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Registry No. PVAc (homopolymer), 9003-20-7.

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Ultrasonic Relaxation Study of Aqueous Solutions of Poly(acrylic acid)

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ABSTRACT: In order to investigate ultrasonic relaxation processes due to segmental motions in aqueous solutions of poly(acrylic acid) (PAA), ultrasonic absorption measurements were carried out as functions of temperature, concentration of polymeric solute, molecular weight of polymers, and degree of neutralization in the frequency range from 0.8 to 180 MHz. The ultrasonic relaxation spectra show two relaxation processes. The relaxation frequencies are located at about 1.4 MHz and about 20 MHz, respectively, for the majority of solutions investigated. Both processes are ascribed to segmental motions of polymer chains. Relaxation processes due to the protolytic reaction of COOH groups in PAA are observed in the ultrasonic relaxation spectra of aqueous solutions of PAA maintained at pH 2–3. Kinetic parameters and magnitudes of volume changes associated with the protolytic reaction are roughly estimated. Site binding between polyion and counterion, Na^+, gives only a slight contribution to the total ultrasonic relaxation spectrum of solutions of sodium polyacrylate compared to segmental motions. Viscous loss also contributes little to the total ultrasonic absorption in solutions of PAA.

The dynamic properties of polyelectrolytes in aqueous solutions have been investigated by a variety of methods, such as NMR,[1-3] dynamic shear viscosity,[4] and dielectric dispersion.[5-8] The ultrasonic relaxation method is also a powerful technique for investigating the dynamics of molecular processes such as conformational changes of polymer chains, protolytic reactions, and ion association processes in the time range of 10^{-5}–10^{-10} s. A number of ultrasonic relaxation studies have been carried out for nonionic polymer solutions by many investigators and the results are summarized in reviews.[9,10]

Ultrasonic studies of polyelectrolytes in aqueous solutions have also been carried out by a few investigators. These studies are well summarized by Zana.[11,12] It was reported in one review[11] that there are two relaxation mechanisms associated with site binding between a polyion and counterions and with hydrogen-bond formation between COOH and COO^- [13,14] in the ultrasonic relaxation phenomena of aqueous solutions of poly(acrylic acid). Contributions of segmental motions and protolytic reaction to ultrasonic absorption of polyelectrolytes are neglected in the review.[11] However, it has been shown[9,10] that segmental motions give an important contribution to ultrasonic absorption in polymer solutions in the megahertz frequency range. Moreover, protolytic reaction contributes to ultrasonic absorption in monomeric carboxylic acids.[15,16] Therefore, the protolytic reaction should also be responsible for ultrasonic relaxation in aqueous solutions of poly(acrylic acid). We speculate that the frequency ranges were not wide enough and the accuracy of the data below 10 MHz was not sufficient in previous work[13,14] to disclose the contributions mentioned above.

In this work, accurate measurements of ultrasonic absorption of aqueous solutions of poly(acrylic acid) have been carried out over a wider frequency range and at lower concentrations than in earlier work to disclose several contributions to ultrasonic absorption such as segmental motions, protolytic reaction, and site binding between a polyion and counterions. Ultrasonic relaxation spectra of aqueous solutions of poly(acrylic acid) were obtained as functions of temperature, concentration, molecular weight, and degree of neutralization of the samples, together with the spectra of acrylic acid and sodium acrylate. Ultrasonic relaxation spectra in aqueous solutions of sodium poly-

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acrylate were measured under the presence of sodium chloride to study the added salt effect. Ultrasonic absorption in aqueous solutions of tetra-*n*-butylammonium polyacrylate was measured as a function of frequency to disclose the contribution of the site binding effect.

Experimental Section

Materials. Three samples of poly(acrylic acid) (hereafter abbreviated as PAA) with different molecular weights were used. Two of them were commercially supplied from Polyscience Inc. and the other having the highest molecular weight was prepared by ion exchange of sodium polyacrylate (hereafter abbreviated as NaPA) commercially supplied from Nakarai Chemicals Co. Ltd. The molecular weights, determined by viscosity measurement in 0.1 mol·L^{-1} NaCl,[17] were 9 × 10^4, 2.5 × 10^5, and 1.5 × 10^6, respectively. The samples of acrylic acid, sodium acrylate, and tetra-*n*-butylammonium hydroxide were also supplied from Nakarai Chemicals and they were used without further purification.

All aqueous solutions investigated were prepared by using water deionized after distillation.

Ultrasonic Absorption Measurements. The ultrasonic absorption coefficient α (Np·cm^{-1}) was measured by using a standard pulse apparatus in the frequency range from 10 to 180 MHz. In the low-frequency range, 0.8–8 MHz, α was measured by a cylindrical resonator method. A more detailed description of the apparatus and experimental procedures was published elsewhere.[18] Deionized water was used as a reference material for the resonator method.

The concentration range of the ultrasonic absorption measurement was from 0.030 to 0.150 monomer mol·L^{-1}. This is about 1 order lower than that in two works reported earlier.[13,14]

Sound Velocity and Density Measurements. The ultrasonic velocity was mainly measured with a cylindrical resonator and occasionally with an ultrasonic interferometer working at a fixed frequency of 4.000 MHz. Density was mainly measured with an Ostwald-type pycnometer of 20-cm^3 capacity and also with a vibrational type densimeter, DMA-02C, manufactured by Anton Paar Co. Ltd., to determine the apparent molar volume in aqueous solution of tetra-*n*-butylammonium polyacrylate (hereafter abbreviated as TBAPA).

The degree of neutralization of solutions was determined by titration with standard NaOH solutions. The pH values of the solutions were measured with a type F7 pH meter manufactured by Horiba Inc.

Data Analysis

The ultrasonic absorption data were analyzed according to the following equation assuming that the results indicate either one or two discrete ultrasonic relaxation processes:

$$\frac{\alpha}{f^2} = \sum_{i=1}^{2} \frac{A_i}{1 + (f/f_{ri})^2} + B \qquad (1)$$

where f represents the measured frequency, f_{ri} the relaxation frequency, A_i the relaxation amplitude, and B the contribution to sound absorption from any other processes that may be occurring at higher frequencies beyond our frequency range. In the case of double relaxation processes, suffixes 1 and 2 refer to the low- and high-frequency processes, respectively.

Equation 1 was fitted by computer to experimental data in the frequency range investigated and best values of the parameters, A_i, f_{ri}, and B, were obtained by assuming either single or double relaxation phenomena were present. A nonlinear least mean squares fit was carried out by using the complete grid search technique. The initial values of the relaxation parameters were chosen by inspection of ultrasonic absorption spectra and then the quantity

$$Q = \sum_{i=1}^{n} \left| \frac{(\alpha/f^2)_{\text{obsd}} - (\alpha/f^2)_{\text{calcd}}}{(\alpha/f^2)_{\text{obsd}}} \right|$$

was minimized. In this equation n represents the number of data points, and suffixes obsd and calcd refer to the observed and calculated values of α/f^2, respectively. An equation of double relaxation processes was required to successfully fit the sound absorption data in all polymer solutions investigated. In most cases the error of fit, defined as $100Q/n$, was less than 2.0 and in the extreme case rose to 2.8.

