Charge Density Effects on Polyelectrolyte Dynamic Rheology

John C. Harrington

Hercules Incorporated, Paper Technologies and Ventures Group, 500 Hercules Road, Wilmington, Delaware 19808

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ABSTRACT: The dynamic rheological properties of an uncharged polymer and charged polyelectrolytes were evaluated in salt-free water at various concentrations above the entanglement concentration. A poly(acrylic acid) homopolymer was used as the uncharged polymer and was ionized to anionic poly(acrylic acid-*co*-sodium acrylate) at five levels of ionization (0.05, 0.10, 0.15, 0.30, and 0.50). The polymers exhibited a terminal region at a low frequency and a plateau region at a high frequency. The dynamic data for the nonionic parent and all charged polymers could be reduced to a master curve, which indicated a similar distribution of relaxation times for the nonionic and charged polymers. The shear modulus, relaxation time, and zero shear viscosity properties exhibited a concentration and charge density dependence. Higher power-law exponents for the rheological properties were noted for the nonionic polymer versus the charged derivatives. The number of mechanically active entanglements per number of chains increased with the polymer concentration and charge density. The total number of mechanically active entanglements per number of chains that occurred because of imposing a charge to the nonionic parent did not change with increased concentration, and this indicated a different entanglement mechanism for charged polymers in comparison with their nonionic parent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 3310–3317, 2008

Key words: polyelectrolytes; rheology; solution properties; viscoelastic properties; water-soluble polymers

INTRODUCTION

Polyelectrolytes are important for solid–liquid separation, dispersion, oil recovery, thickening, and personal care applications, where the charge on the polymer is generally employed to coagulate, flocculate, disperse, or thicken the medium.[1,2] The solution rheological properties of polyelectrolytes will increase upon dilution under salt-free solutions because of repulsion of the charge group and can provide dramatic increases in viscosity in comparison with uncharged polymers.[3] The theoretical basis for the unique behavior of polyelectrolyte solutions has been investigated and reported.[4–8] Scaling theories predict that polyelectrolyte rheological properties will scale with lower exponents in comparison with nonionic polymers in the dilute and semidilute concentration regions.[9,10]

Fully charged polyelectrolytes, where every monomer contains a charge, have been investigated experimentally with steady-shear experiments in the dilute[11] and semidilute[12,13] regions. The effects of a variable charge density have been investigated with steady-shear experiments in the dilute[14–19] and semidilute[20] regions. A series of poly(2-vinyl pyridine-*co*-*N*-methyl-2-vinyl pyridinium chloride)s were studied in ethylene glycol, where the level of ionization (α) varied from 0 to 0.55.[20] A concentration dependence on rheological properties was observed for the polymers and was different for the uncharged and charged polymers. Nonionic poly(2-vinyl pyridine) exhibited the lowest viscosity, whereas samples with α = 0.1–0.55 were identical in solution viscosity because of counterion condensation.

Dynamic oscillation techniques have been used to study the effects of charge density in the dilute region[21–23] and at a constant charge above the entanglement concentration (C_e).[13,24–27] Fully charged homopolymer poly(*N*-methyl-2-vinylpyridinium chloride)[24] and partially charged poly(acrylamide-*co*-sodium acrylate), containing 17 mol % charged monomer,[27] were characterized in salt-free water above C_e with dynamic oscillation techniques. The rheological properties exhibited a concentration dependence. In the semidilute region, the power-law exponents were less than that of a nonionic polymer; in the concentrated region, the values approached that of a nonionic polymer. General agreement with predicted scaling laws was reported.

The dynamic properties of a poly(acrylic acid) aqueous solution, possessing a viscosity-average molecular weight of 7.5×10^5, were evaluated at pHs

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Correspondence to: J. C. Harrington (jharrington@herc.com).

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ranging from 4.6 to 7.0 with an electromagnetic transducer.[28] The storage modulus (G') of the highest 0.081*M* concentration solution increased from 2.8 Pa at pH 4.6 ($\alpha = 0.5$) to a maximum G' value of 1×10^4 Pa at pH 6.4 ($\alpha = 0.98$). The decrease in G' to 0.7 Pa as the pH was further increased from 6.4 to 7.2 was attributed to charge–dipole interactions. The degrees of neutralization were based on a pK_a value of 4.6 for poly(acrylic acid).

