Macromolecules **1994**, *27*, 5123–5128

Water-Soluble Copolymers. 53. Sodium-23 NMR Studies of Hydrophobically-Modified Polyacids: Copolymers of 2-(1-Naphthylacetamido)ethylacrylamide with Acrylic Acid and Methacrylic Acid

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Received June 10, 1993; Revised Manuscript Received May 11, 1994[●]

ABSTRACT: ^{23}Na NMR measurements of the longitudinal (R_1) and transverse (R_2) relaxation rates of copolymers of 1% and 10% 2-(1-naphthylacetamido)ethylacrylamide (NAEAM) with acrylic acid (NAA-1 and NAA-10) and methacrylic acid (NMA-1 and NMA-10) have been performed as a function of the degree of ionization. The transverse relaxation was sufficiently biexponential at low α to extract R_{2s} and R_{2f} for NAA-10, NMA-1, and NMA-10. The correlations times, τ_c, and values of $P_b\chi^2$, the product of the fraction of bound ions and the quadrapolar constant, were determined and indicate conformational transitions in NAA-10, NMA-1, and NMA-10. The incorporation of increasing concentration of hydrophobic NAEAM into the polyacids increases χ at low degrees of ionization. The results of the relaxation studies are shown to be consistent with previous viscosity and fluorescence studies on the same systems.

Introduction

Hydrophobic modification of polyelectrolytes can impart desirable properties to copolymers in aqueous solution. For example, hydrophobic substituents of properly-tailored systems can associate in aqueous solution to form microheterogenous domains. "Closed" or intramolecular associations may induce surface-active qualities, while "open" or intermolecular associations may lead to viscosification in aqueous media. The organization of the microheterogeneous associates and responsiveness to changes in pH and ionic strength dictate the usefulness of such systems in applications ranging from phase transfer to rheology modification. An external probe such as naphthalene or pyrene can be solubilized within these microheterogenous zones, and dynamic information about the environment may be obtained from fluorescence studies. Incorporation of the chromophore as a hydrophobic label allows examination of the internal dynamics of hydrophobically-modified polyelectrolyte systems.[1–5]

Poly(methacrylic acid) (PMA) exhibits conformational reordering as the degree of ionization, α, along the polymer backbone reaches a critical value.[6] The methyl groups associate at low pH, forming a compact coil (hypercoil) with hydrophobic domains. As the degree of ionization increases, Coulombic repulsions overcome weak associations of the methyl groups, expanding the coil. This conformational transition has been observed by fluorescence techniques[6,7] as well as classical methods.[8] Hydrophobically-modified poly(methacrylic acid) has been reported to adopt a "hypercoiled" structure in which the hydrophobes form an inner hydrophobic domain surrounded by ionized carboxylate units.[9,10] These hypercoils may persist even at high degrees of ionization if the pendent hydrophobes have flexible spacers.[1,2,10,11]

The major objective of this work was to investigate via ^{23}Na NMR the behavior of sodium hydroxide-neutralized acrylic and methacrylic acid copolymers which have been prepared with 1 and 10 mol % 2-(1-naphthylacetamido)ethylacrylamide (NAEAM) comonomer (Figure 1). The NAEAM comonomer serves a dual purpose of acting as a "hydrophobe" and a fluorescence label. A further objective of this work was to ascertain whether or not the ^{23}Na NMR method might be useful in probing the pH-responsive domain organization deduced from previous photophysical and viscometric studies.[1,2]