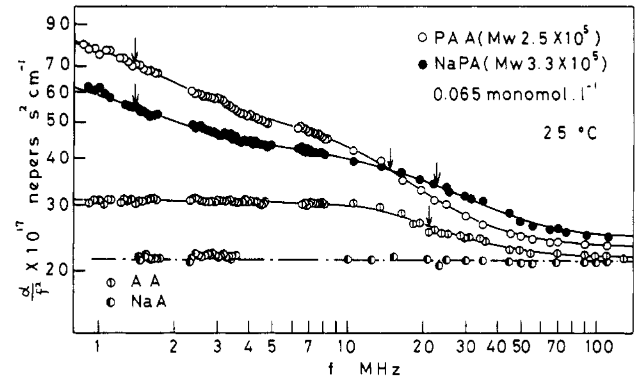

Figure 1. Ultrasonic absorption at 25 °C as a function of frequency for aqueous solutions of PAA (○), NaPA (●), acrylic acid (◐), and sodium acrylate (◐). In Figures 1, 2, and 5, the solid lines represent the calculated relaxation spectra from eq 1 and arrows show the location of relaxation frequencies.

Results

Ultrasonic velocities in aqueous solutions of PAA and NaPA observed in the present work were in good agreement with those reported by Roy-Chowdhury et al.[19]

Figure 1 shows typical results of the ultrasonic absorption measurements for aqueous solutions of PAA and NaPA together with those of acrylic acid and sodium acrylate carried out for comparison. The data are expressed as α/f^2 vs. logarithmic frequency, log f. The solid lines in the figure represent the calculated ultrasonic relaxation spectra from eq 1 and arrows show the location of the relaxation frequencies. All measurements are carried out at the same concentration, 0.065 monomer mol·L^{-1}.

Figure 1 clearly shows that no relaxation is observed in an aqueous solution of sodium acrylate but the relaxation spectrum of acrylic acid can be expressed by a single relaxation equation ($i = 1$ in eq 1). The relaxation frequency, f_r, is located at 22 MHz and the relaxation parameters A and B and sound velocity are 10.0 × 10^{-17} and 21.6 × 10^{-17} Np·s^2·cm^{-1} and 1499 m·s^{-1}, respectively.

Ultrasonic relaxation spectra of aqueous solutions of PAA and NaPA, however, are quite different from those of the corresponding monomer solutions; that is, an equation of double relaxation processes is required to successfully fit the ultrasonic absorption data of PAA and NaPA in the frequency range investigated. Two relaxation frequencies are located at about 1 and 15–23 MHz, respectively. The ultrasonic absorption of PAA is larger than that of NaPA, especially in the frequency range below 10 MHz. All other ultrasonic relaxation spectra of polymer solutions investigated have been well expressed by the equation of double relaxation processes.

Effects of Molecular Weight and Concentration. Figure 2 shows molecular weight dependence of ultrasonic absorption in solutions of PAA and NaPA. As is seen in Figure 2, both ultrasonic relaxation spectra of PAA and NaPA do not depend on molecular weight in the range of molecular weight investigated.

Figure 3 shows the plots of relaxation frequencies and relaxation strengths, r_i, vs. concentration of polymeric solute, C, where r_i is defined as $r_i = (2/\pi)\mu_{\text{max}i}$ and $\mu_{\text{max}i}$ is the absorption maximum per wavelength defined as $\mu_{\text{max}i}$

Table I
Concentration and Molecular Weight Dependences of Ultrasonic Relaxation Parameters[a] and Sound Velocity Data[a] for Aqueous Solutions of PAA and NaPA at 25 °C

$10^{-4}M_w$	C, mon mol·L^{-1}	$10^{17}A_1$, Np·s^2·cm^{-1}	f_{r1}, MHz	$10^{17}A_2$, Np·s^2·cm^{-1}	f_{r2}, MHz	$10^{17}B$, Np·s^2·cm^{-1}	u, m·s^{-1}	$10^5\mu_{max1}$	$10^4\mu_{max2}$	
					PAA					
150	0.065	40.3	1.4	28.0	15	22.7	1497	4.23	3.14	
	0.073	47.8	1.4	28.0	15	22.7	1498	5.01	3.14	
25	0.065	40.3	1.4	28.0	15	22.7	1498	4.22	3.14	
9	0.065	40.3	1.4	28.0	15	22.7	1498	4.22	3.14	
					NaPA					
200	200	0.053	24.2	1.2	14.5	23	24.4	1500	2.18	2.50
	0.065	25.2	1.4	17.7	23	24.4	1501	2.65	3.05	
	0.073	26.2	1.4	19.0	23	24.3	1501	2.75	3.28	
33	33	0.030	23.3[b]	1.4	11.0	23	22.0	1490	2.43	1.88
	0.065	25.2	1.4	17.7	23	24.4	1501	2.65	3.05	
	0.100	37.3	1.4	25.0	23	26.5	1504	3.93	4.32	
	0.150	*c*	*c*	33.0	23	28.7	1508		5.72	

[a] Uncertainties in the relaxation parameters and sound velocity data presented in this report are empirically estimated as follows: A_1, ±2.0 × 10^{-17} Np·s^2·cm^{-1}; f_{r1}, ±0.2 MHz; A_2, ±1.0 × 10^{-17} Np·s^2·cm^{-1}; f_{r2}, ±1.0 MHz; B, ±1.0 × 10^{-17} Np·s^2·cm^{-1}; u, ±0.5 m·s^{-1}. [b] Unusual error was involved (ca. (±7–8) × 10^{-17} Np·s^2·cm^{-1}). [c] Ultrasonic absorption could not be measured in the frequency range 0.8–8 MHz because of too high viscosity of solution.

Table II
Temperature Dependence of Relaxation Parameters for Aqueous Solutions of NaPA[a]

temp, °C	$10^{17}A_1$, Np·s^2·cm^{-1}	f_{r1}, MHz	$10^{17}A_2$, Np·s^2·cm^{-1}	f_{r2}, MHz	$10^{17}B$, Np·s^2·cm^{-1}	u, m·s^{-1}	$10^5\mu_{max1}$	$10^4\mu_{max2}$
15	38.9	1.0	18.0	23	32.1	1470	2.86	3.04
25	24.2	1.2	14.5	23	24.3	1500	2.18	2.50
35	15.8	1.4	12.2	24	18.3	1523	1.68	2.23

[a] M_w = 2.0 × 10^6, C = 0.053 monomer mol·L^{-1}.

