same magnitude was found in complexes of poly(4-hydroxystyrene)/PDMA. It is readily seen from Figure 8 that the fraction of bonded carbonyl in a 1:1 PDMA/PHMP blend film is very small. The bond fraction is significant in the annealed blend but has an even larger value in the complex formed from ethyl acetate. These findings are qualitatively in agreement with the conclusions drawn from infrared and T_g measurements (Figure 6).

Conclusion

Mutual precipitation occurs between PDMA and PHMP from acetone, dioxane, and ethyl acetate solutions. The compositions of the complexes can be represented in most cases by simple molar ratios of the components. The glass transition temperatures of the complexes are higher than the T_g value of either component.

PDMA and *p*-methoxy-PHMP also form complexes. Again the compositions of the complexes can be represented by simple molar ratios. The glass transition temperatures of the complexes are also higher than the component T_g values.

When 40% of the hydroxyl groups in PHMP were methylated, mutual precipitation with PDMA still occurred in dioxane. This observation calls for a reexamination of the requirement of a long sequence of uninterrupted bonding sites in a chain as a prerequisite for complexation.

Blend films cast from hydrogen bond breaking solvents have lower T_g values than the corresponding complexes of the same compositions. But the glass transition temperatures of the blends can be raised by thermal treatment during which a concomitant change in the fraction of bonded carbonyl groups in PDMA occurs. A correlation between T_g and the bonded carbonyl group is suggested. It is estimated from the correlation that at least 53% of the carbonyl group are hydrogen bonded in a 1:1 complex of PDMA/PHMP having a T_g of 144 °C.

^{13}C CP/MAS NMR experiments showed a chemical shift of 3 ppm for the bonded carbonyl absorption. The fractions of bonded carbonyl increase in the order blend < annealed blend < complex, in agreement with T_g data.

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Registry No. PDMA, 26793-34-0; (phenol)(formaldehyde) (copolymer), 9003-35-4; (phenol)(*p*-methoxyphenol) (copolymer), 38639-99-5.

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Rotational Relaxation Time and Conformational Transition of Poly(acrylic acid) As Studied by the Conductance Stopped-Flow Technique

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ABSTRACT: The rotational relaxation time (τ_r) of poly(acrylic acid) (HPAA) in aqueous media of various pH values has been determined by the conductance stopped-flow technique. The effective length of a single chain may be evaluated from the relaxation time, τ_r. The conformation of the macroion chain is found to be highly stretched in the presence of added NaOH. The deionized HPAA chain at α (degree of neutralization) = 0 is stretched by the electrostatic intersegment repulsive interaction and the elongated Debye screening length around the macroions. The chain shrinks significantly with decreasing α in the region of negative α.

Introduction

In preceding papers,[1-3] the author has used the conductance stopped-flow (CSF) and spectrophotometric stopped-flow (SP-SF) techniques to obtain information on the rotational relaxation times and rotational diffusion times of anisotropic macroions such as ellipsoidal colloids of tungstic acid, deoxyribonucleic acid, and sodium poly(styrenesulfonate) in aqueous solution. The rotational relaxation processes of the conductance anisotropy were first discussed for ionic detergents,[4,5] polyphosphates,[6-9] graphitic acid colloids,[5,10] deoxyribonucleic acid,[10] and poly(methacrylic acid)[11] by using the Couette apparatus. In the present paper the rotational diffusion times of poly(acrylic acid) (HPAA) are reported in salt-free ("deionized") solution and in the presence of NaOH or HCl, from which the effective rod length has been evaluated.

Anisotropic molecules are expected to orient themselves along stream lines during continuous flow. When the solution flow is stopped, the molecules revert to a random orientation by a Brownian rotation. The translational motion is not significant in the stopped-flow method, since the flow of the solvent molecules have stopped completely by the time the observation is started. The macroions might be deformed by the flow field, but we assume that at the moment the flow is stopped, the macromolecules

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approach their equilibrium conformation quickly, and then the polymers start to rotate. This assumption is sound, because chain dynamics is much faster than the rotational motion of macromolecules.