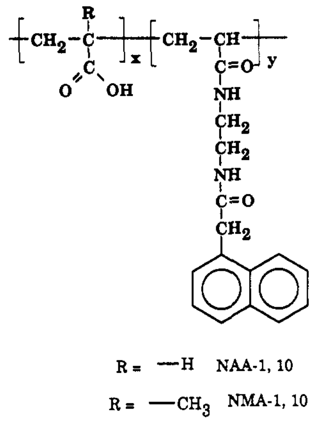

Figure 1. Structures for the NAA and NMA copolymers

Our approach was guided largely by ^{23}Na NMR relaxation rate studies designed to observe conformational changes in poly(methacrylic acid) (PMA)[11] and poly(2-hydroxyethyl methacrylate-*co*-methacrylic acid).[12] Major contributions to the development of the ^{23}Na NMR method, including the key expressions utilized in data analysis, are detailed in the Introduction of the preceding paper in this series. Hereafter, to avoid redundancy, appropriate expressions will be cited. In this approach longitudinal and transverse relaxation rates for sodium counterions have been measured as a function of α (degree of ionization) for the modified copolymers shown in Figure 1. The corresponding correlation times, τ_c, and values for $P_b\chi^2$, the product of the fraction of bound ions and the quadrapolar coupling constant for the Na$^+$ nuclei are calculated using both the ratio of R_1 to R_2 as well as the biexponential transverse relaxation rates in the copolymers. These data indicate that a conformational transition induced by the presence of sufficient hydrophobic label probably occurs at low charge density for both PAA and PMA. These conclusions are supported by previously reported viscosity and fluorescence measurements on these or related systems.[1,2] The correlation time, τ_c, is deter-

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[●] Abstract published in *Advance ACS Abstracts*, July 1, 1994.

0024-9297/94/2227-5123$04.50/0

mined by employing a theoretical estimate for P_b[11-14] or by assuming P_F (the fraction of free ions) $\gg P_b$.[15] Once τ_c is known, $P_b\chi^2$, and χ may be determined. χ is a measure of quadrupolar interactions and is proportional to the magnitude of the electric field gradient experienced by counterion nuclei.

Previous studies on PMA have shown that $P_b\chi^2$ and χ vary substantially with increasing degree of ionization, α, in PMA when using theoretical estimates for P_b. These studies demonstrated that the changes observed in $P_b\chi^2$ could not be solely accounted for by changes in P_b; thus, χ must change with α. Similar variations in both χ and τ_c were observed when determined from the $\Delta(R_1/R_2)$ and $\Delta(R_{2f}/R_{2s})$.[11] (See (9-11) in the preceding paper.)

Experimental Section

Sodium NMR measurements were conducted at 25 °C on a Bruker MSL-400 operating at 105.8 MHz for ^{23}Na nuclei. The glass cylinders supporting the transmitter/receiver coils were replaced with Teflon counterparts to minimize signal interference from sodium borosilicate glass. Teflon NMR tube liners from Wilmad Glass Co. were used in place of glass NMR tubes. Longitudinal relaxation rates (R_1) were measured using the inversion-recovery method. All curves were observed to be single-exponential decays and were fit to (8) (see the Introduction of the preceding paper) using the Bruker SIMFIT program. Transverse relaxation rates (R_2) were measured (nonspinning) using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence and were fit to (4) and (5). In some cases the biexponential relaxation was diminished to the point where the error of the fit to (5) was similar to that of (4), and the relaxation decay was then deemed single exponential. Error bars on the plots are given at the 95% confidence level.

The synthesis of the copolymers (Figure 1) has been previously[2] described with the mole percent of NAEAM incorporated as follows: 0.9% NAEAM in PAA (NAA-1), 9.3% NAEAM in PAA (NAA-10), 1.02% NAEAM in PMA (NMA-1), and 11.8% NAEAM in PMA (NMA-10). Poly(acrylic acid) (PAA; MW = 250 000) and poly(methacrylic acid) (PMA; MW = 15 000) were obtained from Polysciences, Inc. Polymer solutions were prepared to 0.1 g/dL concentration with 5% D_2O to provide a frequency lock. The polymer concentration for these studies was selected to provide a good signal-to-noise ratio with a reasonable number of scans and to fall within the dilute regime in order to minimize possible associative interactions between isolated polymers. The polymers were initially prepared at pH 9 and titrated with 1 M HCl to the desired pH values. Attempts to titrate from an acidic polymer solution using NaOH were unsuccessful due to the insolubility of the 10% NAEAM-labeled polymers at low pH. The degree of ionization was determined from the amount of added acid.

Results and Discussion

In the following discussion, the longitudinal and transverse relaxation rates of PAA, PMA, and the labeled, hydrophobically-modified NAA and NMA series (Figure 1) will be presented.[2] The slow and fast transverse relaxation rates, R_{2s} and R_{2f}, respectively, are included when the relaxation decays displayed biexponential character at low α. At α values above 0.8, biexponential rate behavior was observed; however, these data are not presented since the region of interest for this study is α values less than approximately 0.8. Correlation times, τ_c, are calculated from $\Delta(R_1/R_2)$ since $\omega\tau_c > 0.25$ over the range of all α values. For the NMR series, the biexponential relaxation rates observed at low α were also employed to calculate $P_b\chi^2$.