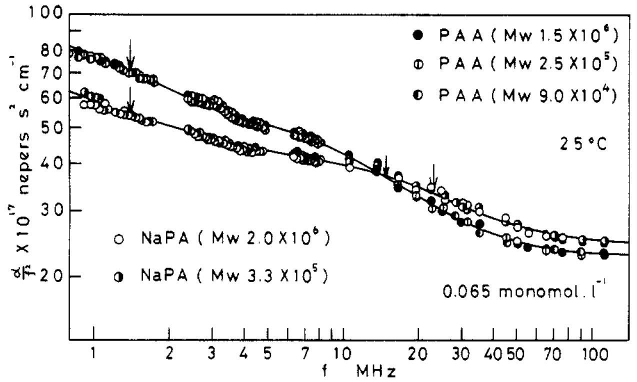

Figure 2. Ultrasonic absorption as a function of frequency for aqueous solutions of PAA and NaPA with various molecular weights: (●) PAA M_w 1.5 × 10^6; (◐) PAA M_w 2.5 × 10^5; (◐) PAA M_w 9.0 × 10^4; (○) NaPA M_w 2.0 × 10^6; (◑) NaPA M_w 3.3 × 10^5.

= $A_i f_{ri} u/2$. Here u represents ultrasonic velocity. Ultrasonic relaxation strengths of solutions of PAA and NaPA increase with increasing concentrations of the polymeric solutes but relaxation frequencies are independent of the concentrations.

Table I summarizes the molecular weight and concentration dependences of relaxation parameters for aqueous solutions of PAA and NaPA.

Effect of Temperature. The temperature dependence of relaxation parameters is summarized in Table II. The absorption maxima per wavelength μ_{max1} and μ_{max2} decrease with increasing temperature. The relaxation frequency, f_{r2}, is almost independent of temperature but f_{r1} trends to shift to the high-frequency side with increasing temperature.

Effect of Degree of Neutralization. Table III gives the relaxation parameters for aqueous solutions of PAA with different degrees of neutralization. In order to investigate the protolytic process in PAA, measurements of ultrasonic absorption were also carried out in aqueous solutions maintained at pH 2.0 and 3.0 with HCl. The relaxation parameters obtained are listed in Table IV.

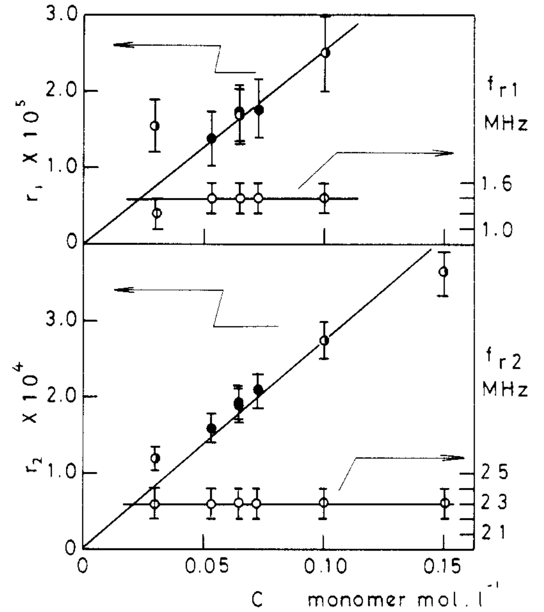

Figure 3. Ultrasonic relaxation strengths r_i (i = 1, 2) and frequencies f_{ri} (i = 1, 2) as a function of concentration of polymeric solute for aqueous solutions of NaPA: (●) and (○) M_w 2.0 × 10^6; (◑ and ◐) M_w 3.3 × 10^5.

In Figure 4 relaxation frequencies f_{ri} and strengths r_i are plotted as a function of pH and/or degree of neutralization, θ, where θ is defined as $\theta = C_{Na^+}/C$. In this definition C_{Na^+} represents the concentrations of Na$^+$. In the low pH region, f_{ri} do not markedly vary with degree of neutralization or pH, but r_i show a maximum near $\theta \approx 0$. The relaxation strength of an aqueous solution of acrylic acid is also plotted in Figure 4 for comparison.

Table III
Relaxation Parameters for Aqueous Solutions of PAA with Different Degrees of Neutralization and a Solution of TBAPA at 25 °C[a]

neut	pH	$10^{17}A_1$, Np·s^2·cm^{-1}	f_{r1}, MHz	$10^{17}A_2$, Np·s^2·cm^{-1}	f_{r2}, MHz	$10^{17}B$, Np·s^2·cm^{-1}	u, m·s^{-1}	$10^5\mu_{max1}$	$10^4\mu_{max2}$
0	2.8	40.3	1.4	28.0	15	22.7	1498	4.22	3.14
0.1	4.0	32.5	1.2	14.8	18	22.7	1499	2.92	1.99
0.2	4.8	32.2	0.8	15.5	18	23.3	1499	1.93	2.09
0.3	5.3	29.0	0.9	18.4	18	23.5	1499	1.95	2.48
0.4	5.9	27.2	1.2	21.2	18	23.6	1499	2.45	2.86
0.6	6.6	25.9	1.2	24.5	19	23.6	1500	2.33	3.49
0.8	7.6	26.2	1.4	23.6	20	24.2	1500	2.75	3.54
0.95	9.0	28.0	1.5	20.0	21	24.0	1501	3.15	3.15
1.0	11.3	25.2	1.4	17.7	23	24.4	1501	2.65	3.05
TBAPA		28.0	1.4	10.0	21	24.6	1514	2.97	1.59

[a] M_w = 2.5 × 10^5, C = 0.065 monomer mol·L^{-1}.

Table IV
Effects of Added Acid and Salt on Relaxation Parameters for Aqueous Solutions of PAA and NaPA[a]

system	pH	$10^{17}A_1$, Np·s^2·cm^{-1}	f_{r1}, MHz	$10^{17}A_2$, Np·s^2·cm^{-1}	f_{r2}, MHz	$10^{17}B$, Np·s^2·cm^{-1}	u, m·s^{-1}	$10^5\mu_{max1}$	$10^4\mu_{max2}$
PAA + 0.001 M HCl	3.0	39.7	1.4	24.3	15	22.5	1498	4.16	2.73
PAA + 0.01 M HCl	2.0	26.7	1.4	17.8	16	23.0	1498	2.80	2.13
NaPA	11.3	25.2	1.4	17.7	23	24.4	1501	2.65	3.05
NaPA + 0.129 M NaCl		34.4	1.4	19.7	18	25.0	1509	3.58	2.68
NaPA + 0.323 M NaCl		65.8	1.4	25.7	14	25.0	1521	6.91	2.74
NaPA + 0.646 M NaCl		77.0	1.4	29.7	12	25.4	1541	8.48	2.75
NaPA + 0.969 M NaCl		118	1.4	29.7	11	24.5	1561	12.5	2.55

[a] M_w (PAA) = 2.5 × 10^5, M_w(NaPA) = 3.3 × 10^6, C = 0.065 monomer mol·L^{-1}.

