Hydrogen Bonding in Poly(maleic acid) upon Charging: A Solvent Deuteron NMR and Fourier Transform Infrared Study

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ABSTRACT: The nuclear magnetic relaxation rates of deuterons in D_2O solutions of poly(maleic acid) were studied as a function of charge. Under the assumption of fast exchange, the relaxation rates of deuterons on the carboxylate groups were calculated. The relaxation is shown to be driven by at least two processes, one having a correlation time much longer than the Larmor period and one much shorter. The contribution of the slow process shows a maximum around degree of neutralization $\alpha = 0.3$, while that of the fast process is much smaller and vanishes between $\alpha = 0.4$ and 0.5. FT-IR spectroscopy was used to determine the fraction of deuterons involved in hydrogen bonding. The C═O stretching vibration is a measure of the amount of free COOD groups on the polymer chain, from which the fraction of hydrogen-bonded carboxylate groups is obtained. This fraction has a maximum at $\alpha \approx 0.35$.

Introduction

Polyelectrolytes containing maleic acid as a (co)-monomer show peculiar behavior on charging. Their potentiometric titration curves show a step at half neutralization, and the nuclear magnetic relaxation rates of quadrupolar counterions increase steeply beyond this point. This behavior is certainly due to the close proximity of pairs of carboxylate groups; otherwise, the behavior of poly(isobutylene-*co*-maleic acid) would resemble that of poly(methacrylic acid), which is not the case. In this paper an attempt is made to obtain information on the behavior of COOD groups in poly(maleic acid), PMA, by the nuclear magnetic relaxation of the deuterons in D_2O solutions of PMA as a function of the degree of neutralization α. As hydrogen bonding is assumed to play a role, the fraction of COOD groups involved in hydrogen bonding was determined by FT-IR.

Over the past decade the dissociation behavior of PMA has been investigated by Kitano and Kawaguchi et al.[1−4] With potentiometric titration and viscometry they found a remarkably different behavior below and above 50% neutralization. An Ising model was used to explain the dissociation behavior. It included short- and long-range interactions, hydrogen bonding, and assumptions about the stereochemistry and the local dielectric constant. However, quantitative agreement was not achieved.

Recently, the titration curves of PMA were satisfactorily fitted[5] to an Ising model using three free parameters: an intrinsic dissociation constant and two excess free energies of nearest-neighbor interaction across a racemic and a mesomeric diad. The stereochemistry as determined by ^{13}C NMR[6] was taken into account by assuming random propagation with 65.5% chance of a racemic diad.

The IR spectra of poly(fumaric acid), the stereoisomer of PMA, and poly(isobutylene-*co*-maleic acid) (PIM) have been analyzed by Kawaguchi et al.[3,7] They resolved the IR spectra into four species: free and H-bonded COOH and COO^-. To describe the IR spectra of PMA, these four species were found to be insufficient. It was proposed that H-bonds are formed over four adjacent groups connected by racemic diads. However, some of the assumptions of Kawaguchi et al. are found to be unrealistic. In particular, it was assumed that the probability of racemic propagation is 50% and that the chain is built up regularly, three racemic bonds alternating with a mesomeric one. The ^{13}C NMR spectrum of PMA shows[6] this probability to be 65.5%, causing 70% of the acid groups occur in racemic stretches of six or more.

When PMA is dissolved in D_2O, deuterons exchange freely between the solvent and the COOD groups. Deuteron nuclear magnetic relaxation is driven by the coupling of its nuclear quadrupole with a fluctuating electric field gradient. Consequently, it should be sensitive to the dynamics of COOD groups and to hydrogen bonding. Therefore, the NMR relaxation rates should yield information on free and D-bonded COOD.

In the present work we analyze the D-NMR relaxation rates of PMA for α from 0 to 0.775 and compare the results with data obtained by FT-IR.

Experimental Section

PMA ($M_w = 17\,600 \pm 300$ g/mol) was synthesized by the method of Lang et al.[8] as described in a previous paper.[6] Half of a stock solution of PMA in H_2O was neutralized with LiOH up to $\alpha = 0.775$; at higher α the polymer precipitates. Both solutions were freeze-dried and redissolved in D_2O (Aldrich, 99.9%) five times to replace all exchangeable protons with deuterons. Final concentrations in both D_2O solutions were 0.1099 N PMA. Intermediate values of α were obtained by mixing the stock solutions. These solutions were used for both FTIR and for NMR relaxation and diffusion measurements. An additional α range was prepared at 0.0103 N and was used for NMR measurements only.