In Figure 2, the transverse and longitudinal relaxation rates for NAA-1 are plotted as a function of the degree of ionization. R_1 and R_2 values are nearly identical for NAA-1 and PAA. Also the values for the latter are consistent with those from previous studies.[13] In ref 13, R_2 has slightly higher values than R_1, indicating that $\omega\tau_c > 0.25$.[11] The data presented in our work also demonstrate that $\omega\tau_c > 0.25$ as evidenced by the inequality of R_1 and R_2 over the range of pH values studied. Both relaxation rates increase smoothly toward $\alpha = 1$. The similarity in the relaxation rates for PAA and NAA-1 demonstrates that incorporation of 1% NAEAM has no observable effect on the ^{23}Na NMR behavior.

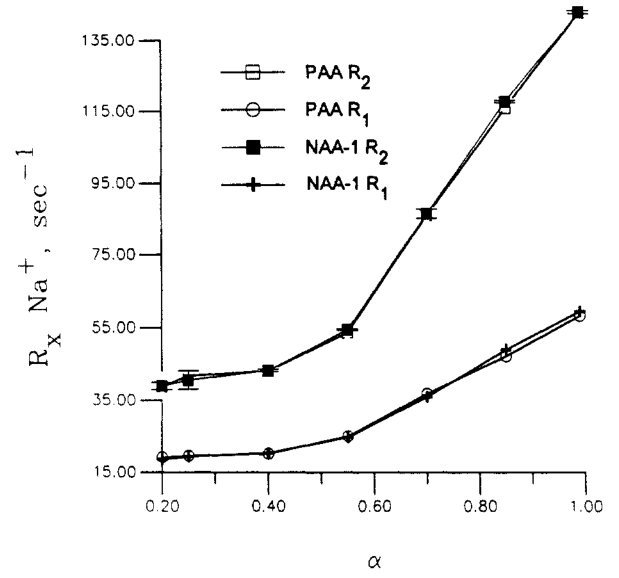

Figure 2. Transverse (R_2) and longitudinal (R_1) relaxation rates of PAA and NAA-1 with increasing α. The polymer concentration is 0.1 g/dL.

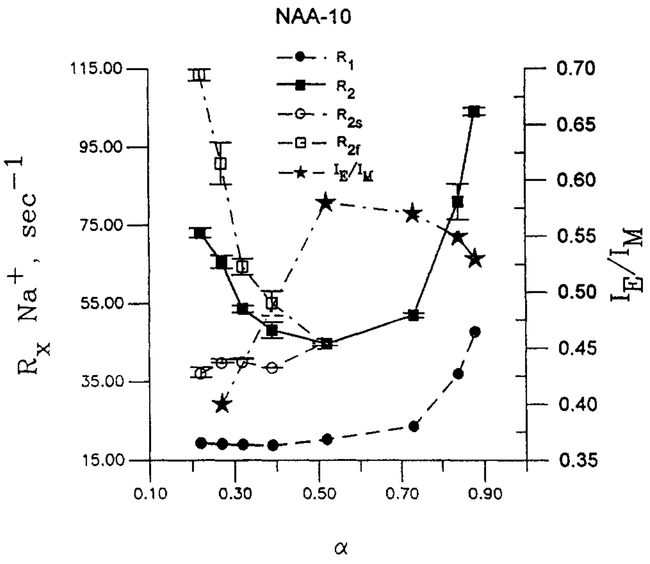

Figure 3. Transverse (R_2) and longitudinal (R_1) relaxation rates of NAA-10 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The ratio of the excimer to monomer fluorescence emission, I_E/I_M, is also depicted. The polymer concentration is 0.1 g/dL.