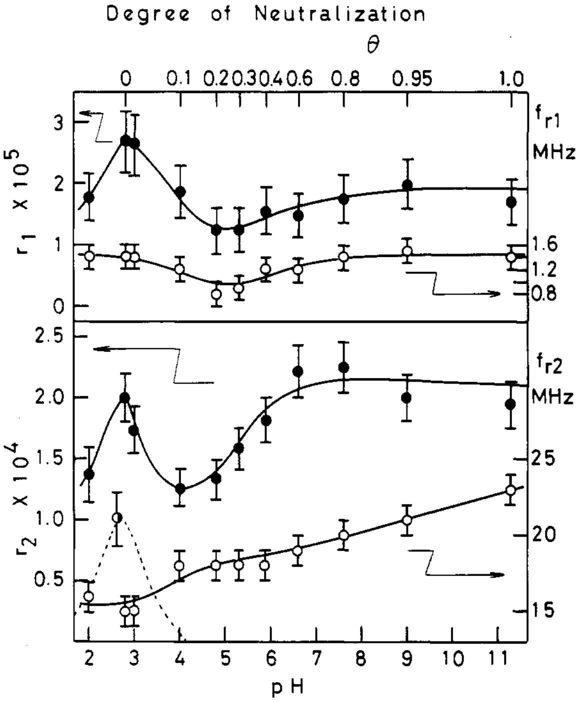

Figure 4. Ultrasonic relaxation strengths r_i (i = 1, 2) (●) and relaxation frequencies f_{ri} (i = 1, 2) (○) at 25 °C as a function of degree of neutralization or pH for aqueous solutions of PAA (M_w 2.5 × 10^5). ◑ represents the relaxation strength for an aqueous solution of acrylic acid and the dotted line represents the calculated relaxation strength from eq 4.

The ultrasonic absorption was measured in an aqueous solution of TBAPA, which was prepared by neutralization of an aqueous solution of PAA with tetra-*n*-butylammonium hydroxide. The relaxation spectrum of an aqueous solution of TBAPA is shown in Figure 8 and relaxation parameters are listed in Table III.

Effect of Added Salt. Figure 5 shows the relaxation spectra in aqueous solutions of NaPA in the presence of added sodium chloride. The relaxation parameters obtained are listed also in Table IV. The relaxation frequencies and strengths are plotted as a function of θ' (= concentration of NaCl/polymeric solute) in Figure 6. As is seen in Figure 6, relaxation frequency f_{r2} shifts to the lower frequency side with increasing concentration of added salt. Relaxation strength r_2 slightly decreases, while r_1 increases as the concentration of NaCl increases.

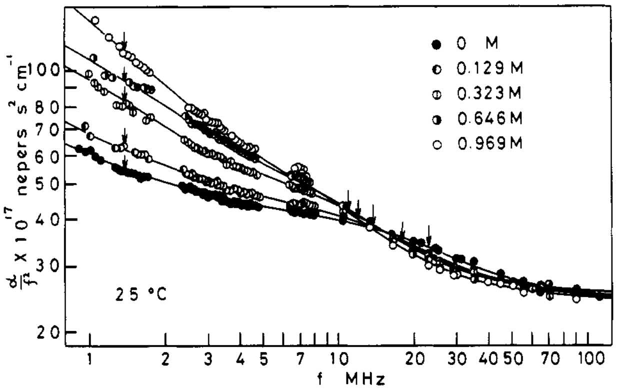

Figure 5. Ultrasonic absorption at 25 °C as a function of frequency for aqueous solutions of NaPA in the presence of added sodium chloride: (●) 0 M NaCl; (◐) 0.129 M NaCl; (◑) 0.323 M NaCl; (◑) 0.646 M NaCl; (○) 0.969 M NaCl.

Discussion

There are a number of possible mechanisms which give rise to the ultrasonic relaxation in aqueous solutions of PAA and NaPA. They may be segmental motions of polymer chains, protolytic reaction of the COOH group, ion binding between COO$^-$ and counterions, hydrogen-bond formation between COOH and COO$^-$, and so on. We will discuss these possible ultrasonic relaxation mechanisms in detail.

Protolytic Reaction of COOH Groups in PAA. Considering the results of ultrasonic relaxation studies of aqueous solutions of univalent carboxylic acid,[16] it is rea-

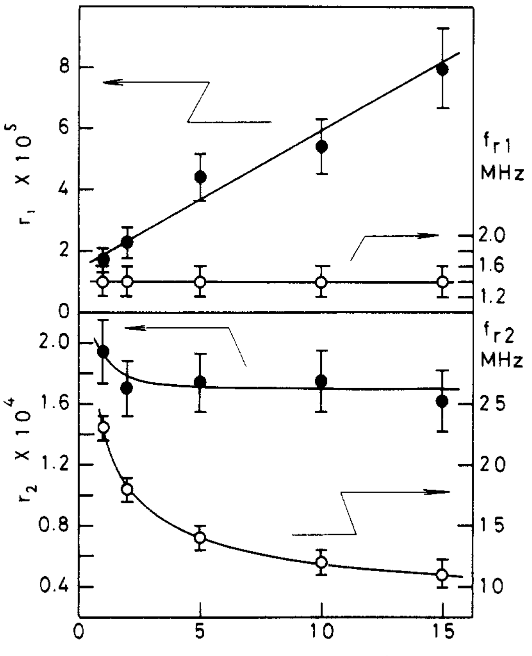

Figure 6. Relaxation strengths r_i (i = 1, 2) (●), and relaxation frequencies f_{ri} (i = 1, 2) (○), as a function of θ'. θ' is the ratio of concentration of NaCl to polymeric solute, C_{Na^+}/C, for aqueous solutions of NaPA.

sonable to assume that the ultrasonic relaxation due to protolytic reaction should be observed in the spectrum of an aqueous solution of acrylic acid.