The NMR measurements were performed on a Bruker AM 200 WB spectrometer at 4.7 T at 25.0 ± 0.1 °C. D_2O self-diffusion was measured by the pulsed field gradient method,[9] using the stimulated echo sequence.[10] Gradients up to 2.95 T m^{-1} were generated by an actively shielded gradient coil (Doty Scientific Inc.). Current pulses with carefully controlled rise and fall times (about 100 μs) were delivered by a Techron 7570 amplifier in constant current mode, controlled by the spectrometer computer. Samples were contained in 5 mm o.d. NMR tubes. The filling height was about 6 mm to ensure good gradient homogeneity over the sample volume.

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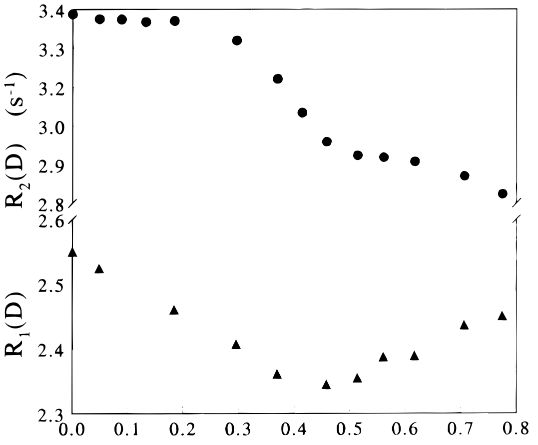

Figure 1. Longitudinal (R_1) and transversal (R_2) deuteron nuclear magnetic relaxation in D_2O solutions of 0.1099 N PMA as a function of the degree of neutralization.

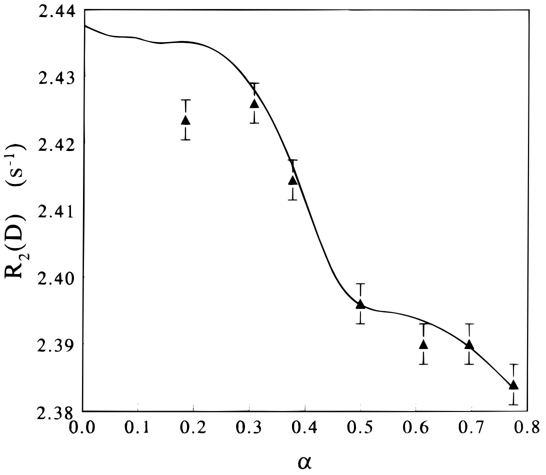

Figure 2. Transversal (R_2) deuteron nuclear magnetic relaxation in D_2O solutions of 0.0103 N PMA. The solid line is calculated from R_2 in 0.1099 N PMA.

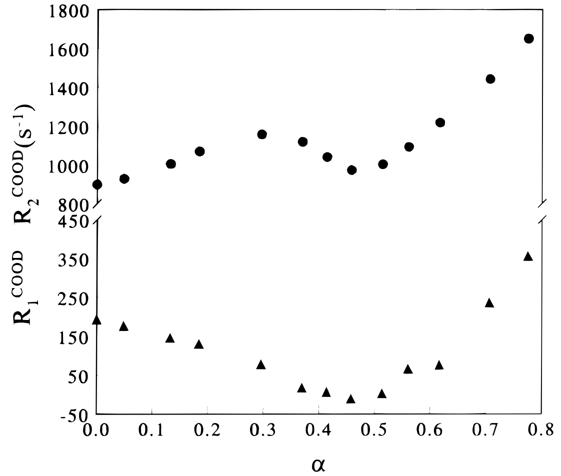

Figure 3. Deuteron relaxation rates in the carboxylic acid groups (R_1^{COOD} and R_2^{COOD}) as calculated with eq 2 for D_2O solutions of 0.1099 N PMA.

Longitudinal relaxation rates R_1 were measured by the inversion recovery method using 32 points; transversal relaxation rates R_2 were measured by Carr Purcell−Gill Meiboom sequences, recording only the even echos. Both R_1 and R_2 were also measured at 6.3 T, but no differences were observed outside experimental error.

IR spectra were obtained with a BIORAD FTS-60A FT-IR spectrophotometer using a CaF_2 cuvette of 109.6 μm at 22.5 ± 0.1 °C. The spectra were corrected for D_2O and HDO. Four bands with a fixed baseline were fitted to the spectra over the whole α range. The Gaussian/Lorentzian character of the bands was left free.