Polyelectrolytes have also been modified with hydrophobic monomers, where the resultant hydrophobic associations provide unique rheological properties.[29,30] Although increased charge density generally results in an increase in the solution viscosity or modulus,[31] a decrease in solution rheological properties has been observed in some associative systems with increased polymer charge density; this decrease has been attributed to a reduction in the number of associations resulting from intermolecular electrostatic repulsion or increased polymer solubility.[32]

For this study, a high-molecular-weight poly (acrylic acid) homopolymer was systematically ionized to five different charge densities, and the dynamic properties were determined in salt-free water at various concentrations above C_e. Poly(acrylic acid) was used as the nonionic parent because its ionization permits evaluations of the rheological properties of uncharged polymers and charged polymers of various charge densities with the same parent polymer. The concentration and charge density dependence on the rheological properties are reported.

EXPERIMENTAL

Sample preparation

A high-molecular-weight ($> 10^6$ Da) poly(sodium acrylate) homopolymer (EM 1030NA, SNF Floerger, Riceboro, GA), produced via inverse emulsion polymerization, was used as the parent polymer. A high-molecular-weight polymer was used to provide differentiation of the charged and uncharged species due to differences in the terminal relaxation time.[27] A polymer produced by the inverse emulsion process was employed to provide a very high molecular weight polymer.[33]

The parent emulsion polymer was first precipitated with acetone as the nonsolvent to remove residual surfactant, oil, and low-molecular-weight species. After several precipitation cycles, the precipitated polymer was collected on a 1.5-μ glass fiber filter (934AH, Whatman, Maidstone, England) and rinsed thoroughly with additional acetone. The collected polymer powder solids were allowed to dry at 40°C for 24 h to remove any residual solvent. The resultant powder was then dissolved in nanopure water (< 2 μS/cm) under low-shear conditions and then converted from the sodium salt to the protonated acid form by contact with a strong acid ion-exchange resin (Amberlite IR-120H, Rohm & Haas, Philadelphia, PA). Ion exchange was repeated until a solution pH of 2.2 was achieved and no sodium was detected by sodium-selective electrodes. The solution was then exhaustively dialyzed with a dialysis membrane having a molecular weight cutoff of 12,000–14,000 Da (Cellusep T-3, Membrane Filtration Products, Inc., Seguin, TX) and with nanopure water as the continuous phase. This was repeated until the dialyzate was equal in conductivity to the nanopure water. The polymer solution was then rotovaped under a low pressure and temperature.

Five separate poly(acrylic acid-*co*-sodium acrylate) polyelectrolytes were prepared from the nonionic poly(acrylic acid) parent polymer by the addition of a calculated amount of 1.0*M* sodium hydroxide (Aldrich, Milwaukee, WI) to the parent polymer. The reported α value was based on the equivalents of sodium hydroxide added per acrylic acid monomer and was defined as $\alpha = y/(y + x)$ from the formula $(CH_2CHCOOH)_x$-*co*-$(CH_2CHCOONa)_y$. The effective charge density of the resultant polyelectrolytes was likely lower than the calculated degree of ionization due to counterion condensation.[19]

Molecular weight determination

The weight-average molecular weight (M_w) of the parent homopolymer was determined by batch multi-angle laser light scattering (MALLS) with a Dawn DSP laser photometer and Optilab DSP interferometric refractometer system (Wyatt Technology, Santa Barbara, CA). In the MALLS batch mode, polymer solutions of several concentrations in 1*M* $NaNO_3$ were analyzed to extrapolate light scattering and refractive-index data to very low scattering angles and concentrations. Zimm plots were then constructed with the light scattering data from several polymer concentrations and detection angles to obtain M_w.

