaged molecular weight of PMA was 0.22×10^6. Syndiotactic PMA was synthesized by hydrolysis of the corresponding methyl ester, PMMA, by means of heating a solution of PMMA in concentrated H_2SO_4, (96 vol %), at a temperature of 65°C and during a period of 4 h in a nitrogen atmosphere. Afterwards the solution obtained was poured onto ice, diluted with water and the precipitate was filtered off. A pure PMA solution in water was obtained by repeatedly dialysing the mixture of the precipitate and fresh water. The syndiotactic PMMA was kindly provided by Dr D. Heikens (Department of Chemical Technology, Technische Hogeschool, Eindhoven, The Netherlands). The synthesis and fractionation of the syndiotactic PMMA is described elsewhere[8]. The viscosity-averaged molecular weight of syndiotactic PMMA was 0.24×10^6 and the percentage of syndiotactic triads was 85%, as determined by integration of the methyl proton magnetic resonance spectrum at 100 MHz and 80°C of a $CDCl_3$ solution of PMMA. All n.m.r. samples were prepared by mixing calculated amounts of stock solutions of the polyacid and the sodium polysalt in D_2O, using acid and salt solutions of the same concentration. Due to the relatively fast relaxation rates of the PMA methyl protons it is unnecessary to replace dissolved oxygen by nitrogen or helium. CW n.m.r. spectra were obtained from samples contained in tubes of 5 mm diameter, while self-diffusion experiments were performed with sample tubes of 10 mm diameter. Sample volumes were approximately 0.7 and 1.5 cm^3, respectively.

The CW proton spectra of PMA were recorded on a Varian DA-60 spectrometer, operating in the field sweep mode and using such H_1-field strengths, sweep rates and filter settings that no distortion of the proton resonances occurred. The magnetic field/RF frequency relation was maintained by locking internally on the signal from the protons exchanging between water and polyacid. The field inhomogeneity was approximately 0.2 Hz, as determined by the proton linewidth of *o*-dichlorobenzene. Sample temperature was controlled by the use of a Varian temperature unit, using nitrogen gas, whose temperature was thermostatically controlled.

The PMA self-diffusion coefficients were obtained from the results of the pulsed gradient technique, using a Bruker pulsed gradient apparatus and a Bruker spectrometer. The experiments were performed in a Varian 12 inch magnet, controlled by a Varian flux stabilizer and a Bruker pulsed

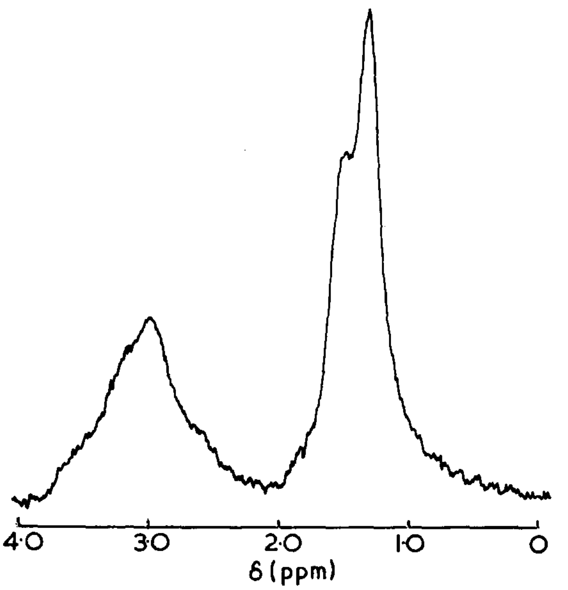

Figure 1 The 60 MHz ^1H spectrum of a-PMA in a D_2O solution at 80°C: $\alpha' = 0.21$ and $X_2 = 1.4 \times 10^{-3}$