Figure 3 illustrates the dependence of R_1 and R_2 on α for NAA-10. The behavior is quite different from that observed in PAA and NAA-1. Below $\alpha = 0.5$, R_2 can be resolved into slow and fast (R_{2s} and R_{2f}) components. It is interesting to note that a substantial decrease in R_{2f} is matched by a marked increase in I_E/I_M (the fluorescence intensity ratio of excimer to monomer designated by the stars in Figure 3) as α approaches 0.5. These superimposed data are from previous studies[2] on this polymer by our group. This behavior is consistent with the adoption of a pseudomicellar conformation with high values of I_E/I_M.[2]

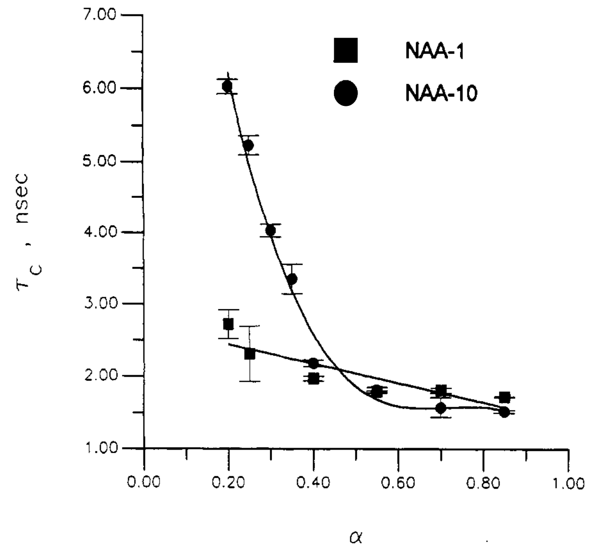

Figure 4. Correlation times, τ_c, with increasing degree of ionization, α, for NAA-1 and NAA-10. These data were derived from (8) using the P_b from Anders et al.[16]

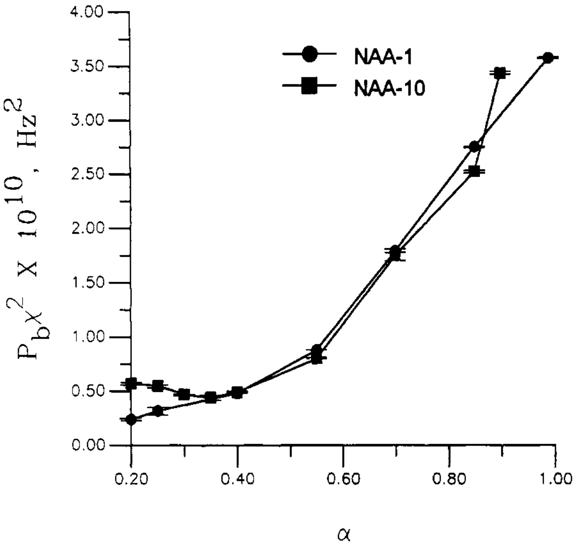

Figure 5. Values of $P_b\chi^2$ for NAA-1 and NAA-10 derived from (7) using τ_c from Figure 4 and the values of P_b from Anders et al.[16]

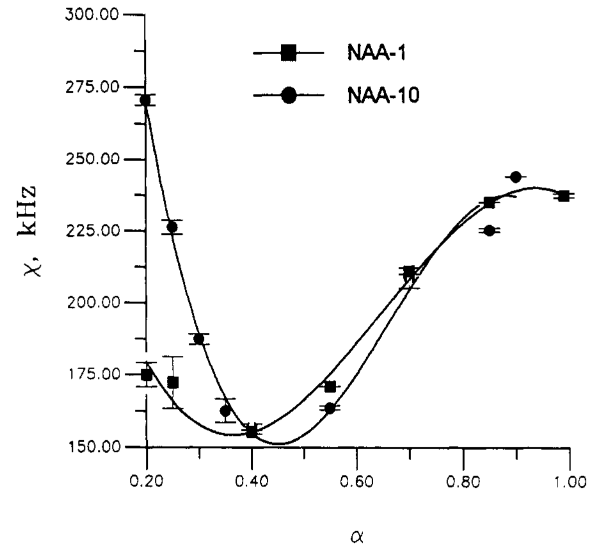

Figure 6. Values of χ for NAA-1 and NAA-10 derived from (7) using τ_c from Figure 5 and the values of P_b from Anders et al.[16]