Solution rheology

Rheological tests were conducted with a Haake RheoStress-75 controlled stress rheometer (Fisher Scientific, Newington, NH) with a cone and plate geometry with a 60-mm diameter and a 2° angle. The temperature was controlled at a constant value of 25°C with an external circulator. The polymer sample was placed into the geometry, and the solution was allowed to remain unperturbed for 20 min before testing. A thin film of light mineral oil was applied to the solution surface to minimize water evaporation.

Dynamic oscillation studies were conducted first by the subjection of each sample to a stress sweep at a constant angular frequency to ensure that the frequency sweep studies were conducted in the linear viscoelastic region (LVR). A frequency sweep was then conducted over 4 decades of frequencies with a stress value in the LVR. The storage modulus (G') and loss modulus (G'') values were determined from the oscillatory data with the RheoWin 3.2 instrument software according to the following:

$$G' = (\tau_0/\gamma_0)\cos\delta \tag{1}$$

$$G'' = (\tau_0/\gamma_0)\sin\delta \tag{2}$$

where τ_0 is the stress amplitude, γ_0 is the strain amplitude, and δ is the phase angle shift between the stress and strain amplitude. A characteristic modulus [shear modulus (G_0)] was determined from the modulus value at which G' and G'' intersect.[34] The relaxation time (τ) was determined from the reciprocal frequency values at which G' and G'' intersect [critical oscillation frequency (ω_C)]. The zero-shear viscosity (η_0) was determined by the limit of $G''(\omega)/\omega$ as $\omega \rightarrow 0$, where ω is the oscillation frequency.

RESULTS AND DISCUSSION

Polymer characterization

Sample identification and M_w for the six polymers are listed in Table I. M_w of the nonionic parent homopolymer was determined by light scattering; M_w of the charged polymers was then calculated with the weight-average degree of polymerization and the respective monomer formula weights.[35] The sample nomenclature used throughout this report is PAA-0 for the nonionic poly(acrylic acid) parent; the respective poly(acrylic acid -*co*-sodium acrylate) charged polymers for α values of 0.05, 0.10, 0.15, 0.30, and 0.50 are identified as PAA-5, PAA-10, PAA-15, PAA-30, and PAA-50.

TABLE I
Polymer Properties

Identification	α	$M_w \times 10^6$ (g/mol)[a,b]
PAA-0	0	4.90
PAA-5	0.05	4.98
PAA-10	0.10	5.05
PAA-15	0.15	5.13
PAA-30	0.30	5.35
PAA-50	0.50	5.65

[a] The parent poly(acrylic acid) had an M_w value of 4,900,000, as determined by light scattering. The weight-average degree of polymerization (DP_w) was 68,056.

[b] The M_w value of the charged polymers was determined from $M_w = (\alpha DP_w \times 94) + [(1 - \alpha)(DP_w)(72)]$, where 94 was the sodium acrylate monomer weight and 72 was the acrylic acid monomer weight.

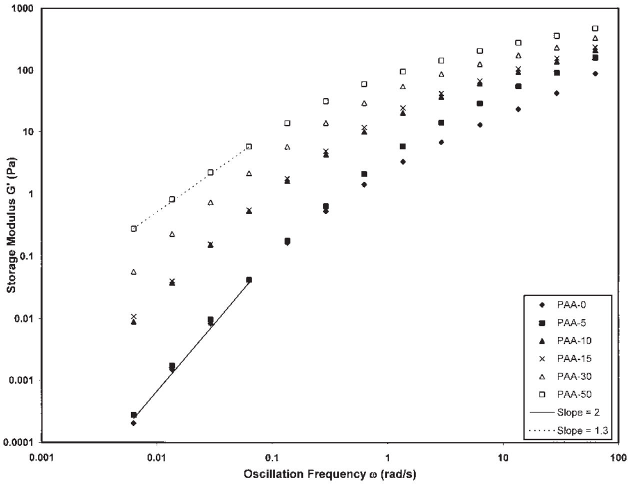

Figure 1 G' as a function of ω for the 4% polymer solutions.

Rheological properties

Typical frequency sweep data are presented in Figures 1 and 2 with 4% polymer concentrations, where the respective G' and G'' values of the six polymers are presented. G' and G'' exhibit a charge density dependence: a higher modulus was observed with increased charge density over the full frequency range.