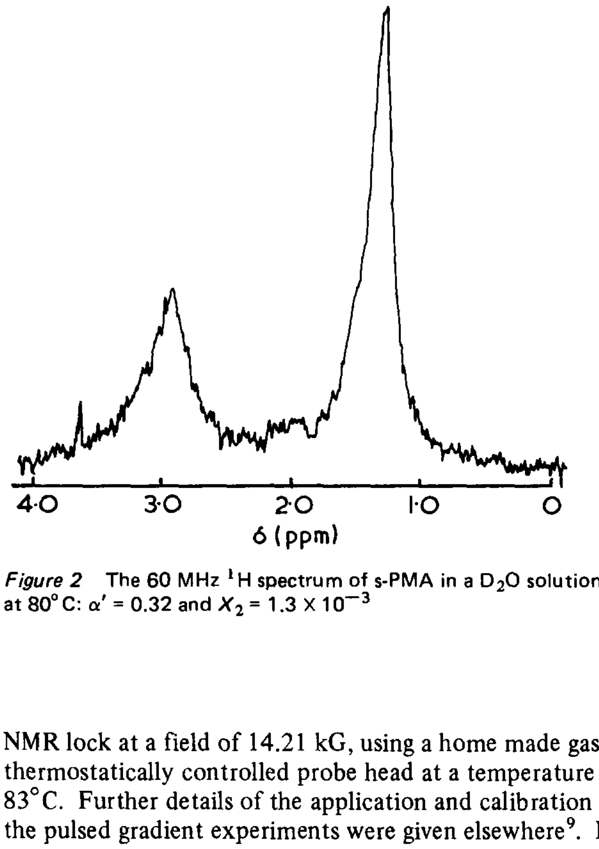

Figure 2 The 60 MHz ^1H spectrum of s-PMA in a D_2O solution at 80°C: $\alpha' = 0.32$ and $X_2 = 1.3 \times 10^{-3}$

NMR lock at a field of 14.21 kG, using a home made gas thermostatically controlled probe head at a temperature of 83°C. Further details of the application and calibration of the pulsed gradient experiments were given elsewhere[9]. In contrast to the procedure reported in ref 9, we have obtained an absolute scale of the diffusion coefficient by measuring the echo attenuation of polymer protons and heavy water deuterons using, except for the Larmor frequency, identical settings (the only difference in probe head configuration was the addition of an extra capacitor which switches the probe head resonance condition between 60 and 9.2 MHz). The impossibility of calibration on an H_2O sample is caused by the narrow gradient pulses required in the H_2O experiments. For PMA self-diffusion experiments approximately 3 msec gradient pulses are used, while in H_2O experiments the pulse length is only 0.5 msec.

RESULTS AND DISCUSSION

Figures 1 and *2* show the n.m.r. spectra of solutions of atactic (a-PMA) and syndiotactic (s-PMA) PMA in D_2O at 60 MHz and 80°C at $\alpha' = 0.21$ and 0.32, respectively and at concentrations $X_2 = 1.4 \times 10^{-3}$ and 1.3×10^{-3}, respectively, where X_2 is the PMA molar fraction on a monomeric base. Although the spin–spin coupling of the methyl protons to the methylene protons is too small to be relevant in the present work, the methyl and the methylene proton resonances show multiplet structure, due to differences in configuration. In first order the CH_3 and CH_2 multiplets can be interpreted in terms of triads (three monomeric units) and dyads (two monomeric units), respectively.

According to this triad and dyad statistics, the magnetic non-equivalence of the protons yields three CH_3 singlets, due to isotactic, heterotactic and syndiotactic triad placements, a CH_2 singlet, due to syndiotactic dyad placements and a CH_2 double doublet, due to isotactic dyad placements. While in PMMA, the methyl ester of PMA, the multiplet structure of the CH_3 and CH_2 resonances are clearly observable, this is not so in pyridine, formamide or dimethyl sulphoxide solutions of PMA, due to the broadness of the resonance lines. In dimethylformamide solutions of PMA, however, one observes well resolved resonance lines of the CH_3 and CH_2 protons[10]. In D_2O solutions of a-PMA the resonance line of the methyl protons is broadened and sometimes split in two resonances (of methyl protons in heterotactic and syndiotactic configurations), depending on the value of α'; the resonance of the CH_2 protons remains one broad signal at all α'-values.