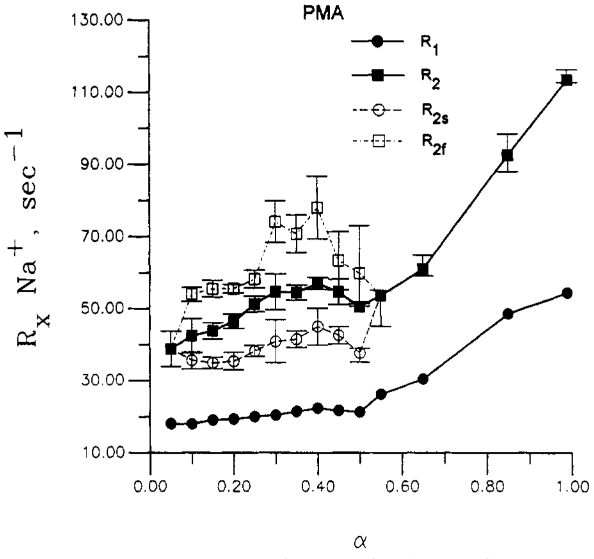

Figure 7. Transverse (R_2) and longitudinal (R_1) relaxation rates of PMA (NMA-0) with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The polymer concentration is 0.1 g/dL.

The "micellelike" or hypercoil structure persists at still higher values of α up to 0.7, beyond which R_2 increases dramatically and I_E/I_M decreases slightly. The number of ions bound and the strength of the binding in the "hypercoil" play roles in the observed changes.

In Figure 4, τ_c is plotted as a function of α for NAA-1 and NAA-10. The data for PAA (not included) are virtually identical to that for NAA-1. The correlation times were determined using (8) (preceding paper) and the P_b values for PAA provided by Ander et al.[16] The slope of the τ_c vs α for NAA-10 is greater than that of NAA-1, indicating that the local motions of the Na$^+$ counterions are slowed in the NAA-10 copolymer. The P_b values determined by Ander[16] are from an electrophoretic technique and may arguably not reflect the same fraction of ions bound on the NMR time scale. However, rather than employing theoretical estimates for P_b,[11-14] we have chosen this experimental measure for P_b. As shown by Lindman and co-workers,[15] the precise values of P_b may not be important for an unambiguous interpretation of the relaxation data.

The values of $P_b\chi^2$ (Figure 5) and χ (Figure 6) were determined from the derived τ_c values using (7) (preceding paper). Higher values of $P_b\chi^2$ and χ at $\alpha < 0.3$ are observed for the NAA-10 copolymer compared to NAA-1. This increase in $P_b\chi^2$ for NAA-10 can be largely attributed to changes in χ, as clearly established by considering the extreme limits of $P_b\chi^2$ from (7) assuming that all of the ions are bound ($P_b = \alpha$) or that none of the ions are bound ($P_b = 0$). This behavior might be projected from a decrease in the local dielectric constant within the hydrophobic domain affecting the bound sodium ions and is consistent with the I_E/I_M data in Figure 3. This will be discussed further in the section to follow on the NMA copolymers.

In Figures 7–9, the relaxation rates for PMA, NMA-1, and NMA-10, respectively, are presented with increasing α. There are maxima in both R_1 and R_2 at low α for each of the polymers (PMA, NMA-1, and NMA-10). Similar maxima are observed in the behavior of R_{2s} and R_{2f}. This behavior is analogous to that observed for PMA by other researchers.[11] As with NAA-1, the incorporation of 1% NAEAM into the copolymer has no observable effect on the relaxation rates.

Biexponential relaxation rates are observed at low α and disappear with increasing degree of ionization. The

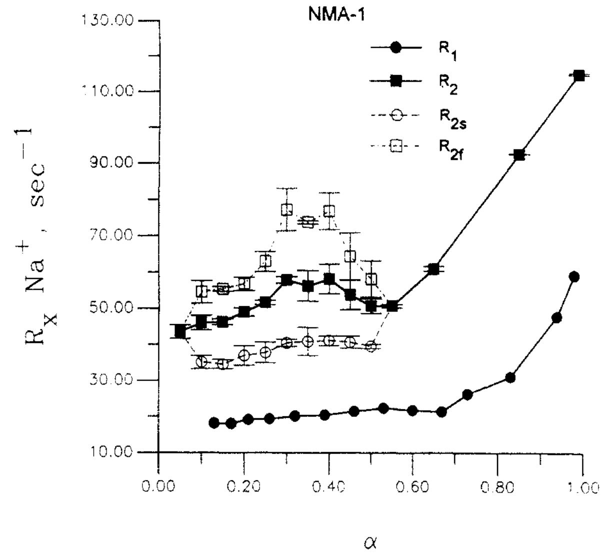

Figure 8. Transverse (R_2) and longitudinal (R_1) relaxation rates of NMA-1 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The polymer concentration is 0.1 g/dL.