The data demonstrate that the experimental frequency range of 0.0063–63 rad/s covers the terminal to the plateau region. The materials exhibit liquidlike behavior in the low-frequency terminal region, as $G'' > G'$. The materials also exhibit a frequency dependence in the terminal region that is consistent with rheological models,[36] as $G'' \sim \omega$ for all polymers.

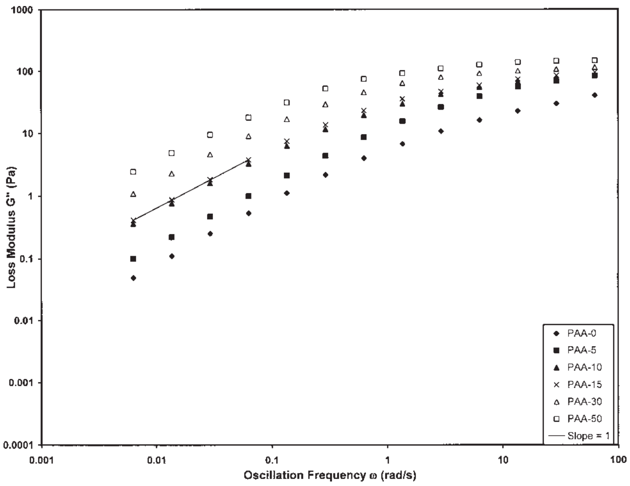

Figure 2 G'' as a function of ω for the 4% polymer solutions.

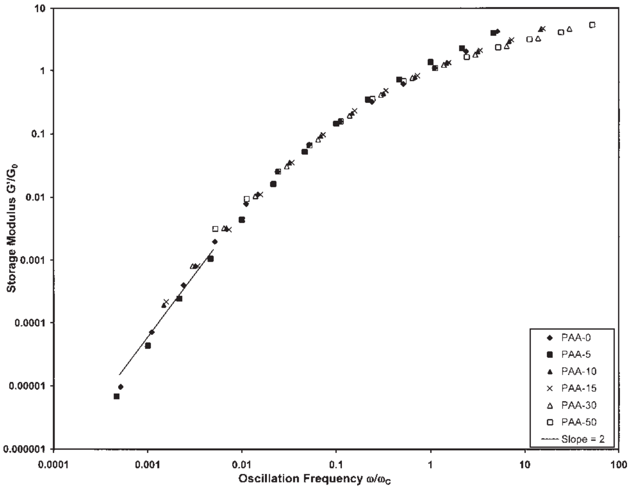

Figure 3 Reduced master curve of G'/G_0 as a function of ω/ω_C for the 4% polymer solutions.

G' for the nonionic polymer PAA-0 and the lowest charge density polymer PAA-5 scales with the frequency as $G' \sim \omega^2$ in this region, which is also consistent with rheological models. The charged polymers with $\alpha > 0.05$ exhibit a frequency dependence in this region but do not exhibit model behavior within the experimental frequency range. The nonmodel behavior in the terminal region is best exemplified by the highest charge density polyelectrolyte PAA-50, which scales with the frequency as $G' \sim \omega^{1.3}$.

With increased frequency, a crossover of the moduli occurs, and a plateau region is observed in which $G' > G''$. Above the crossover frequency, the materials exhibit predominantly elastic behavior. A well-defined plateau region, in which G' is invariant with frequency or a G'' inflection occurs, is not observed. The absence of a definite plateau region has been observed in previous rheological characterizations of polyelectrolytes.[24,27]

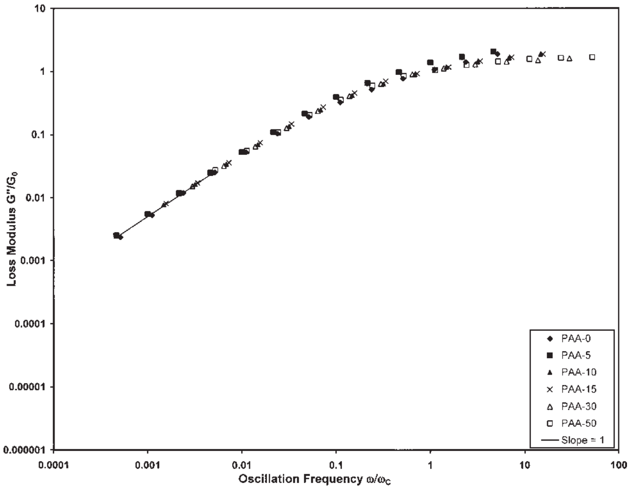

Figure 4 Reduced master curve of G''/G_0 as a function of ω/ω_C for the 4% polymer solutions.

