Photon Correlation Spectroscopic Studies of Poly(vinyl acetate) above the Glass Transition Temperature

G. Fytas[†]

Max-Planck-Institut fur Polymerforschung Mainz, 6500 Mainz, West Germany

C. H. Wang*

Department of Chemistry, University of Utah, Salt Lake City, Utah 84112

G. Meier and E. W. Fischer

Max-Planck-Institut fur Polymerforschung Mainz and Institut fur Physikalische Chemie der Universitat Mainz, 6500 Mainz, West Germany. *Received September 20, 1984*

ABSTRACT: Homodyne photon correlation spectroscopic measurements of poly(vinyl acetate) at temperatures between 31.8 and 64.5 °C have been carried out. Over this narrow temperature range, the mean relaxation time changes by more than 5 orders of magnitude. The light scattering (photon correlation) results are compared with the mechanical and dielectric relaxation data. Good agreement is found between the light scattering and the dynamic compressibility data, in support of a recent theoretical analysis.

Introduction

Dynamic light scattering is a useful technique for the study of relaxation processes of amorphous polymers above glass transition temperatures.[1] By use of existing digital electronic correlators to process the scattered light, a wide frequency range from 0.1 Hz to 1 MHz can be covered. Information obtained in this frequency range is very valuable in understanding the dynamics of the glass transformation for amorphous polymers. Above the glass transition temperature (T_g), segments of amorphous polymer chains stochastically jump from one position to another. A detailed theoretical treatment of such a type of segmental motion is very difficult, and in order to simplify the description, the free volume concept is frequently used to account for the relaxation peak observed in the viscoelastic or dielectric relaxation spectra of amorphous polymers or glass-forming liquids.

In a recent paper,[2] we have shown, using linear response theory, that at *all* frequencies the dynamic light scattering spectrum arising from density fluctuations is proportional to the imaginary part of the complex longitudinal compliance. Above T_g, the shear modulus of the amorphous polymer is known to be 1 or 2 orders of magnitude smaller than the bulk modulus;[3] thus, above T_g the longitudinal compliance $D(t)$ can be approximated by the bulk compliance $B(t)$. Since bulk compliance data in the dynamic range of 1–10^{-6} s are rarely reported in the literature, due apparently to experimental difficulty, dynamic light scattering provides a useful technique for determining the bulk compliance of amorphous polymers above T_g. The suitability of the dynamic light scattering technique for obtaining the bulk compressibility data has recently been evaluated and compared[4,5] with the dynamic compressibility data of poly(vinyl acetate) at 50 °C by Mckinney and Belcher.[6]

The purpose of the present work is to investigate the photon correlation spectra of poly(vinyl acetate) (PVAc) at different temperatures above but in the vicinity of the glass transition. In order to elucidate the nature of the relaxation process, we have compared the light scattering result with the mechanical and dielectric data previously published. During the course of this work, a paper dealing with dynamic light scattering of PVAc by Tribone, Jamieson, and Simha[7] appeared. Their results are, however, not in agreement with the ones presented in this paper. In a later section we discuss possible causes for the disagreement.

Experimental Techniques and Data Analysis

Homodyne photon correlation functions at different temperatures (32–57 °C) are measured at a scattering angle of $\theta = 90°$. The excitation light source is an argon ion laser (Lexel) operating at 5145 Å with about 400 mW of power. The depolarized scattering intensity of PVAc is small; the polarized scattering intensity was analyzed with a 28-channel Malvern Loglin correlator (K7027) to obtain the single-clipped photo-count autocorrelation function $G_k(t)$, where k indicates the clip level. With the present log-delay correlator, the correlation function $G_k(t)$ in a dynamic range of 4.3 decades in time (using the far-point extension) is simultaneously obtained, without the need of matching several sections of the time correlation function obtained by using different delay times in a manner similar to the method previously used.[1] With the proper setting of delay times, the measured base line of the correlation function of PVAc at each temperature investigated is found to be equal to the calculated one, thus suggesting good quality of the measurements.

The PVAc sample used in this study was supplied through the courtesy of Dr. C. Kemenater of Wacker Chemie, Burghansen, West Germany. The viscosity-average molecular weight is 1.5×10^4, with an unknown molecular weight distribution. The glass transition temperature of our sample determined by DTA is low (17 °C) in comparison with the generally accepted T_g value of 29–32 °C.[8] The low value obtained here is due to the low molecular weight of our sample and not due to the presence of impurity. At this molecular weight our T_g value agrees with the literature value.[9] It is interesting to note that our T_g value is similar to that of the PVAc sample used in the dynamic compressibility experiment[6] in which the presence of small amount of plasticizer is expected to affect the results.[6] Since we shall compare the light scattering result with both mechanical and dielectric relaxation data, the deviation from the conventional T_g value will not affect the interpretation, provided that the effect of different T_g values is taken into account.