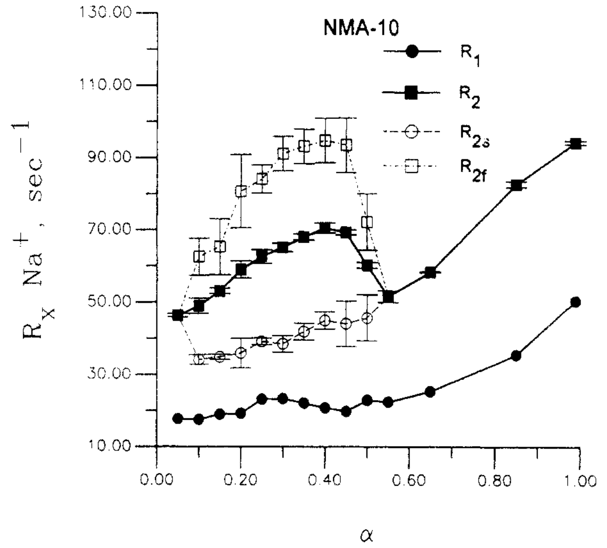

Figure 9. Transverse (R_2) and longitudinal (R_1) relaxation rates of NMA-10 with increasing α along with the biexponential transverse relaxation rates (R_{2s} and R_{2f}). The polymer concentration is 0.1 g/dL.

magnitude of the relaxation rates is somewhat lower than that observed by Lindman et al.[11] and may be due to the differences in the neutralization procedures employed or the polymer concentration. For both NMA polymers, a decrease in R_2 (and R_{2f}) occurs between α = 0.45 and 0.60, coinciding with an increase in I_E/I_M observed for these systems.[2] This behavior is consistent with the formation of a hypercoil structure like that reported by Guillet.[9,10] Unlike the NAA-10 copolymer however, increased α (increase in R_2) does not significantly affect the hydrophobicity of the hypercoil.

In Figures 10 and 11, the correlation times, τ_c, are plotted as a function of the degree of ionization for NMA-1 and NMA-10. τ_c was determined as before, using (7) (preceding paper) and the values for P_b from Ander.[16] A decrease in τ_c is observed with increasing α, as previously reported for PMA[11] (only the data for NMA-1 are presented in Figure 10, due to the similarity of the calculated τ_c values to those determined for PMA). In Figure 11, τ_c for NMA-10 is observed to increase for α values between 0.3 and 0.55. This, in turn, is manifested as an increase in $P_b\chi^2$ for NMA-10 vs NMA-1 (Figure 12). Values for $P_b\chi^2$ calculated from (10) and (11) (preceding paper) are also shown in Figure 12. These values are somewhat higher than those calculated from (7) and (8), consistent with previous investigations.[11]

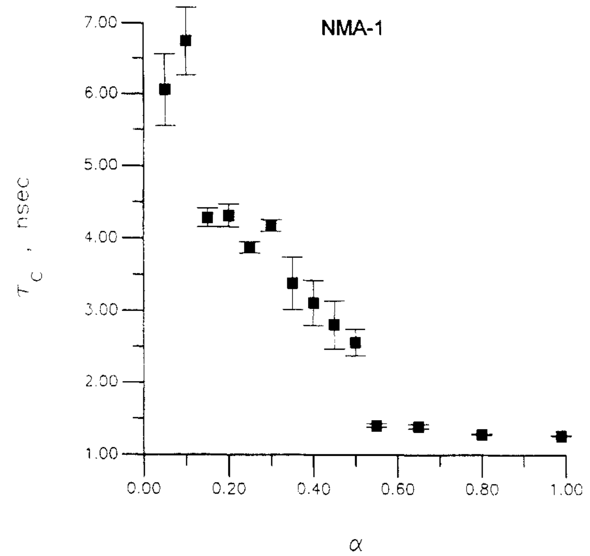

Figure 10. Correlation times, τ_c, with increasing degree of ionization, α, for NMA-1. These data were derived from (8) using P_b from Anders.[16]