It has been shown that the configuration of the vinyl polymers discussed in this paper can be described by a single parameter σ, which gives the probability for an isotactic placement[11]. In the present case we have measured spectra of a-PMA and s-PMA. Integration of the α-CH_3 resonance lines in $CDCl_3$ solutions of the methyl ester of a-PMA and s-PMA gives the value of σ in the two cases; values of 0.25 and 0.08, respectively, were obtained. Using the value obtained for σ one can calculate the amount of CH_3 and CH_2 groups in each of the triad and dyad configurations. Besides the distribution of CH_3 or CH_2 groups among the different configurations, the relative shifts and linewidths within a group of CH_3 or CH_2 resonance lines will determine the overall shape of the CH_3 or CH_2 resonance. Although it is found in toluene solutions of PMMA that carbons differing in configurational placement have unequal ^{13}C longitudinal relaxation rates[12], we will use the same value for the methyl proton linewidths of methyl protons in syndiotactic, heterotactic and isotactic placements. Since the amount of isotactic placements is low (6 and 1% at $\sigma = 0.25$ and 0.08, respectively, the values in a-PMA and s-PMA) and since the difference in ^{13}C relaxation rates is substantial only between isotactic and syndiotactic/heterotactic carbons, the use of a single value for the individual methyl linewidth will cause only a minor error.

In PMA, as in small weak acids, the chemical shifts will depend on the degree of neutralization, α'. For instance, the magnetic difference between the two CH_2 protons disappears at increasing α', leading to a collapse of the isotactic CH_2 double doublet; the chemical shift difference between the CH_3 and CH_2 protons in s-PMA at $\alpha' = 0.00$ or $\alpha' = 1.00$ is approximately 0.9 or 0.7 ppm, respectively. We have made the following estimate for the α'-dependent chemical shift differences between CH_3 protons in syndio- and hetero-

Table 1 Observed overall CH_3-linewidth and fit-CH_3 linewidth in three PMA solutions as a function of the temperature at 60 MHz

	a-PMA, $\alpha' = 0.50$ $X_2 = 2.0 \times 10^{-2}$		s-PMA, $\alpha' = 0.07$, $X_2 = 1.3 \times 10^{-3}$		s-PMA $\alpha' = 0.18$, $X_2 = 1.3 \times 10^{-3}$	
T (°C)	$\Delta\nu$-obs. (Hz)	$\Delta\nu$-fit (Hz)	$\Delta\nu$-obs. (Hz)	$\Delta\nu$-fit (Hz)	$\Delta\nu$-obs. (Hz)	$\Delta\nu$-fit (Hz)
50	16	10	–	–	–	–
60	14	8	22	19	16	13
70	13	7.5	18.5	15	13.5	11.5
80	12.5	7	15	12.5	10.5	9.5
88	11	6	–	–	–	–
96	11	5.5	12.5	10	8	7.5

tactic placements: 0.15 ppm at $\alpha' = 0.00$, 0.10 ppm at $\alpha' \geqslant 0.25$ and a linear α'-dependence in the range 0.00–0.25. This estimate was based on the slope of the α'-dependent chemical shift of the CH_2 protons in an isotactic placement (the relative shift of the two non-equivalent protons is accurately known at the low α'-values involved) and the use of the observed shift between CH_3 protons in syndiotactic and heterotactic placements found in a 220 MHz spectrum of a D_2O solution of s-PMA at $\alpha' = 0.18$ and 75°C (in that case, the different CH_3 resonances are distinctly separated) to scale the shift in ppm. The result is in fair agreement with literature data of ^1H chemical shifts in PMMA solutions[10,11]. Because of the complicated structure of the CH_2 resonance and the strong dependence of the multiplet structure on α', only the α-CH_3 resonance lines will be discussed.