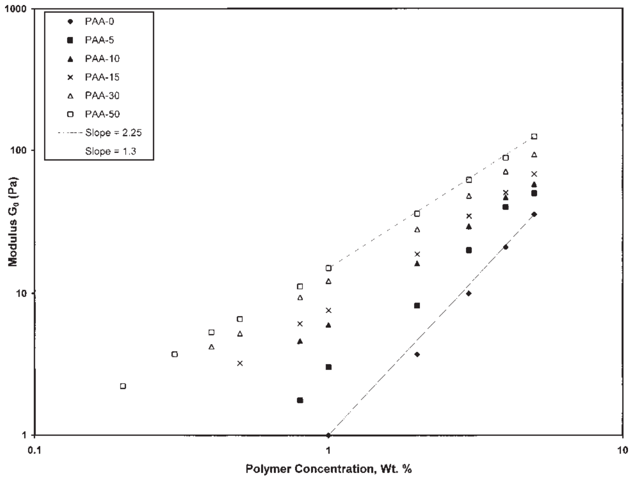

Figure 5 G_0 as a function of concentration for the uncharged and charged polymers.

Figures 3 and 4 illustrate master curves of the 4% concentration modulus curves, where the modulus has been shifted by G'/G_0 or G''/G_0 and the frequency has been shifted by ω/ω_C. It is noted that the dynamic data all superimpose onto one master curve. The master curve was developed classically with time–temperature–superposition for molten polymers[37] and has since been observed for polymer solutions as a function of temperature[38] and concentration.[24] The reduction of dynamic data over a wide frequency range onto a master curve for polyelectrolytes at various charge densities has not been presented previously. This master curve indicates that introducing a charge species onto a nonionic polymer does not affect the fundamental polymer dynamics; it merely shifts to a higher modulus and lower frequency. The master curve data also indicate a similar distribution of relaxation modes for the nonionic and charged polymers and show that additional relaxation times are not produced by the induction of a charge to a nonionic polymer. The nonmodel behavior of G' for the higher charge polymers in the terminal region can be explained by the master curve. The dynamic spectra of the higher charge polymers were shifted to a longer relaxation time and higher modulus and, therefore, did not reach the terminal region within the studied frequency range.

G_0, η_0, and τ as a function of the concentration are presented in Figures 5–7. C_e occurs at a relative viscosity ($\eta_r = \eta/\eta_s$, where η is the polymer solution viscosity and η_s is the solvent viscosity) of approximately 50.[10] The lowest measured η_r value in this study was on the order of 100, above C_e.

As stated in the Experimental section, a stress sweep was conducted to establish a LVR. The pres-

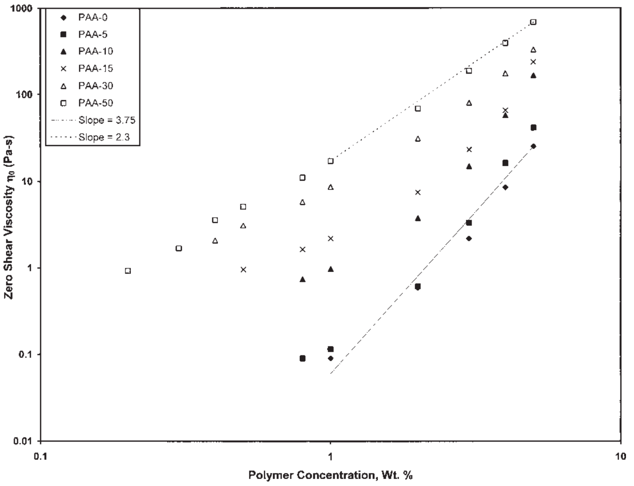

Figure 6 η_0 as a function of concentration for the uncharged and charged polymers.