Results and Discussion

R_1 and R_2 of 0.1099 N PMA in D_2O are shown in Figure 1, and R_2 in 0.0103 N PMA is shown in Figure 2. R_1 shows a shallow minimum at $\alpha = 0.45$. R_2 shows two plateaus connected by a region of fairly steep decrease for α between 0.3 and 0.5. To interpret these relaxation rates, it is realized that the deuterons exchange between a number of distinct environments: bulk D_2O, D_2O hydrating the polymer and the counterions, and free and D-bonded COOD groups. Certainly the exchange between the D_2O environments is fast.[11,12] Therefore, all D_2O can be treated as a single species having relaxation rates that are averages over the three environments. As no data are available about hydration D_2O, the usual assumption[13,14] is made that in dilute solution the rotational dynamics, which determines relaxation, and translation are influenced identically by the solute. Then the average relaxation rates in the D_2O phase may be written $R_{1,2} = R_0(D_0/D)$ where R_0 and D_0 are the relaxation rate and self-diffusion coefficient in pure D_2O, and D is the deuteron self-diffusion in the solution. If moreover exchange between the D_2O and COOD phases is at 25.0 ± 0.1 °C assumed to be rapid, the observed relaxation rates are given by[15]

$$R_{1,2}^{\mathrm{obs}} = PR_0\frac{D_0}{D} + (1 - P)R_{1,2}^{\mathrm{COOD}} \qquad (1)$$

where $R_{1,2}^{\mathrm{COOD}}$ are the average relaxation rates in the COOD groups and P is the probability to find the deuteron in a D_2O environment. This expression may be rewritten as

$$R_{1,2}^{\mathrm{obs}} = \frac{x_1}{x_1 + (1 - \alpha)x_2}R_0\left(\frac{D_0}{D}\right) + \frac{x_2(1 - \alpha)}{x_1 + (1 - \alpha)x_2}R_{1,2}^{\mathrm{COOD}} \qquad (2)$$

where x_1 and x_2 are the mole fractions of D_2O and PMA monomer units in the polymer, respectively. The factor D_0/D in 0.1099 N PMA is measured and found to depend weakly on α according to $D_0/D = 1.021 + 0.013\alpha$; in 0.0103 N PMA it equals 1 within experimental error. With eq 2 the dependence of R_1^{obs} and R_2^{obs} on α and concentration is analyzed. The solid line in Figure 2 is R_2^{obs} in 0.0103 N PMA calculated from R_2^{obs} in 0.1099 N PMA by substituting x_2 and α for constant R_0 and R_2^{COOD}. This fits the measured data points well and shows that R_2^{COOD} has no visible concentration dependence over this range. The calculated R_1^{COOD} and R_2^{COOD} are shown in Figure 3. Both rates have a minimum at $\alpha = 0.45$, and a local maximum is observed in R_2^{COOD} at $\alpha \approx 0.3$.

Relaxation is driven by fluctuation processes. Such a process is characterized by its time autocorrelation function (ACF) or equivalently by the spectral density which is the Fourier transform of the ACF. Generally the ACF decays exponentially, leading to a Lorentzian spectral density. In terms of the spectral density $J(\omega)$, D relaxation rates may be written as

$$R_1 = C(J(\omega) + 4J(2\omega))$$

$$R_2 = C\left(\frac{3}{2}J(0) + \frac{5}{2}J(\omega) + J(2\omega)\right) \qquad (3)$$

where C is proportional to the mean-square interaction strength and ω is the Larmor frequency. When the correlation time τ of the process is very short with respect to the Larmor period ω^{-1}, i.e., $\omega\tau < 0.1$, one obtains $J(0) = J(\omega) = J(2\omega) = C\tau$ and R_1 and R_2, and the relaxation is in the extreme narrowing limit. When $\omega\tau$ approaches 1, the rates become frequency dependent and $R_2 > R_1$. When $\omega\tau > 10$, $J(0) \gg J(\omega) \approx J(2\omega)$; $R_2 \gg R_1$ and the frequency dependence vanishes again.

In the present case the relaxation in the COOD groups is outside the extreme narrowing limit, but R_2 is only slightly larger than R_1 while between 30.7 and 41.5 MHz no frequency dependence is seen. Therefore, it is necessary to assume that the relaxation is driven by at least two processes. One must be so fast as to be in the extreme narrowing limit at 41.5 MHz, while the other must be so slow as to show no dispersion at 30.7 MHz. This frequency independence is unfortunate as it allows only the product $C\tau$ and a bound on τ to be determined. It may therefore only be concluded that the correlation time of the fast process must be much shorter than 0.2 ns, while that of the slow process is longer than 50 ns. Information on the slow process may be obtained by measurements at (much) lower frequencies. For PAA at $\alpha = 0$ a slight frequency dependence was found below 10 MHz,[7] but unfortunately lower fields are not available to us at present.