The CSF technique has been applied to analyze various fast interionic reactions, i.e., micellar equilibria of ionic detergents,[12] conformational transitions of poly(carboxylic acid),[13] macroion complexations with neutral polymers,[13] metal ions,[14] and oppositely charged macroions,[15] enzymatic reactions,[16] metal–cryptand inclusional reactions,[17] and other chemical reactions.[18–20]

Experimental Section

Materials. Poly(acrylic acid) (HPAA) with a molecular weight (MW) of 2 × 10^6 was purchased from Aldrich Chemical Co. (Milwaukee, WI). HPAA of MW = 4 × 10^6 was obtained from Polyscience Inc. (Warrington, PA). The samples were purified seven to 10 times with pure water by using an ultrafiltration cell (Model 202, membrane; Type PM-10, Amicon, Co., Lexington, MA) until the filtrate ceased to show UV absorbance at wavelengths higher than 200 nm. The solution was then stirred with a mixed bed of ion-exchange resins, AG501-X8(D) (Bio-Rad Lab., Richmond, CA), for more than 10 days. The concentration of the resulting stock solution was determined by conductance titration. The water used for the purification and preparation of solutions was obtained from a Milli-Q water system (Type I, Millipore, Ltd., Bedford, MA).

Electric Conductance, pH, and Conductance Stopped-Flow (CSF) Measurements. Electric conductance was measured on a Wayne-Kerr autobalance precision bridge, mark II, at a frequency of 1592 Hz (Model B331, Bognor Regis, Sussex) with a thermostated conductivity cell (25 ± 0.05 °C). The cell was cleaned as completely as possible by a chromic acid wash followed by thorough rinsing with pure water. Potentiometric titrations were measured on a Horiba pH meter (type F8L, Kyoto) in the conductivity cell.

The details of the CSF apparatus have been described previously.[12,20] The sample solution from the mixer, which was made of Teflon and was a four-jet type, flowed between platinum plates. The platinum plate electrodes (2 mm × 10 mm) were fixed on opposite walls (2 mm apart) inside the observation cell made of epoxy resins. For each run, about 0.2 cm^3 of solution was required. A value of 1.30 cm^{-1} was obtained for the cell constant. An ac current of 50 kHz was applied to the Wien bridge. The applied voltage across the cell was kept at 2 V (root mean square). The time change of the solution conductance was amplified in two stages and monitored by a memoriscope and/or digital memory and an X–Y recorder after rectification. The dead time was 1 ms.

Results and Discussion

The conductance stopped-flow (CSF) method for the determination of the conformation of a polyelectrolyte is based on the phenomenon that the electrical conductivity of a solution of charged anisotropic molecules is also anisotropic if flow induces a preferred molecular orientation.[6,21,22] With charged anisotropic molecules an increase in conductivity occurs in the direction of flow and a decrease occurs perpendicular to the flow.[8] After the flow is stopped (at time $t = 0$) in a CSF measurement, the induced orientation decreases until a random distribution is reestablished. Consequently the induced anisotropy of the electrical conductivity decreases to zero. This change in conductance provides a convenient means of detecting rotational movement of anisotropic polyelectrolytes. The rotational relaxation depends on the dimensions of the molecules and can be described by a relaxation function:

$$\kappa - \kappa^+ = (\kappa_0 - \kappa^+) \exp(-t/\tau_r) \qquad (1)$$

Here, the relaxation time constant, τ_r, can be described by

$$\tau_r = 1/(6D_r) \qquad (2)$$

where κ_0 is the electrical conductivity at the initial state of orientation, caused by the flow in the observation cell. κ^+ is the conductivity at $t = \infty$, and κ is the conductance at time t. τ_r is the rotational relaxation time. For monodisperse anisotropic molecules of uniform size in sufficiently dilute systems, eq 1 and 2 hold.[23] In the case of nonuniform molecular sizes the relaxation is a superposition of processes of eq 1 with different D_r values.[10] From single-exponential curves of conductance values, τ is easily obtainable. We believe that the electric field applied, i.e., $2V$ (rms) is not strong enough to influence the rotational relaxation.

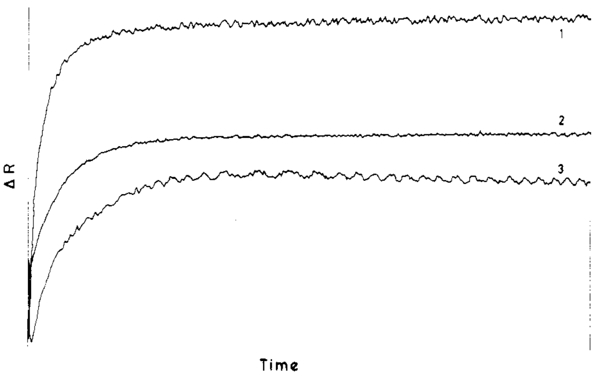

Figure 1. Typical traces of CSF relaxation measurements for HPAA + NaOH (1), HPAA + H_2O (2), and HPAA + HCl (3) mixtures at 25 °C. [HPAA] = 5.66 × 10^{-4} M after mixing; (1) $\alpha = 0.177$ after mixing, full scale time = 50 s; (2) $\alpha = 0$, 10 s; (3) $\alpha = -0.707$, 0.5 s.