ence of an LVR was determined to be polymer concentration and charge density dependent. For each polymer species, as the concentration was reduced via serial dilution, a concentration was encountered at which an LVR was not present. As this concentration was encountered for each polymer species, no further rheological experiments were performed with that sample. As illustrated in Figures 5–7, this lower concentration limit of the LVR decreases with increasing polymer charge density. The specific lower concentration limit of the LVR is a function of the minimum instrument torque (1 μNm for this instrument) and geometry. This lower concentration limit of the LVR would be present experimentally for all polymer solutions but would shift according to a different concentration based on the minimum instrument torque and geometry. The LVR of the highest charge polymer PAA-50 is extended nearly a decade in concentration compared to that the nonionic parent PAA-0, from 1 to 0.2%, by the induction of a charge to the nonionic parent.

The rheological properties all exhibit a concentration and charge density dependence, increasing with a higher polymer concentration and polymer charge density. Increased modulus and viscosity values and longer relaxation times are observed for the charged polymers compared to the nonionic parent. Within the charged species, higher modulus and viscosity values and longer relaxation times result with increased charge density. The greatest modulus, viscosity, and relaxation times are observed at 5% concentration and with the highest charge density polymer PAA-50; concurrently, the lowest values are observed with the nonionic parent polymer PAA-0.

The net increase in rheological properties with increased charge was concentration-dependent, with a greater difference between the charged polymers and nonionic parent observed at a lower concentration. As the concentration increases, the difference between the charged polymers and nonionic parent decreases, and the lines move toward convergence. This has been explained by scaling laws,[9] which predict that nonionic polymers will scale with higher exponents than charged polymers at concentrations below a concentration transition (C_D). Above C_D, the electrostatic blobs of the polyelectrolytes entangle, and the behavior of charged polymers is that of a neutral system.[10] As shown by the best-fit line slopes in Figures 5 and 6, the charged polymers clearly scale with lower exponents than the nonionic parent. Large data scatter is observed with the nonionic parent PAA-0 relaxation times, therefore, a best-fit slope was not presented for comparison with the highest charged polymer PAA-50. The large data scatter, also observed with the lowest charged polymer PAA-5, is likely due to instrument inertia effects because of the low polymer viscosity.

The chain expansion of polyelectrolytes with increased charge density has been studied extensively in the dilute region, resulting either in increases in solution viscosity[14–18] or in increases in the relaxation time due to a slowing of the polymer chain dynamics.[22–23] The polymer chain expands with higher charge density because of interchain and intrachain electrostatic repulsion resulting in an increase in the hydrodynamic volume and chain entanglements and a concurrent change in the rheological properties. The increase in the modulus, viscosity, and relaxation time with a higher charge density in aqueous systems has been reported in the concentration regions below C_e.[14–19] The rheological properties of the charged polymers are clearly higher than those of the uncharged polymer in the concentration region above C_e in this study. The effects of longer relaxation times and

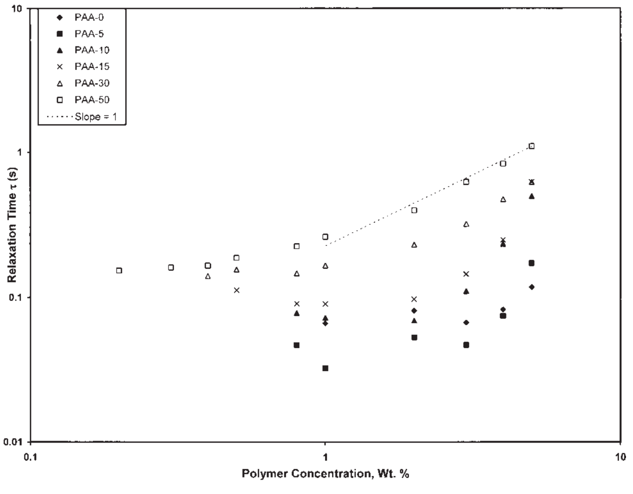

Figure 7 τ as a function of concentration for the uncharged and charged polymers.