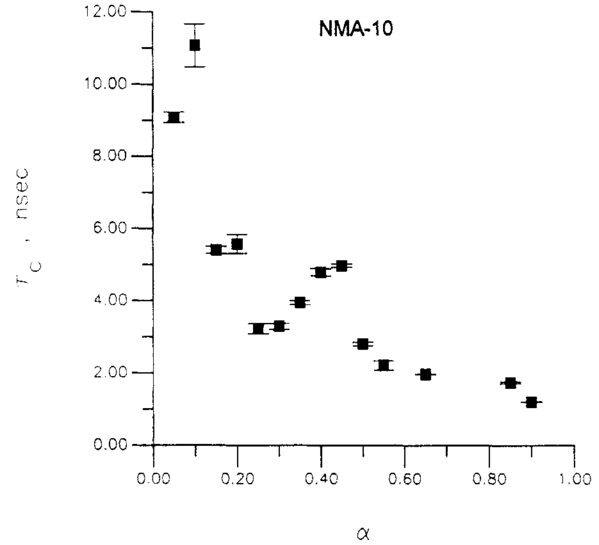

Figure 11. Correlation times, τ_c, with increasing degree of ionization, α, for NMA-10. These data were derived from (8) using P_b from Anders et al.[16]

The variation in $P_b\chi^2$ with α for many polymer systems is often rationalized by assuming χ to be constant. Therefore, as α increases, changes in $P_b\chi^2$ would be due only to changes in P_b.[14,17] This assumption appears to be consistent with experimental data as long as a conformational change does not occur over the range of α values studied. For PMA, however, for which conformational changes have been demonstrated by a number of classical techniques, variations in $P_b\chi^2$ may be due to significant changes in χ as a function of α. As discussed by Lindman et al.[11] for PMA, an increase in P_b alone is not sufficient to account for the increase in $P_b\chi^2$ with increasing α. A similar argument is applied to the differences in $P_b\chi^2$ for NMA-10 compared to NMA-1. At $\alpha \approx 0.3$, $P_b\chi^2$ ranges from 0.347 to 0.768 × 10^{10} Hz^2 (for values of $P_b = 0$ and $P_b = \alpha$, respectively) for NMA-1 and 0.61 to 0.971 × 10^{10} Hz^2 for NMA-10. Thus, if χ were constant for NMA-1 and NMA-10, a near doubling of P_b for NMA-10 compared

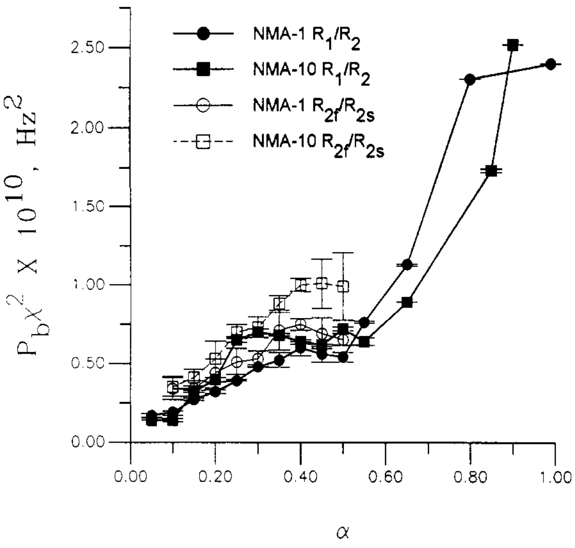

Figure 12. Values for $P_b\chi^2$ for NMA-1 and NMA-10 derived from (6) and (7) using τ_c from Figures 10 and 11 and P_b from Anders.[16]

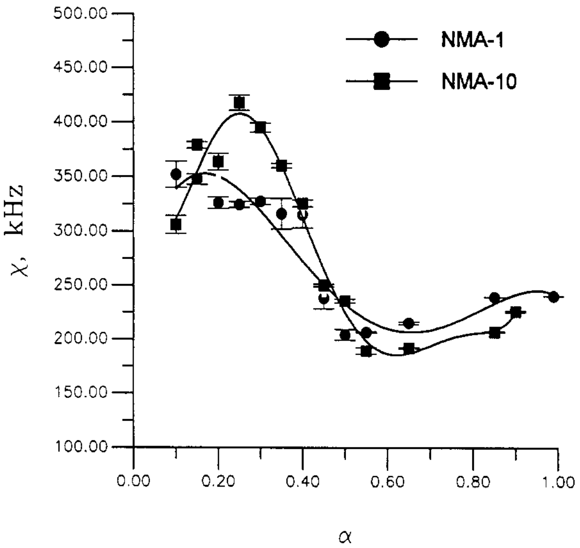

Figure 13. Quadrapolar coupling constants, χ, for NMA-1 derived from (6) and (7) using τ_c from Figure 8 and P_b from Anders.[16]

to NMA-1 would be necessary to account for the increase in $P_b\chi^2$; obviously this is not possible.