For the ultrasonic relaxation due to the protolytic reaction

$$\mathrm{COOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{COO^-} + \mathrm{H^+} \qquad (2)$$

the ultrasonic relaxation frequency, f_r, and the relaxation strength, r, can be expressed by eq 3 and 4, respectively,

$$\begin{aligned} 2\pi f_r &= k_1 + k_{-1}([\mathrm{H^+}] + [\mathrm{COO^-}]) \\ &= k_{-1}([\mathrm{H^+}] + [\mathrm{COO^-}] + K) \end{aligned} \qquad (3)$$

$$r = \frac{\rho u^2(\Delta V)^2}{RT}\left\{\frac{1}{[\mathrm{H^+}]} + \frac{1}{[(\mathrm{COO^-}]} + \frac{1}{[\mathrm{COOH}]}\right\}^{-1} \qquad (4)$$

where $K = k_1/k_{-1}$, k_1 and k_{-1} are the forward and backward reaction rates, respectively, and ΔV expresses the volume change with protolytic reaction. R and T have their usual meaning and ρ is the density. Some additional data are required to estimate the kinetic parameters, k_1, k_{-1}, and ΔV, from the obtained relaxation parameters, μ_{max} and f_r. These data for acrylic acid are pK_a = 4.26 (from the literature[20]) and [H$^+$] = 2.51 × 10^3 (from concentration and measured pH values). Using the above data in eq 3 and 4, we obtain $k_1 = 1.9_7 \times 10^6$ s^{-1}, $k_{-1} = 3.5_6 \times 10^{10}$ mol^{-1}·L·s^{-1}, ΔV = 11 cm^3·mol^{-1}. These values are in good agreement with those obtained for aqueous solutions of univalent carboxylic acid.[15,16]

It has already been confirmed that the pH dependence of r calculated from eq 4 agrees well with experimental results of univalent carboxylic acids.[16] Therefore, using the above parameters, one can calculate the relaxation strength as a function of pH from eq 4. The dotted line in Figure 4 shows the calculated values.

Since a similar maximum is observed in the plot of r vs. pH for PAA in Figure 4, one can speculate that the maximum in the vicinity of pH 3 is due to the protolytic reaction of COOH. The ultrasonic relaxation spectra for solutions maintained at pH above 4 or below 2 may be free from the protolytic reaction of COOH. However, curve fitting cannot distinguish an additional relaxation process due to protolytic reaction in the ultrasonic relaxation spectrum of PAA. Not only the spectra of solutions of polymers without protolytic reaction but also the spectra of the solutions of PAA, which should reflect the relaxation mechanism of protolytic reaction, can be expressed by the equation of double relaxation processes. This may be because the relaxation frequency of protolytic reaction would be located close to that of the relaxation process due to segmental motion (see below) and the relaxation strength would be weak.

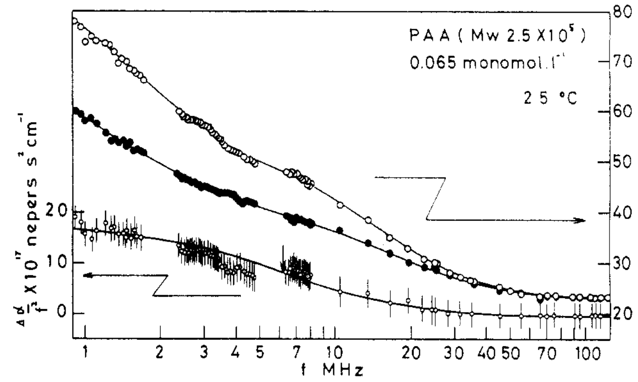

Figure 7. Ultrasonic absorption as a function of frequency for aqueous solutions of PAA at pH 2.8 (○) and pH 2.0 (●). In Figures 7 and 8, ϕ show excess ultrasonic absorption as a function of frequency and bars show the experimental error. The solid line in excess ultrasonic absorption data represents the calculated relaxation spectra from eq 1 with i = 1. The arrow shows the location of relaxation frequency.

In order to investigate the ultrasonic absorption due to protolytic reaction, let us make a crude assumption that the subtraction of ultrasonic absorption observed at pH 2.0 from that at pH 2.8 as a function of frequency can eliminate all of the contributions other than that of protolytic reaction. The excess ultrasonic absorption spectrum due to protolytic reaction thus obtained can be exprressed by an equation for a single relaxation process as shown in Figure 7. The relaxation parameters for the excess spectrum are f_r = 6.3 MHz and $\mu_{max} = 0.77 \times 10^{-4}$. The following kinetic parameters are estimated from these relaxation parameters and experimental conditions for the protolytic reaction in PAA: $k_1 = 2.0 \times 10^5$ s^{-1}, $k_{-1} = 1.0_4 \times 10^{10}$ mol^{-1}·L·s^{-1}, ΔV = 8 cm^3·mol^{-1}. For a pK_a value of PAA, 4.72[21] was used in the calculation. These kinetic parameters of PAA are reasonable if they are compared with those of acrylic acid. Since PAA has many COOH groups, an interaction between COOH groups may decrease the rates of protolytic reaction and volume change, ΔV.[15,16]

Atkinson et al.[22] pointed out that an ultrasonic relaxation process due to hydrogen-bond formation was observed in aqueous solutions of acetic acid at concentrations from 3.6 to 17.4 mol·L^{-1}. Zana et al.[13] reported that the ultrasonic relaxation of PAA in the low pH range might be due to hydrogen-bond formation between COOH and COO$^-$. In the work of Atkinson et al.,[22] the relaxation frequency shifted to the low-frequency side and the relaxation strength increased with the increasing pH value of solutions. As is seen in Figure 5, our experimental results, however, do not show the pH dependence reported by Atkinson et al. Moreover, since the concentrations of solutions investigated here are about 1 order lower than those reported by Zana et al.[13] and by Atkinson et al.,[22] protolytic reaction seems to be more reasonable than hydrogen-bond formation for explaining our experimental results.

Segmental Motion. The ultrasonic absorption due to the protolytic reaction is not included in the ultrasonic relaxation spectra of PAA observed above pH 4. All spectra observed above pH 4 have similarities to those of nonionic polymers in organic solvents, which are attributed to the segmental motions of polymer chains:[9,10,23-25] (i) Both the relaxation spectra of PAA and those of nonionic polymers can be well expressed by an equation for double relaxation processes. (ii) The relaxation frequencies are both located at about several megahertz and several tens of megahertz. They are almost independent of concentrations and molecular weights of polymers. (iii) Both relaxation strengths are linearly proportional to polymer concentration.

These similarities suggest that the segmental motions of polyelectrolyte chains may mainly contribute to the ultrasonic relaxation processes in aqueous solutions of PAA. Segmental motions should arise principally as a result of conformatonal changes of the backbone structure of the polymer. There are many possible types of segmental motions but a lack of definite information concerning the conformational changes of polyelectrolyte segments makes it difficult to unequivocally identify what kinds of segmental motions are involved in the two relaxation regions characterized by f_{r1} and f_{r2}. Therefore, the picture of the segmental motions, at this stage, must be obscure and speculative.