The sample used in our light scattering experiment was prepared by a procedure described elsewhere.[10] It is dust free and optically homogeneous. The sample displays light scattering intensity consistent with pure thermal density fluctuations, as demonstrated by the low value of the

---

[†] Permanent address: Department of Chemistry, University of Crete, Crete, Iraklion, Greece.

0024-9297/85/2218-1492$01.50/0

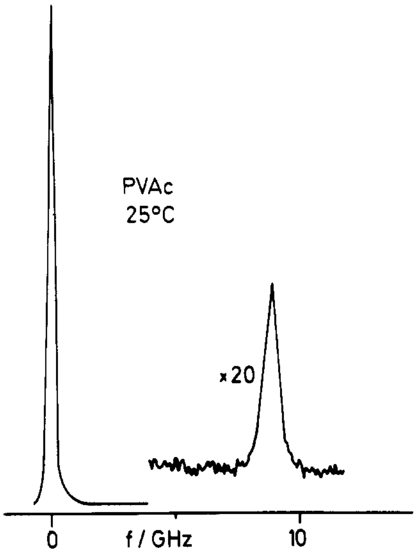

Figure 1. Rayleigh–Brillouin spectrum of poly(vinyl acetate) at 25 °C and at 90° scattering angle. The spectrum shows a low Landau–Placzek ratio.

Landau–Plazcek ratio in the Rayleigh–Brillouin spectrum. Shown in Figure 1 is the Rayleigh–Brillouin spectrum of the present sample at 25 °C at $\theta = 90°$. The Landau–Plazcek ratio is approximately equal to 8.

A detailed description of the method of data analysis of the measured single-clipped photoelectron-count autocorrelation function $G_k(t)$ was given in ref 1. Here we describe only briefly the method used in the present work.

When the scattering intensity is due to density fluctuations, $G_k(t)$ is related only to a part of the density time correlation function $g(t)$ by

$$G_k(t) = A[1 + b|g(t)|^2] \tag{1}$$

where A is the background factor which can be computed or measured by using long delay times. In the present work, the measured and computed A values agree to within 1.6% (the mean value of all correlation functions measured). The parameter b is equal to $B\alpha_r^2$, where B is determined by the characteristics of the correlator such as the clip levels, the delay time, and the effective photocathode area. The B factor can in principle be calculated if the spatial coherence factor of the optical system is known, but in practice, this is difficult. Thus, we determined the B factor by calibrating the optical system with pure CCl_4 and with a solution of polystyrene in CCl_4 at room temperature. The factor α_r is known as the relaxation strength and it accounts for that part of density fluctuations that is detected by the correlator due to the fact that the shortest sample time of the correlator is limited to about 100 ns.

It is customary to determine the b factor by fitting the function $[G_k(t) - A]/A$ according to some assumed function. In the present case, we assume that

$$(Gk(t) - A)/A = b \exp\{-2(t/\tau_0)^{\beta}\} \tag{2}$$

treating b, β, and τ_0 as fitting parameters. The background factor A used is a fixed value corresponding to the measured base line and not a fitting parameter. Note in eq 2 that we have assumed $g(t)$ to be represented by a fractional exponential, which is known to describe well the normalized correlation function $g(t)$ with a proper set of values, β and τ_0.[12] Here β is between 0 and 1.

The relaxation strength α_r obtained from the fitting parameter b is calculated to be equal to 0.52, indicating that only about a half of the intensity arising from density fluctuations of PVAc is probed by our correlator. The other half (48%), not accessible to the shortest time window ($\simeq 10^{-7}$ s) of our correlator, is associated with the hypersonic wave, thermal diffusion, and fast segmental motion. All of these processes do not contribute to the time correlation function $g(t)$, but only to the background factor A.

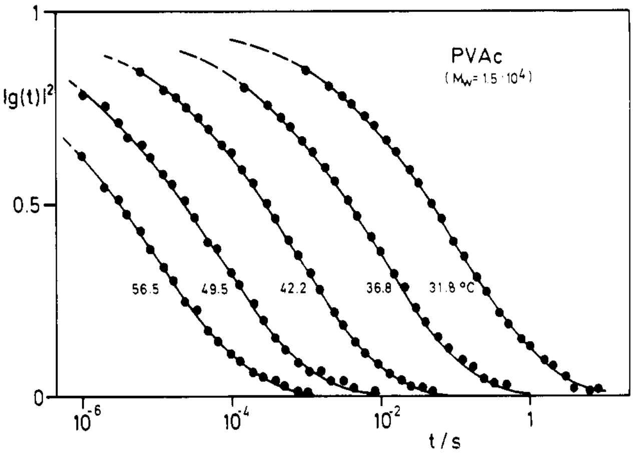

Figure 2. Normalized correlation functions $|g(t)|^2$ determined at various temperatures plotted vs. log t.