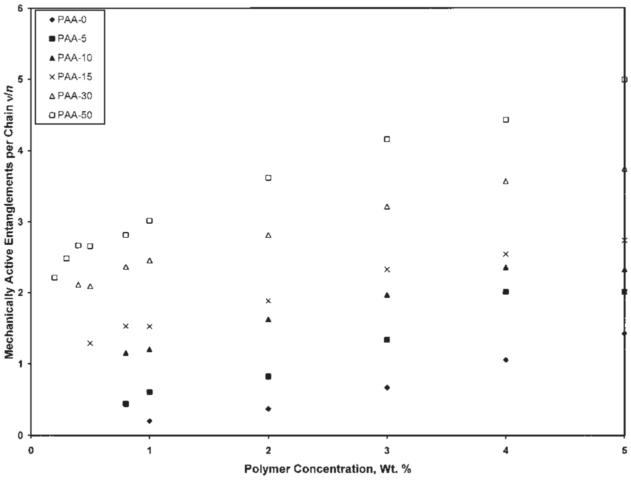

Figure 8 Fraction of mechanically active entanglements (ν) per total number of chains (*n*) as a function of the polymer concentration.

higher moduli with increasing polymer charge are also illustrated in Figures 3 and 4, where the charged polymers have been shifted to superimpose upon the nonionic parent to form a master curve.

The concentration of mechanically active entanglements (ν) can be determined from the theory of rubber elasticity, which was extended to transient networks by Green and Tobolsky:[39]

$$G_0 = \nu kT \tag{3}$$

where G_0 is the modulus, k is the Boltzmann constant, and T is the absolute temperature.

As the modulus increases with the charge density at a constant polymer concentration, eq. (3) indicates that the concentration of mechanically active entanglements is increasing. Thus, the chain expansion that is occurring with a higher charge density is providing an increased number of entanglements and a concurrent increase in the modulus.

Yamaguchi et al.[25] applied the reptation model with consideration of the hydrodynamic interactions between entanglement points along the chain to derive the following:

$$\tau = (\eta_s/kT)(Na/\mathrm{n})^3 \tag{4}$$

$$\eta_0 = \eta_s(N/\mathrm{n})^3 \tag{5}$$

where N is the number of segments along the polymer chain, a is the chain dimension divided by the entanglement points, and n is the number of segments between entanglement points. Although the molar mass of the studied polymers is increasing with charge substitution because of sodium salt formation, N is constant. The only factor in eqs. (4) and (5) that changes with increased charge density is n, which is decreasing to allow for the increase in the values of the rheological properties. Thus, the increase in the modulus, viscosity, and relaxation time with increased charge density can be accounted for by a decrease in segments between entanglement points or, conversely, can be depicted as an increase in entanglements per chain.

Equation (3) can be used to estimate the fraction of mechanically active entanglements (ν) per total number of chains (n) from the following equation:

$$\nu/n = G_0/MN_AkT \tag{6}$$

where M is the molar concentration of the solution and N_A is Avogadro's number. As shown in Figure 8, the total number of mechanically active entanglements per total number of chains increases with the concentration and charge density. The values of ν/n range from less than 1 for the nonionic PAA-0 to 3–5 for the highest charge PAA-50.

As the ν/n values as a function of concentration appear to be parallel (see Fig. 8), the increase in the number of entanglements due solely to introducing a charge to a nonionic polymer is of interest. The number of entanglements due to contributing species is additive,[40] and the entanglements can be differentiated as follows:

$$\nu = \nu_0 + \nu_\alpha \tag{7}$$

where ν is the total entanglement density, ν_0 is the entanglement density of the nonionic parent, and ν_α is the total number of mechanically active entanglements from electrostatic effects.