For a process characterized by f_{r2} we may be able to imagine a rotational motion of a segment of PAA similar to the "crankshaft"[38,39] motion of polystyrene in organic solvents or a normal-mode motion[40-44] of the Rouse–Zimm type expressed in terms of internal viscosity and internal rotation of the polymer chain. Six to ten monomer units are necessary[38,45-47] before the motion of the chain becomes truly representative of internal segments in solutions of polystyrene[38,45,46] and in those of styrene and α-methylstyrene–alkane copolymers.[47] Therefore, we may be able to consider that a similar extent of monomer units is involved in the segmental motion of PAA. A similar motion may be in for the process characterized by f_{r1}. Then segments longer than that of f_{r2} should be considered because the process has longer relaxation time and remains unaffected by the increase in salt concentration.

Since the polymer chain is more extended by an electrorepulsive force with increasing charge density, segmental motions of PAA should become easier and their relaxation frequencies should shift to the higher frequency side as the degree of neutralization increases. This explains the ultrasonic relaxation behavior of PAA shown in Figure 4. Above pH 4, relaxation frequencies f_{r1} and f_{r2} shift to the high-frequency side with increasing degree of neutralization, i.e., with increasing charge density of the polymer.

There is a shallow minimum at $\theta = 0.2$–0.3 in the plot of f_{r1} vs. degree of neutralization (Figure 4). A few studies[5,26-28] indicate that PAA undergoes a conformational change from a tightly coiled structure to a loose, open coil at degree of neutralization 0.2–0.3. Therefore, the minimum of f_{r1} may reflect the influence of conformational change. Since the addition of NaCl reduces the electrorepulsive force between charged groups, the relaxation frequencies should shift to the low-frequency side with increasing concentration of NaCl (Figure 5). As is seen in Figures 5 and 6, ultrasonic absorption at frequencies below 10 MHz and relaxation strength r_1 increase with increasing salt concentration. In the frequency range below 1 MHz, i.e., the kilohertz region, a few kinds of ultrasonic relaxation processes have been observed in nonionic polymers in organic solvents[18,23,29] and they have been attributed to motions of larger units in the polymer chain than those considered here, for example, the rotational motion of the polymer as a whole[23] and normal-mode motions of the Rouse–Zimm type.[18,29] The relaxation processes in the kilohertz region should be more strongly affected than those in the megahertz region by the change of electrostatic force with addition of salt, because they depend on the shape and size of the molecule. Indeed, similar behavior has been observed in a dielectric study.[6] Therefore, the increases of ultrasonic absorption and relaxation strength r_1 may reflect some "tail" effect of a relaxation process in the kilohertz region. In any event, it is clear that conclusive identification requires additional ultrasonic studies, especially, in the kilohertz region.

One difference between the ultrasonic relaxation behavior of PAA and nonionic polymers is the temperature dependence. The relaxation frequencies of the ultrasonic relaxation spectra for nonionic polymers in organic solvents[9,10,25] depend on temperature. On the other hand, for aqueous solutions of PAA, they are almost independent of temperature and the relaxation spectra are not sensitive to temperature. Hence, this may appear in contradiction with our argument that the ultrasonic relaxation processes in aqueous solutions of PAA are primarily due to the local segmental motions of polymer chains. This should be discussed here.

In general, an ultrasonic relaxation strength, r, can be written as[30]

$$r = \frac{C_p^{\,0}}{C_p^{\,\infty}}\left[\left(\frac{\beta_T^{\,\mathrm{r}}}{\beta_s^{\,0}}\right)^{1/2} - \left\{(\gamma - 1)\frac{C_p^{\,\mathrm{r}}}{C_p^{\,0}}\right\}^{1/2}\right]^2 \qquad (5)$$

where β_s, β_T, and C_p are isoentropic and isothermal compressibilities and the heat capacity at constant pressure, respectively. The superscript r denotes the relaxation quantity and the superscripts 0 and ∞ mean the values at the limits of low and high frequencies, respectively. γ is the ratio of heat capacities C_p/C_v. C_v is the heat capacity at constant volume. If the first term is predominant on the right-hand side of eq 5, the relaxation process is called "volume" relaxation, while if the second term is predominant, it is called "thermal" relaxation. For aqueous solutions of ionic polymers, two facts should be considered in eq 5. The first is the fact that the ratio of specific heats, γ, becomes approximately unity in most dilute aqueous solutions at room temperature. This seemingly reduces the term of thermal relaxation, $(\gamma - 1)C_p^{\,\mathrm{r}}/C_p^{\,0}$, in magnitude even if $C_p^{\,\mathrm{r}}$ is very large in eq 5. The second is concerned with the term of volume relaxation. In addition to the thermal term, the volume term is important for explaining ultrasonic relaxation processes in ionic polymer solutions, since there are many kinds of volume changes responsible for ultrasonic relaxation, such as protolytic reaction, hydrogen-bond formation (these are already discussed above), and site binding between polyion and counterions and so on. The two facts mentioned above may make the relaxation frequencies and relaxation spectra insensitive to temperature.

One more experimental result will be presented to support our argument for segmental motions. It has been widely accepted that the volume change associated with site binding between polyion and counterions can be negligible in aqueous solutions of TBAPA.[31-33] Consequently, it can be considered that there is no ultrasonic

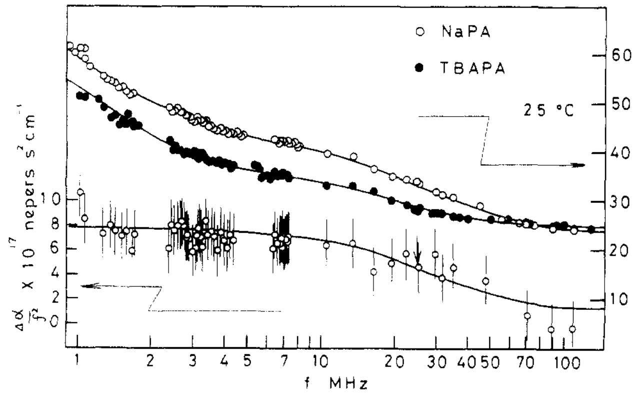

Figure 8. Ultrasonic absorption as a function of frequency for an aqueous solution of TBAPA (●) and for aqueous solutions of NaPA (○).

absorption due to site binding in the solution. Figure 8 shows the ultrasonic relaxation spectrum for a solution of TBAPA. Its relaxation parameters are listed in Table III. For comparison, the spectrum of NaPA is also shown in Figure 8. The following information leads us to conclude that the relaxation processes due to segmental motions mainly contribute to the ultrasonic absorption in aqueous solutions of PAA. (1) The relaxation spectrum of TBAPA also can be expressed by the equation for double relaxation processes, and relaxation frequencies f_{r1} and f_{r2} show little change in comparison with those of NaPA (Figure 8 and Table III). (2) The ultrasonic absorption for the solution of TBAPA has ca. 85% of the magnitude of that for the solution of NaPA (Figure 8). If we assume the difference in ultrasonic absorption between the two solutions is due to site binding, this in turn indicates that the site binding gives only a small contribution to the total ultrasonic absorption in aqueous solutions of NaPA.