Computer simulations were made of α-CH_3 proton resonances on the basis of Lorentzian lineshapes, using as a parameter the same linewidth for the protons in the three triad placements. The relative intensities were determined by the value of the tacticity parameter σ, and the relative chemical shifts were derived from the relation given above (assuming additionally that the chemical shift difference between protons in isotactic and heterotactic placements is the same as between protons in heterotactic and syndiotactic placements). It should be noted that in ref 6, the *total* CH_3 linewidths in D_2O solutions of atactic PMA are given (and not the CH_3 linewidth in terms of *one* triad placement); they were obtained by applying a computational procedure to resolve the overlapping CH_3 and CH_2 resonances (at 35°C and 100 MHz). At 80°C, the CH_3 and CH_2 resonances are sufficiently narrow to eliminate this overlap, even at 60 MHz. The influence of the temperature on the observed total methyl linewidth and on the linewidth of a methyl group in one triad placement (denoted by $\Delta\nu$-fit) in three PMA solutions is given in *Table 1*.

Arrhenius plots of $\Delta\nu$-fit, in the small temperature range involved, yield energies of activation of 3.0, 3.9 and 4.1 kcal/mol for a-PMA, ($\alpha' = 0.50$), s-PMA ($\alpha' = 0.07$) and s-PMA ($\alpha' = 0.18$), respectively. In *Figure 3* we have plotted $\Delta\nu$-fit as a function of α' for D_2O solutions of a-PMA at three concentrations ($X_2 = 1.4 \times 10^{-3}$, 4.7×10^{-3} and 1.1×10^{-2}), 60 MHz and 80°C. Before discussing these linewidths in terms of macromolecular dynamics, one has to show that the contribution from water protons to the methyl proton relaxation is negligible. *Table 2*, in which five observed linewidths and their corresponding $\Delta\nu$-fit are given as a function of the D_2O/H_2O composition, shows that this water contribution is indeed negligible. There exists, however, a more serious problem connected with the interpretation of $\Delta\nu$-fit in terms of PMA dynamics. The transverse relaxation of PMA methyl protons is dominated by magnetic dipolar interaction, but neither all the relevant protons involved in the dipolar interactions nor the motions of these proton–proton vectors are known. The knowledge of the PMA configuration is not sufficient to determine the time-dependent length and direction of the vectors between a CH_3 proton and protons of other CH_3 and CH_2 groups, since all those vectors change by internal rotations. The number of relevant protons interacting with the CH_3 proton is limited by their distance to the CH_3 proton and by the time dependence of the orientations of those vectors.

Two papers will be published shortly, in which we report on the frequency dependent longitudinal and transverse relaxation of CH_3 protons, CD_2 deuterons and COOD deuterons in water solutions of selectively deuterated, syndiotactic PMA, s-PMA[13,14]. It turns out that it is not possible to describe the rotation of the 'interaction vector' (*viz*. H–H vectors in CH_3 groups; C–D vector in CD_2 group; O–D vector in COOD group) by a single correlation time. It is necessary to introduce an anisotropic motion of the backbone carbon atom (represented by the two elements of a cylindrically symmetric rotational diffusion tensor) and to