Figure 9 presents ν_α/n, the charge induced mechanically active entanglements per total number

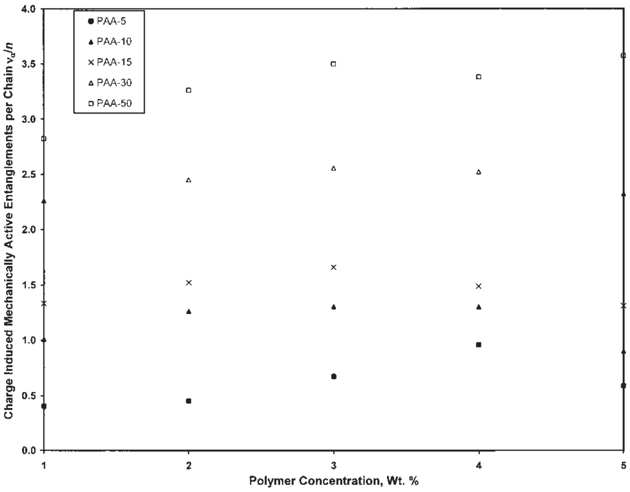

Figure 9 Total number of mechanically active entanglements due to charge effects (ν_α) per total number of chains (n) as a function of the polymer concentration. The calculated values of ν_α/n were invariant with increased concentration.

of chains, as a function of concentration for the five charged polymers, determined according to eq. (7) by the subtraction of ν_0 from ν. The data indicate a higher ν_α/n value with a higher charge density at a constant concentration, whereas ν_α/n is generally independent of the concentration at a constant charge density. Although the total number of entanglements per number of chains (ν/n; as shown in Fig. 8) increases with the concentration, the mechanically active entanglements per total number of chains that occurs because of imposing a charge to the polymer (ν_α/n) does not change with increased concentration. The data suggest that as a charge is induced upon a nonionic polymer at a fixed concentration, the chain will expand because of electrostatic repulsion, resulting in a new conformation and an increase in entanglements. As the concentration increases, this new conformation will not result in any additional entanglements above those that would occur with the uncharged polymer.

Boris and Colby[12] proposed that less flexible, charged polymers would form entanglements less effectively than uncharged polymers. Their work involved the assumed universal number of chains required to form an entanglement (**n**), which could vary with the persistence length of the chain, and as such **n** would be different for charged and uncharged polymers. These data demonstrate different entanglement effects with the uncharged and charged polymers, using the same uncharged parent polymer for comparison with charged polymers, and support their proposal that polyelectrolytes form entanglements less effectively than uncharged polymers. As polyelectrolytes are less flexible than their uncharged counterparts, the rigid conformation of the charged polymers may account for the difference in entanglement development.

CONCLUSIONS

The linear viscoelastic properties of an uncharged polymer and charged polyelectrolytes were characterized in salt-free water. The materials exhibited model viscoelastic behaviors, including a terminal region at a low frequency and a plateau region at a higher frequency. The dynamic data for the nonionic parent and the charged polymers could be reduced to a master curve, demonstrating that as increased levels of charge are imposed upon an uncharged polymer, a similar distribution of relaxation modes is present.

The G_0, τ, and η_0 values derived from the dynamic data exhibited a concentration and charge density dependence. Higher power-law exponents for the rheological properties as a function of concentration were noted for the nonionic polymer compared to the charged derivatives. Higher modulus and viscosity values and longer relaxation times were encountered with increased polymer concentration and charge density. The difference in the rheological properties between the charged and uncharged polymers was greater at lower concentrations, and this phenomena is best explained by scaling laws, which state that uncharged polymers will scale with greater exponents than charged polymers at concentrations below C_D.

The total number of mechanically active entanglements per number of chains was calculated and determined to increase with the concentration or charge density. The total number of mechanically active entanglements per number of chains that occurs because of imposing a charge to the nonionic parent does not change with increased concentration, and this indicates a different entanglement mechanism for charged and uncharged polymers. This supports calculations in which charged polymers form entanglements less effectively than uncharged polymers.

These studies indicate that the rheological properties of a polyelectrolyte can be easily modified by a change in the degree of neutralization. This translates into the ability to meet the specific requirements of an application with the use of a single polymer by the addition of a suitable ionizing agent.

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