Therefore, two quantities can be obtained from D relaxation: $J(0)$ of the fast and the slow processes. As a function of α, these may be obtained trivially from R_1 and R_2; the results are shown in Figure 4.

The fast process is seen to disappear at $\alpha = 0.45$. At this value of α the solution is neutral. Possibly this process is sensitive to the presence of D^+ and OD^- as was already observed for deuteron exchange processes in polyacid solutions in D_2O by Lankhorst et al.[16,17] With the method used by Lankhorst it should be possible to determine whether exchange plays a role, but the experiments are time-consuming and extremely expensive because highly enriched $D_2{}^{17}O$ is needed as a solvent.

The slow process is seen to be responsible for the local maximum in R_2^{COOD}. This maximum is located below $\alpha = 0.5$, i.e., in the range of linear charge density spanned by PAA for α from 0 to 1. For this polyacid no such features are found; however, R_2^{COOD} is found to be constant for $\alpha > 0.2$. Undoubtedly, the close proximity of the carboxylic acid groups in PMA is responsible for this maximum, but for interpretation more information is needed. Therefore, FT-IR spectroscopy was used to determine the extent of intramolecular D-bonding.

IR spectra of 0.1099 N PMA in D_2O as a function of α are shown in Figure 5. In the range 1710−1570 cm^{-1} three main absorption frequencies can be distinguished. The C=O stretching vibration, $\nu^{\mathrm{C=O}}$, is found around 1700 cm^{-1}. With increasing α its intensity decreases, and the asymmetric COO$^-$ stretching vibration, ν_a^{OCO}, appears at 1590 cm^{-1}. Between those two main frequencies another absorption band is present which is assigned to carboxylates that share a deuteron, ν^{bonded}. The bands ν^{bonded} and ν_a^{OCO} overlap and cannot be resolved unambiguously. However, $\nu^{\mathrm{C=O}}$ can be resolved readily. The relative peak area and the frequency maximum of the $\nu^{\mathrm{C=O}}$ band are shown as a function of α in Figure 6.

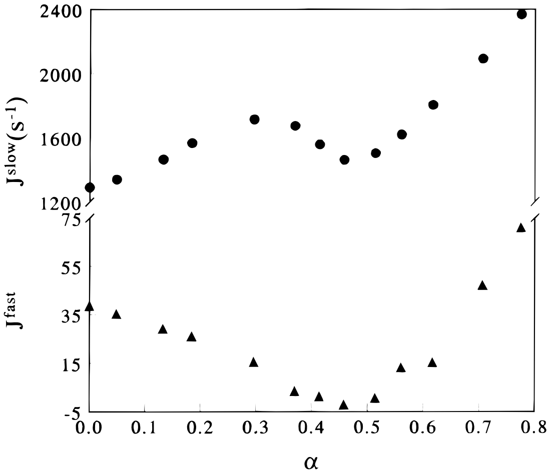

Figure 4. Spectral densities due to the fast and slow processes in the deuteron relaxation in D_2O solutions of 0.1099 N PMA as a function of the degree of neutralization.

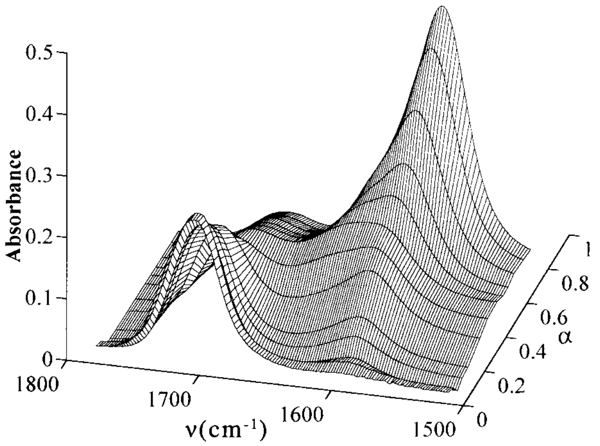

Figure 5. Infrared spectra in D_2O solutions of 0.1099 N PMA as a function of degree of neutralization, corrected for D_2O and HDO.