Typical traces of the relaxation effects in the CSF measurements of HPAA + NaOH ($\alpha = 0.177$ after mixing), HPAA + H_2O ($\alpha = 0$), and HPAA + HCl ($\alpha = -0.707$) mixtures are shown in Figure 1. Usually, a simple and strong relaxation trace appeared. However, in many cases very slow and small traces were observed besides the fast relaxations. Since the fast and slow relaxation times differ more than 10-fold in magnitude, the data are easily deconvoluted into two exponentials to obtain reliable relaxation times. The main, fast relaxations are the rotational relaxations. The slow relaxations are ascribed to concentration fluctuations. When two identical solutions were mixed, the relaxation traces obtained were the same as those shown in Figure 1. The absolute conductance values, which are not necessary for the relaxation analysis, were not known in our experiments in order to get the sensitivity. The relaxation times (τ_r), which were obtained from the first-order plots, decreased sharply as α decreased.

The τ_r values obtained for HPAA are shown in Figure 2 as a function of α, in which negative values of α are in acid solution. Clearly, τ_r first increased gradually and then sharply as α increased. This sharp increase in τ_r corresponds to the conformational transition of a HPAA molecule from a coil to a stretched rod.

The effective length (L) of rodlike HPAA molecules of the neutralized state can be estimated from the τ_r values assuming a simple rod model:[10]

$$L = (48kT\tau_r/\pi\eta_0)^{1/3} \qquad (3)$$

where k and T are the Boltzmann constant and the absolute temperature of the solution and η_0 is the viscosity of the solvent. The results are shown in Figure 3 for HPAA samples of MW = 4 × 10^6 and 2 × 10^6. At $\alpha < -0.2$, L is ca. 1 μm, shorter than the contour lengths (13.9 and 6.94 μm for MW = 4 × 10^6 and 2 × 10^6, respectively) calculated from the monomer length (0.25 nm) and the degrees of polymerization. This means that the conformation of HPAA is coillike or expanded coillike when the acid groups are not ionized. However, for HPAA at high degree of

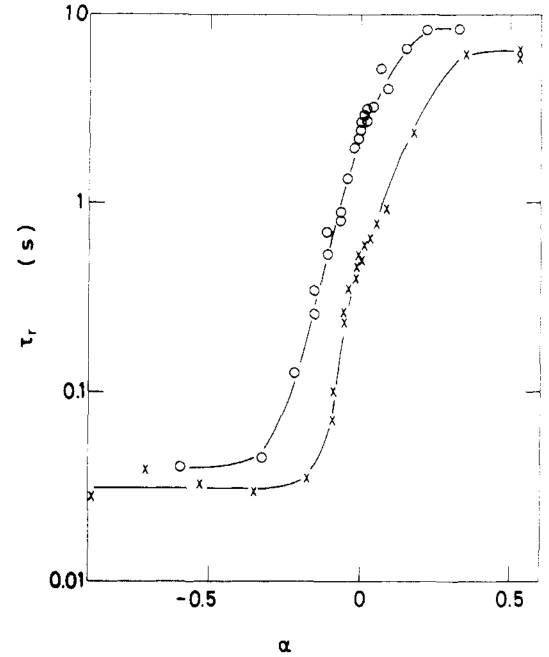

Figure 2. Rotational relaxation times of HPAA by CSF measurements at 25 °C: (○) MW = 4 × 10^6, [HPAA] = 4.60 × 10^{-4} M after mixing; (×) MW = 2 × 10^6, [HPAA] = 5.66 × 10^{-4} M after mixing.