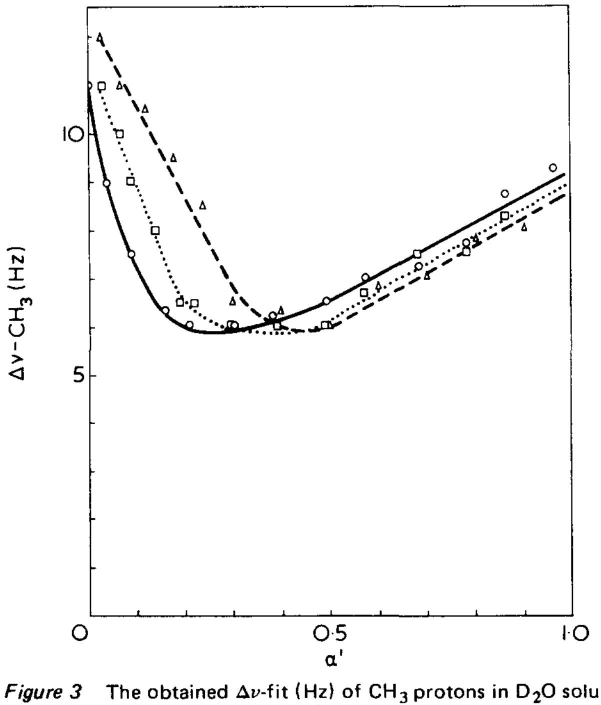

Figure 3 The obtained $\Delta\nu$-fit (Hz) of CH_3 protons in D_2O solutions of a-PMA at 60 MHz and 80°C as a function of α' at three different a-PMA concentrations. ○, $X_2 = 1.4 \times 10^{-3}$; □, $X_2 = 4.7 \times 10^{-3}$ and △, $X_2 = 1.1 \times 10^{-2}$

Table 2 Observed overall CH_3-linewidth and fit-CH_3 linewidth in five atactic PMA solutions as a function of the isotope composition of water (D_2O/H_2O): 60 MHz, 80°C, $\alpha' = 0.50$ and $X_2 = 2.0 \times 10^{-2}$

$\frac{[H_2O]}{([H_2O] + [D_2O])}$	$\Delta\nu$-obs. (Hz)	$\Delta\nu$-fit (Hz)
2.7×10^{-2}	12.4	7.0
0.16	12.2	7.0
0.37	12.5	7.0
0.48	12.1	7.0
0.69	12.5	7.0

contribute an additional internal rotation to the CH_3 group, relative to the backbone motion. Even in the limit of only intra CH_3 group dipolar interaction one obtains the following expression for the methyl proton transverse relaxation rate (neglecting cross-correlation):

$$T_2^{-1}(\omega) = \frac{3}{10}\,\frac{\gamma^4\hbar^2}{r^6}\sum_{k=0,1,2}\;\sum_{l=0,2} c_{kl}\tau_{kl}f_2(\omega_0, \tau_{kl}) \qquad (1)$$

where ω_0 is the Larmor frequency, r is the H–H distance, c_{kl} are functions of the angle between the diffusion tensor symmetry axis and the C–CH_3 bond, and τ_{kl} are functions of the three diffusion constants ($D_\perp$ and $D_\parallel$ for the 'backbone tensor' and D for the internal rotational diffusion). The frequency function $f_2(\omega_0, \tau_{kl})$ is given by:

$$f_2(\omega_0, \tau_{kl}) = \left[\frac{3}{2} + \frac{5}{2}\,(1 + \omega_0^2\tau_{kl}^2)^{-1} + (1 + 4\omega_0^2\tau_{kl}^2)^{-1}\right] \qquad (2)$$

Further details on the model used, and the precise definition of c_{kl} and τ_{kl} can be found in refs 14 and 15.

In the present case the transverse relaxation rate is obtained at one frequency (60 MHz) only, according to $T_2^{-1} = \pi\Delta\nu$. Apart from the necessity to introduce anisotropic reorientation, as described in equation (1), one should in principle take account of the interactions between CH_3 protons and CH_2 protons; the latter protons were absent in the s-CD_2PMA used in the study on the frequency dependent CH_3 proton relaxation[14]. Assuming that these additional interactions are of minor importance only, the possibility of a meaningful interpretation of the α'-dependence of the *one* available quantity ($\Delta\nu$-fit) is still questionable.