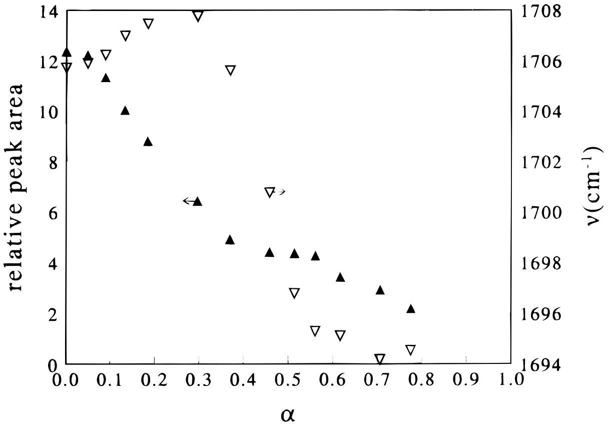

Figure 6. Area and wavenumber of the C=O stretching vibration, $\nu_{\mathrm{C=O}}$, in the IR spectra in D_2O solutions of 0.1099 N PMA as a function of degree of neutralization.

By comparison with the IR spectra of PAA,[11] the $\nu^{\mathrm{C=O}}$ band is assigned to free COOD. In the spectra of PAA two absorption bands are found between 1550 and 1750 cm^{-1} and have been assigned to free COOD and free COO$^-$. The maximum of the $\nu^{\mathrm{C=O}}$ band in PAA

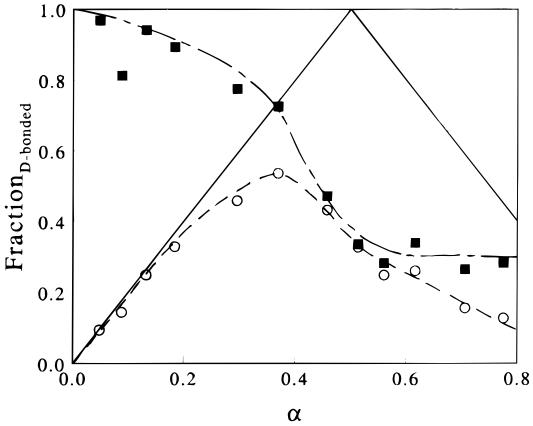

Figure 7. Fraction of D-bonded carboxylic acid groups in D_2O solutions of 0.1099 N PMA (open circles), maximum possible fraction (full line), and the ratio actual/maximum (filled squares) as a function of degree of neutralization. Broken lines are drawn as an aid to the eye.

shifts by 8 cm^{-1} over the α range from 0 to 1, which equals the shift of the $\nu^{C=O}$ of PMA in the corresponding α range from 0 to 0.5. Using this assignment, the fraction of D-bonded groups can be calculated from

$$\text{fraction}_{\text{D-bonded}} = 2\left(1 - \alpha - \frac{A_\alpha}{A_{\alpha=0}}\right) \qquad (4)$$

where A_α is the area at given α and $A_{\alpha=0}$ that at $\alpha = 0$, as obtained by extrapolation. The results are shown in Figure 7, together with the maximum possible fraction and the ratio actual/maximum. Up to $\alpha = 0.2$ about 90% of all possible D-bonds are formed. From $\alpha = 0.2$ to 0.5 this ratio decreases to 30% and stays roughly constant with further increase of α.

In PIM all possible hydrogen bonds are formed over the whole α range.[11] The reason for the strong decrease of the D-bonded fraction in PMA beyond $\alpha = 0.2$ is presumably sterical. PIM may be considered a string of dibasic acids connected by flexible and apolar spacers, and clearly it behaves accordingly. In contrast, a space-filling model of PMA shows it to consist chiefly of helical stretches where COOD groups are crowded on the same side of the backbone, leading to much greater stiffness.

Comparing Figures 4 and 7, it is striking that the local maximum in the spectral density practically coincides with the maximum in the fraction of carboxylates involved in D-bonding. This strongly suggests that D-bonding causes the maximum in the spectral density. Two mechanisms are conceivable: stiffening of the chain leading to slower dynamics and an increase in τ, or increase in the average interaction strength leading to an increase in C. Which mechanism dominates can only be decided when field strengths are accessible where the spectral density of the slow process is frequency dependent, allowing separation of C and τ.

Conclusions

The extent of intramolecular deuterium bonding in PMA has been determined by FT-IR spectroscopy. The deuteron NMR relaxation in the COOD groups has been shown to be driven by at least two fluctuating processes, the slower of which is presumably influenced by D-bonding. It remains to be determined whether chemical exchange has an influence on the relaxation, and low-frequency measurements should clarify the effect of D-bonding on NMR relaxation.

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