Site Binding between Polyion and Counterions. As has already been pointed out by Zana et al.[11,12] and Atkinson et al.,[14] site binding between polyion and counterions is also responsible for volume relaxation processes in aqueous solutions of PAA. If we assume that the excess absorption between solutions of NaPA and TBAPA is due to site binding, the following analysis is possible.

Similarly to the case of protolytic reaction, the excess ultrasonic absorption can be calculated and is expressed in Figure 8 as a function of frequency. The excess absorption data can be expressed by a single relaxation equation and the relaxation parameters A, B, and f_r are 6.5×10^{-17} and 1.2×10^{-17} Np·s^2·cm^{-1} and 25 MHz, respectively. For site binding between polyion and a counterion, Na

$$\mathrm{COO^- + Na^+ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} COONa} \tag{6}$$

the relaxation frequency can be expressed by eq 7

$$2\pi f_r = k_2([\mathrm{COO^-}] + [\mathrm{Na^+}] + K^{-1}) \tag{7}$$

where k_2 and k_{-2} represent the forward and backward reaction rates, respectively, and K is defined as $K = k_2/k_{-2}$. The volume change associated with the site binding, ΔV_s, can be related to relaxation strength r by eq 4, in which the concentration terms, [H$^+$] and [COOH], should be replaced by [Na$^+$] and [COONa], respectively. Using the relaxation parameters of the excess absorption spectrum and other experimental data, one can estimate the following kinetic parameters and the value of the volume change associated with the site binding in aqueous solutions of NaPA: $k_2 = 2.7 \times 10^9$ mol^{-1}·L·s^{-1}, $k_{-2} = 3.3 \times 10^7$ s^{-1}, $\Delta V_s = 3.1$ cm^3·mol^{-1}. In the calculation, the amount of counterions bound to polyion was roughly estimated at 65% of the total concentration of counterions at degree of neutralization 1 according to the report of Huizenga et al.[34]

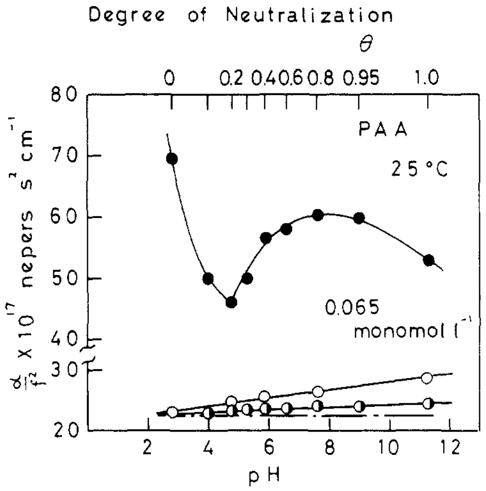

Figure 9. Contribution of dynamic shear viscosity $(\alpha/f^2)_{\mathrm{vis}}$ (○), estimated from eq 8: (●) ultrasonic absorption coefficient at 1.4 MHz; (◑) relaxation parameter B; (—·—) average value of ultrasonic absorption coefficient of water in the literature.[37]

On the other hand, one can estimate the value of volume change associated with site binding from the volumetric study on the basis of the method proposed by Tondre et al.[35] The values of apparent molar volumes of TBAPA and TBA$^+$ in aqueous solutions have been determined by us in this study and by Franks et al.[35] as 299.7 ± 0.3 and 275.6 cm^3·mol^{-1}, respectively. Using these values, we can estimate the volume change associated with site binding at 11.3 cm^3·mol^{-1}. At this stage, however, we cannot explain why the value estimated from the ultrasonic study is smaller than that of the volumetric study.

In order to determine the contribution of site binding more clearly, it is necessary to indicate with eq 7 that the relaxation frequency of the excess relaxation spectra increases linearly with increasing concentration of Na$^+$. For this purpose trial subtractions were made to obtain a series of excess relaxation spectra between ultrasonic absorption in solutions of TBAPA and those of PAA with different degrees of neutralization. The excess absorption was, however, too small in magnitude and the data were too scattered to determine the relaxation parameters except for the solution of NaPA. Therefore, the discussion of relaxation frequency as a function of degree of neutralization from 0.2 to 1.0 should be postponed until more accurate data are available.

Viscous Loss. Viscous loss is also a possible mechanism of ultrasonic absorption since the viscosity of polyelectrolyte solutions is extremely high. Okamoto et al.[4] have reported the measurement of dynamic shear viscosity of dilute aqueous solutions of PAA at frequencies from 2 to 500 kHz. The ultrasonic absorption due to viscous loss can be estimated from eq 8 by substituting the data of Okamoto et al. for excess dynamic shear viscosity, $\Delta\eta'(\omega)$ $(=\eta'(\omega) - \eta_{\mathrm{water}})$

$$\left(\frac{\alpha}{f^2}\right)_{\mathrm{vis}} = \frac{8\pi^2}{3\rho u^2}\Delta\eta'(\omega) + \left(\frac{\alpha}{f^2}\right)_{\mathrm{water}} \tag{8}$$

Estimated values from eq 8 are shown in Figure 9 as a function of pH and/or degree of neutralization together with the values of α/f^2 observed at 1.4 MHz. Clearly the

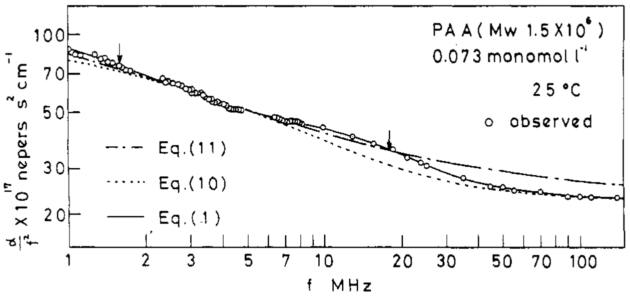

Figure 10. Comparison of the ultrasonic absorption data (○) with calculated relaxation spectra from various equations: (—) eq 1; (- - -) eq 9; (—-—) eq 10.

dynamic shear viscosity does not contribute to ultrasonic relaxation spectra for aqueous solutions of PAA in the frequency range studied.