It was shown previously that the α'-dependence of the observed transverse relaxation rate (and so of $\Delta\nu$-fit) is to a large degree determined by the change in one correlation time, $\tau_{00}(= [6D_\perp]^{-1})$, at least in the α'-range below 0.40 [14]. Therefore some information may be obtained from the line width data. The dependence of $\Delta\nu$-fit on α' (for $\alpha' < 0.4$) and on the concentration, as given in *Figure 3*, can be interpreted as the behaviour of τ_{00}. *Figure 3* shows that τ_{00} decreases strongly with α' at constant concentration, and increases with the concentration at a constant α'-value. The small component ($D_\perp$) in the effective diffusion tensor therefore increases when the polymers unfold. The effects on $\Delta\nu$-fit in the higher α'-range suggest that $\Delta\nu$-fit decreases with the concentration at constant α'. Since the frequency dependent study was performed at one concentration[14], and since the effects found at high α' are small, we are at present unable to given an interpretation.

In *Figure 4* we have plotted $\pi\Delta\nu$-fit of s-PMA as a function of α', at 60 MHz, 80°C and $X_2 = 1.3 \times 10^{-3}$; together with T_2^{-1} at 60 MHz, 80°C and $X_2 = 5.8 \times 10^{-3}$ (according to results given in ref 14).

Inspection of $\Delta\nu$-fit, as given in *Figures 3* and *4*, shows that the decrease of $\Delta\nu$-fit with α' is much slower in a solution of s-PMA than in a solution of a-PMA at a corresponding concentration (in fact the minimum value of $\Delta\nu$-fit is in an a-PMA solution reached at the same α'-value for an approximately ten-fold higher concentration than in a s-PMA solution). The minimum values of $\Delta\nu$-fit are, however, about equal (~6 Hz); *Figure 3* shows that in a solution of a-PMA this minimum value is independent of the concentration. The transverse relaxation rate, T_2^{-1}, obtained from

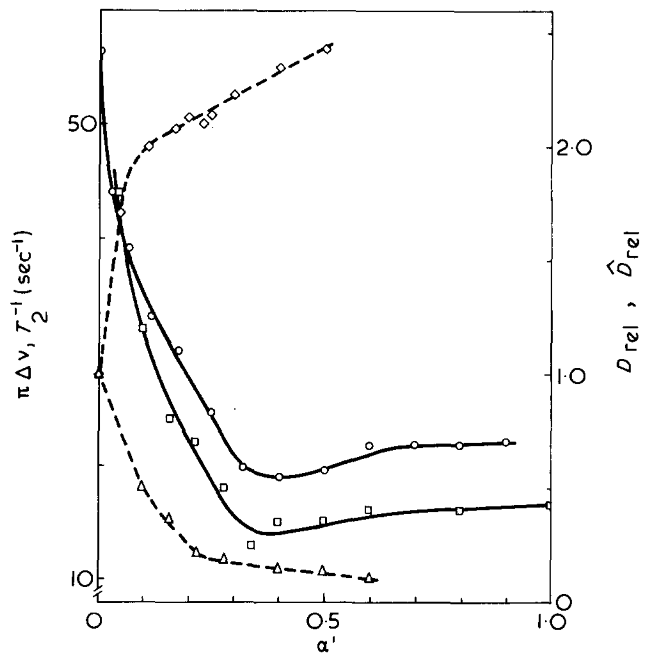

Figure 4 The transverse relaxation rate, as given by $\pi\Delta\nu$-fit and T_2^{-1} (sec^{-1}), of CH_3 protons in D_2O solutions of s-PMA at 60 MHz and 80°C; the relative self-diffusion coefficient, D of s-PMA at 83°C and the relative diffusivity, $\hat{D}$, of a-PMA at 25°C as function of α' ○, $\pi\Delta\nu$-fit, $X_2 = 1.3 \times 10^{-3}$; □, T_2^{-1}, $X_2 = 5.8 \times 10^{-3}$; △; D-relative, $X_2 = 6.9 \times 10^{-3}$ and ◇, $\hat{D}$-relative