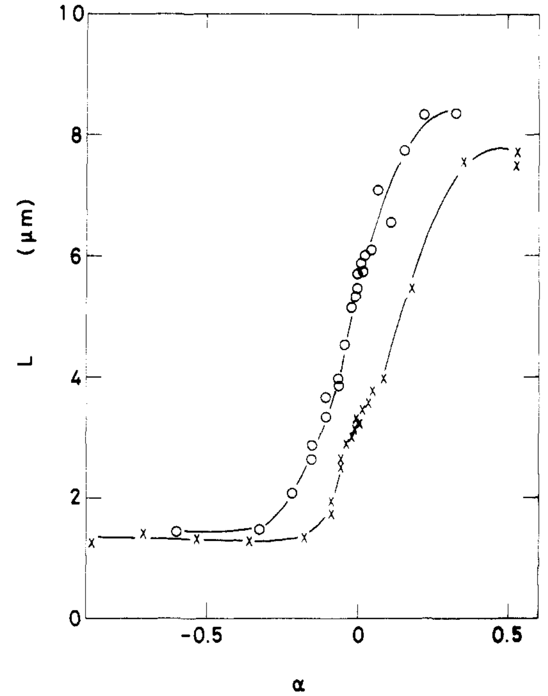

Figure 3. Rod length of HPAA estimated from the CSF measurements at 25 °C: (○) MW = 4 × 10^6; (×) 2 × 10^6.

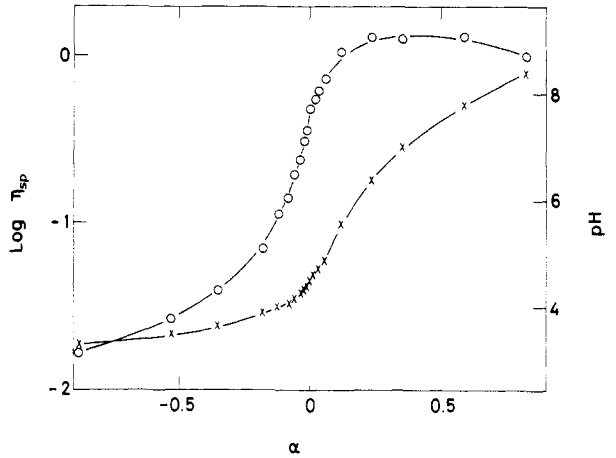

Figure 4. Specific viscosities and pHs of HPAA solution at 25 °C. MW = 2 × 10^6; [HPAA] = 5.66 × 10^{-4} M after mixing; (○) η_{sp}, (×) pH.

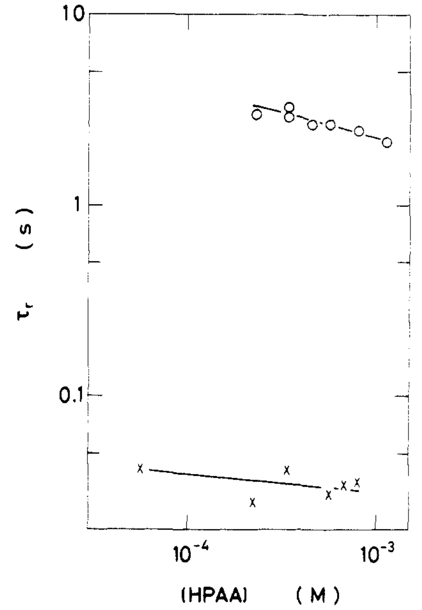

Figure 5. Rotational relaxation times of HPAA by the CSF measurements at 25 °C: MW = 2 × 10^6; (○) α = 0.177; (×) −0.707.

neutralization, L is close to the contour lengths, especially for HPAA of MW = 2 × 10^6. This strongly suggests that the conformation is rodlike.

The conformation of HPAA can also be studied by measurements of viscosity. Figure 4 shows plots of log η_{sp} (η_{sp}: specific viscosity, $\eta_{sp} = \eta/\eta_0 - 1$, where η and η_0 are viscosities of the solution and the solvent) and pH values against α for HPAA of MW = 2 × 10^6. The specific viscosity increased 100-fold with increasing α, which means that the conformation of HPAA transforms from coillike at negative α to a stretched rod at positive α.

It should be noted here that the conformation of HPAA at $\alpha = 0$ is rodlike, which is clearly seen in Figures 2–4, especially for the sample of MW = 2 × 10^6. Our samples of HPAA at $\alpha = 0$ were deionized as completely as possible by treating with mixed beds of cation- and anion-exchange resins for more than 10 days. For a completely deionized solution, the thickness of the electrical double layer of H^+ ions around the macromolecules (Debye screening length) should be large. The conformation may be extended by the electrostatic repulsion between a few ionized segments of a HPAA molecule.