Using the values for P_b provided by Ander for PAA,[16] a more reasonable dependence of χ on α is shown in Figure 13. A significant increase in χ for NMA-10 compared to NMA-1 at low values of α is observed. It has been independently established for the NAA and NMA series that the hydrophobicity of the domains that form at low values for α increases with an increasing amount of NAEAM in the NMA copolymer.[2] An increase in the hydrophobicity of the domains should result in lowering the local dielectric constant, increasing the strength of the ionic bond between Na^+ and the carboxylate moieties, and concomitantly increasing χ. Thus, an increase in χ at low α to account for the increases in $P_b\chi^2$ is consistent with results from previous fluorescence studies.[2] The $P_b\chi^2$ values derived from $\Delta(R_{2f}/R_{2s})$ show the same trend as those from $\Delta(R_1/R_2)$, although the relative error is much larger.

As α increases beyond 0.5, $P_b\chi^2$ increases substantially. Some researchers have demonstrated that this increase is consistent with changes in P_b only.[14,17] As shown in Figures 6 and 13, χ increases only slightly for both NAA and NMA at $\alpha > 0.5$ when using experimental P_b values.[14] In this region of α, the increases in $P_b\chi^2$ (Figures 5 and 12) cannot, at least for these copolymers, be attributed specifically to one parameter (P_b or χ). It is interesting that the increase in $P_b\chi^2$ for both polymer systems is significant in the region of α between 0.5 and 0.6, near Manning's theoretical prediction of α = 0.65 for the onset of counterion condensation. This may be coincidental considering that local dielectric constant values in microphase domains must surely be different from those in the bulk solution. However, further study of this observation should be attempted. Also warranting study is Manning's suggestion that the onset of global polymer transitions may be related to the presence of locally folded structures that become extended as the linear charge density parameter, ξ, exceeds 1.[18]

Conclusions

The data from this study demonstrate that sufficiently large concentrations of hydrophobic groups in PAA and PMA copolymers can cause pH-dependent associations affecting relaxation rates of the Na^+ counterions. The increase in $P_b\chi^2$ for NAA-10 over that in NAA-1 implies a stronger binding of Na^+ to the carboxylate sites, consistent with a decreased dielectric constant in the hydrophobic domains. Similar behavior is observed for the NMA-1 and NMA-10 copolyelectrolytes. An increase in the amount of NAEAM in the NMA polymer is reflected in the calculated values of τ_c and $P_b\chi^2$. The $P_b\chi^2$ values of NMA-10 pass through a maximum as α increases, suggesting that an increase in χ is responsible for the observed behavior. These results are consistent with those previously obtained from fluorescence studies.[2]

Interpretation of the $P_b\chi^2$ vs α behavior for the NAA and NMA copolymers should be approached with some caution for the following reasons. Theoretical models (such as Manning's theory or the Poisson–Boltzmann "cell" model) can be used for the estimation of P_b values. However, these models predict different P_b values and do not address local dielectric constant changes. In our paper, an experimental measure of P_b for PAA was used for the determination of τ_c, $P_b\chi^2$, and χ. It has been pointed out that an electrophoretic technique was employed to measure these values of P_b. Furthermore, it has yet to be established that such measured values of P_b would be accurately accommodated by the two-site model used in interpretation of ^{23}Na NMR since the respective time scales of the measurements are significantly different.

Acknowledgment. Support for this research by the Department of Energy, the Office of Naval Research, and Defense Advanced Research Projects Agency is gratefully acknowledged. We recognize Amoco Oil Co. for their contribution in the form of a research fellowship. The authors also thank Dr. William Jarrett and Porter Shannon for assistance with the NMR experiments, as well as Dr. Robert Lochhead for helpful discussions.

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