spin-echo experiments on solutions of s-CD_2PMA, but at much higher concentration ($X_2 = 5.8 \times 10^{-3}$ instead of 1.3×10^{-3}) is, above an α'-value of approximately 0.10, smaller than $\pi\Delta\nu$-fit. This result is in contrast with the concentration dependence shown in *Figure 3*, in the α'-range 0.10–0.50. This may be due to the possible contribution of the CH_2 protons to the relaxation of the CH_3 protons in the lower α'-range where the conformations of PMA are known to be relatively compact.

This would explain the observed differences at low α'-values, while at high α'-values the previously noted (in solutions of a-PMA) tendency of decreasing relaxation rate with concentration is consistent with the results in *Figure 4*.

For nuclei in small molecules, the relaxation rate often shows a linear dependence on the reciprocal of the self-diffusion coefficient in a range of temperatures (e.g. deuteron relaxation in D_2O). In these situations one normally finds also a linear dependence on the viscosity in a range of temperatures. Since it is well known that the viscosity of PMA solutions increases strongly on changing α' from 0.00 to 0.40 [1], and since the $\Delta\nu$-fit is strongly decreasing in that region, it is of some interest to know the α'-dependence of the self-diffusion constant, D, of PMA.

We have measured, by means of the pulsed gradient technique, the D of s-PMA molecules in a D_2O solution at a concentration of $X_2 = 6.9 \times 10^{-3}$ and a temperature of 83°C in an α'-range of 0.00–0.60. The results, relative to the value at $\alpha' = 0.00$ ($D = 8.4 \times 10^{-7}$ cm^2/sec), are plotted in *Figure 4*. The α'-dependence of D^{-1} is opposite to the one found for $\Delta\nu$-fit. Therefore, neither the viscosity, nor the reciprocal self-diffusion constant, has an α'-dependence, relative to the α'-dependence of the relaxation rate, that is similar to the ones encountered with small molecules. Finally we have plotted the results of Kern and Anderson (interdiffusion of two PMA solutions with concentrations

$X_2 = 6.3$ and 0.63×10^{-4} and with a viscosity-averaged molecular weight, $M_v = 0.36 \times 10^6$) as the diffusivity $\hat{D}$, relative to the value at $\alpha' = 0.00$ ($\hat{D} = 2.4 \times 10^{-6}$ cm^2/sec)[16]. From their values and from their α'-dependence, it is quite clear that the transport properties in a concentration gradient differ qualitatively and quantitatively from properties obtained without a concentration gradient.

CONCLUSIONS

Only a careful analysis of the observed linewidths (i.e. disentanglement of the CH_3 resonances) admits an interpretation which is consistent with the relaxation studies.

Experiments on PMA solutions differing in solvent isotopic compositions (*viz.* $^1H/^2H$ ratio) demonstrated that the contribution of the magnetic dipolar interaction, between water protons and methyl protons to the relaxation of the methyl protons is negligible.

It was found that the methyl proton linewidth of PMA molecules in aqueous solutions decreases rapidly upon increasing α', up to α' values in the range 0.35–0.50, depending on the concentration and the stereochemical nature of the PMA. This confirms the expected important influence of tacticity on the microdynamics of the polymer. In contrast with the results in ref 6, we did not observe an initial slow decrease, a difference caused by the use of the overall methyl linewidth in ref 6, while here the linewidth of a methyl group in one triad placement has been used. A qualitative discussion in terms of the slow backbone atom motion involved was given and it was shown that linewidth experiments at one Larmor frequency yield rather limited information.

In three cases, energies of activation were determined which have magnitudes in agreement with the results of more extensive relaxation studies on the same system[13,14]. The α' dependence of the self-diffusion coefficient of PMA was reported in the α' range 0.00–0.60 and its difference with the concentration gradient results was shown.

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