The Debye length, D_1, in the absence of foreign salt is given by $(4\pi Bn)^{-1/2}$. Where B is the Bjerrum length (0.719 nm at 25 °C in water) given by $e^2/\epsilon kT$, where e is the electronic charge, ϵ is the dielectric constant of the solvent, and n is the concentration (cm^{-3}) of the counterions (H^+ ions). The concentration of the protons is roughly estimated to be ca. 3 × 10^{-5} M from the pH at $\alpha = 0$ in Figure 4. Thus, the Debye length at $\alpha = 0$ is estimated to be ca. 80 nm for HPAA of MW = 2 × 10^6. This value of D_1 is longer than the monomer length (0.25 nm). Any ionized groups on the polymer are unshielded by ions in the double layer so that the repulsion between them extends the chain. The importance of this Debye length has often been pointed out for the solution properties of deionized colloidal particles and polyelectrolytes, such as ordered suspension structures,[24-28] the conformation of flexible polyelectrolytes,[29-31] and dynamic properties of macroions.[32,33]

Figure 5 shows the concentration dependencies of the rotational relaxation times of HPAA. The τ_r's decreased slightly (especially for HPAA of $\alpha = 0.177$) as the polymer concentration increased. This means that the conformation of HPAA begins to shrink with increasing concentration, which is reasonable if we take into account the increased effect of electrostatic shielding on the intramacroion repulsion with polymer concentration.

It should be emphasized here that the relaxation times observed by the CSF method do not always give only the fast rotational relaxation times (τ_r). The slower relaxations, which are usually over 10 times larger, are often observed, especially for low molecular weight HPAA samples. The slow process is identified tentatively as the fluctuation of local assemblies of macroions in solution. Regrettably, the values of relaxation times reported previously for HPAA solution[13] were slow steps, not the fast rotational ones, because the previous relaxation time data were too large compared with those expected from the theory, eq 3.

In conclusion, the rotational relaxation times of poly(acrylic acid) are observed by the conductance stopped-flow technique. The conformation of the macroion is found to be highly stretched at high degrees of neutralization (α). The chain shrinks with decreasing α. The highly deionized HPAA molecules at $\alpha = 0$ are stretched.

Registry No. HPAA, 9003-01-4.

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Dielectric and Mechanical Relaxations in Cycloaliphatic Polyformal Networks

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ABSTRACT: Poly(*cis/trans*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) (PCDO) chains, obtained by condensation of the cis, cis/trans (28/72), and cis/trans (10/90) isomers of 1,4-cyclohexanedimethanol with formaldehyde, were cross-linked with an aromtic triisocyanate. The networks exhibit a well-developed α process associated to the glass–rubber transition, whose location is relatively independent of the substitution (eq–ax or eq–eq) of the cyclohexane ring. The cis isomer presents a mechanical subglass absorption, labeled β, centered at –60 °C at 1 Hz and a weak γ relaxation. The fact that a similar β process also appears at the same temperature and frequency in poly(*cis*-1,4-cyclohexanedimethanol sebacate) (*cis*-PCDS) suggests that the relaxation is caused by molecular motions associated to the glycol residue. The dielectric relaxation spectra exhibit, in addition to the glass–rubber relaxation, two subglass peaks whose maxima are located at –30 (β) and –74 °C (γ), at 0.5 kHz. Since the activation energy of the dielectric β peak is 18.1 kcal mol^{-1}, the absorption would be centered at ca. -65 °C, at 1 Hz, almost at the same temperature as the mechanical one, suggesting that similar molecular motions produce both relaxations. The mechanical subglass region in the relaxation spectra of *cis/trans*(10/90)-PCDO networks resembles that of poly(*trans*-1,4-cyclohexanedimethanol sebacate) (*trans*-PCDS) in that a broad and diffuse relaxation, extending in a temperature span of more than 100 °C, appears. An inspection of this region in the *cis/trans*(28/72)-PCDO networks indicates that complex molecular motions involving more than a single structural unit are responsible for the mechanical β relaxation. Two peaks centered at –30 (β_1) and –60 °C (β_2) are detected in the subglass dielectric relaxation of the networks with the highest *trans*-cyclohexylene units content. Finally, the free volume interpretation gives a good account of the mechanical and dielectric relaxation processes that take place in the glass–rubber transition.

Introduction

The study of the secondary relaxations in polymers containing six-membered saturated rings bonded to the chains has been the subject of numerous investigations in the past.[1-9] As far as the subglass relaxations are concerned, polymers with cyclohexyl rings anchored to side groups show a prominent relaxation process at a frequency around 1 Hz at temperatures in the vicinity of –80 °C,

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