The values of $(\alpha/f^2)_{\mathrm{vis}}$, however, are comparable to those of the relaxation parameter B and both $(\alpha/f^2)_{\mathrm{vis}}$ and B show a similar dependence on pH. This presumably suggests that the viscous loss predominantly contributes to the ultrasonic absorption at higher frequencies beyond the frequency range investigated.

Distribution of Relaxation Times. It is reasonable to assume that any dynamic process in polymers should have a distribution of relaxation times. As is well-known, the dielectric dispersion spectra of polymer solutions in the megahertz frequency range can be expressed by an equation containing a distribution function of relaxation times, for example, a distribution function of the Cole–Cole type.[5] Indeed a distribution of the Cole–Cole type was employed in a few studies[14,29] of ultrasonic relaxation in polymer solutions. Therefore, one may suppose that an equation of the Cole–Cole type is preferable to eq. 1 in order to analyze the ultrasonic relaxation spectra observed in aqueous solutions of polyelectrolytes.

The following two equations of the Cole–Cole type have been proposed:

$$\frac{\alpha}{f^2} = \frac{A \sin(\pi\beta/2)(f/f_r)^{\beta-1}}{1 + 2(f/f_r)^{\beta}\cos(\pi\beta/2) + (f/f_r)^{2\beta}} + B \qquad (9)$$

$$\frac{\alpha}{f^2} = \frac{A[1 + (f/f_r)^{\beta}\cos(\pi\beta/2)]}{1 + 2(f/f_r)^{\beta}\cos(\pi\beta/2) + (f/f_r)^{2\beta}} + B \qquad (10)$$

Equation 9 was proposed by Atkinson et al.,[14] while eq 10 was proposed by Pethrick et al.[29] In eq 9 and 10, β is a parameter which indicates the distribution of relaxation times. Parameter A represents the relaxation amplitude and B the contribution to sound absorption from any other processes that may be occurring at higher frequencies beyond our frequency range. If we fit eq 9 and 10 to ultrasonic absorption data using a least mean squares program, these equations cannot express the relaxation behavior over the full range of frequencies investigated (Figure 10). Especially, they fail to express the convex curve of relaxation spectra at frequencies from 7 to 50 MHz with a reasonable value of β.

If the distribution of relaxation times is taken into account, it may be necessary to assume a distribution around each relaxation frequency f_{r1} and f_{r2}. However, at present such an assumption is not necessary.

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Registry No. PAA (homopolymer), 9003-01-4; NaPA, 9003-04-7.

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Calculation of the High-Pressure Phase Diagram of Polyethylene

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ABSTRACT: The pressure–temperature phase diagram of polyethylene is distinguished by a partially ordered phase which interposes between the melt and orthorhombic crystal for pressure greater than 3.5 kbar. This phase, called the high-pressure intermediate phase (HPIP), is characterized by a hexagonal lattice of highly extended chains. Despite the high extension of the chains, rotational fluctuations about the single bonds are significant. This paper is a calculation of the phase boundary between the crystal and HPIP phases. The latent heat of the first-order crystal–HPIP phase transition is also calculated. Elements of the model are entropy and energy associated with the rotations about the single bonds and the energy associated with interchain interaction. Treatment of the bond rotational degrees of freedom is based on the distribution function calculated in an earlier publication. The remaining degrees of freedom are considered in a simple potential energy approximation. The results for the location and slope of the phase boundary are in good agreement with experiment. The calculated values of the latent heat and volume discontinuity of the phase transition fall between the experimental values recorded in the two literature data sets.

I. Introduction

The phase diagram of polyethylene at high pressure has been the subject of a number of experimental investigations.[1-3] The most important feature of this phase diagram is the extent of the domain of stability of the high-pressure intermediate phase (HPIP). This phase, for which the generic nomenclature "condis crystal" has been suggested,[4] interposes between the melt and the orthorhombic crystal for pressures greater than 3.5 kbar. In the HPIP, the polymer chains are very highly extended and oriented. The phase is hexagonal with the chain axes along the unique direction. Although the structure is apparently well ordered, the thermodynamic data indicate that there is a fair amount of dihedral angle disorder in the HPIP. The physical picture is that while in the crystal the fluctuations of the bond rotations away from the trans position are small, in the HPIP the fluctuations in these rotations are significant. In two earlier papers[5,6] a model calculation for this dihedral angle disorder was developed. This model is based on the idea that the structural effect of the interchain interactions is to confine a polymer chain to a cylindrical cavity of infinite length and fixed cross-sectional area. The entropy associated with dihedral angle disorder can be calculated as a function of the cross-sectional area on the basis of this model. While this approach is capable of obtaining the magnitude of the discontinuity in entropy at the HPIP–orthorhombic phase transition, it must be augmented by a model of the interchain energetics in order to form the basis for a full calculation of the phase boundary between the HPIP and the orthorhombic crystal. The calculation of the interchain energetics and of the HPIP–orthorhombic phase boundary is the subject of this paper. The approach used here is based on an analysis of the equation of state of crystalline polyethylene by Pastine.[7] The augmented calculation is the first statistical mechanical analysis of the HPIP. Earlier theoretical work[8-10] has been confined to thermodynamic phenomenology.

The calculation of this paper draws on numerical results contained in ref 5–7. These numerical results are parameterized by quantities related to the cross-sectional area per chain. In order to make the presentation of this paper as straightforward and self-contained as possible, all of the required numerical results are brought into the form of analytic functions of the same parameter. This parameter is R, the radius of the cylinder confining the skeleton of the polymer chain divided by the length of the carbon–carbon bond. In order to do this, the numerical results which appear in tabular or graphical form are fit to simple analytic functions of R.

This approach has the merit that all of the contributions to the free energy appear as simple functions of R. It is then an easy matter to minimize the free energy with respect to R. It is found that for a certain range of values of the temperature and pressure, there are two minima of the free energy as a function of R. One minimum corresponds to the HPIP, and the other to the orthorhombic crystal. There should be a third minimum corresponding to the melt phase. However, the method of calculation used in ref 6 does not allow calculation of the dihedral angle entropy in the region of R appropriate to the melt phase. Consequently the results of this calculation are limited to the calculation of the HPIP–orthorhombic crystal phase boundary. The calculated slope of this boundary and its intercept with the experimentally determined phase boundary of the melt phase are in excellent agreement with experiment.

The organization of this paper is as follows. Section II discusses the parameterization of the free energy and the dihedral angle distribution function in terms of R. This section also discusses how the numerical results of ref 5 and 6 are incorporated. Section III is concerned with the contribution due to the degrees of freedom external to the chain. Results and conclusions are presented in section IV.

II. Parameterization of Statistical Quantities in Terms of *R*

A. Free Energy. The Gibbs free energy, G, of the polymer chain may be thought of as the sum of five contributions. The first is the average van der Waals energy associated with interchain interaction, E_0. This contri-