Table I
Values of the Parameters β and τ_0 and Mean Relaxation Times $\bar{\tau}$ for PVAc at Various Temperatures

T/°C	β	τ_0/s	τ/s
31.8	0.37	0.86	3.6
36.8	0.37	6.4×10^{-2}	2.7×10^{-1}
39.8	0.36	1.54×10^{-2}	7.3×10^{-2}
42.2	0.37	4.9×10^{-3}	2.1×10^{-2}
49.5	0.35	4.7×10^{-4}	2.3×10^{-3}
56.5	0.34	4.8×10^{-5}	4.0×10^{-4}
64.5	0.36	1.0×10^{-5}	4.4×10^{-5}

Results and Discussion

The normalized correlation functions $|g(t)|^2$ at a series of temperatures varying from 31.8 to 56.6 °C are plotted vs. log t in Figure 2. Points represent the experimental data and the continuous curves are the fitted functions. The parameters τ_0 and β used to fit the time correlation functions are given in Table I. One notes in Table I that while the primary relaxation time τ_0 decreases rapidly with increasing temperature, the shape parameter β remains unchanged, equal approximately to 0.36–0.37 for T between 31.8 and 64.5 °C. The shape parameter is a measure of the width of the distribution of relaxation times. Constancy in the shape parameter is a good indication that only one type of relaxation process is manifested in $g(t)$ over the temperature range studied.[11]

Despite the distribution of relaxation times, it is useful to characterize the dynamic data by a mean relaxation time $\bar{\tau}$ given by

$$\bar{\tau} = \int_0^{\infty} \mathrm{d}t \exp\{-(t/\tau_0)^{\beta}\} = \tau_0/\beta\Gamma(1/\beta) \tag{3}$$

where $\Gamma(1/\beta)$ is the gamma function. The mean relaxation times computed by using the β and τ_0 values are also given in Table I at various temperatures. The results for $\bar{\tau}$ are also shown in Figure 3. Over the temperature range 31.8–69.5 °C, the temperature variation of $\bar{\tau}$ does not follow the Arrhenius equation with a constant activation energy. We now compare the present light scattering results with those of previous studies. In ref 7, Tribone et al. used a

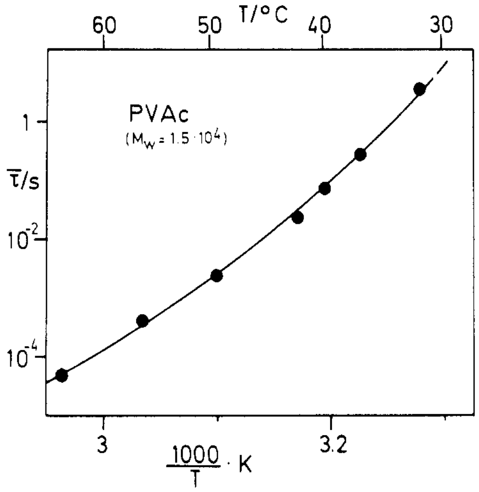

Figure 3. Mean relaxation time $\bar{\tau}$ is plotted as a function of temperature in an Arrhenius manner.

linear correlator to collect autocorrelation function data with different sample time segments. They then matched overlapping segments to obtain a composite autocorrelation function covering five to seven decades in time. In this manner, they obtained a composite autocorrelation function described by eq 2. However, their β value is 0.45, considerably higher than our 0.36–0.37 value. The quoted τ_0 value at 39.3 °C is also larger than ours. When their photon correlation results are compared with the mean retardation times for volume compliance, a disagreement is found, the volume compliance data being longer by at least more than 2 orders of magnitude. This is in contrast to the present result in which we have found that the retardation time for volume compliance is in good agreement with that of the photon correlation data. Recently an elaborate analysis involving first numerically calculating the retardation spectrum from the time correlation function obtained from dynamic light scattering and then using the retardation spectrum to calculate the real and imaginary parts of the dynamic compliance in PVAc has yielded a good agreement.[5]

It appears that the data reported by Tribone et al. need to be corrected. The origin of their difficulty may arise from improper data processing dealing with matching the correlation functions. As discussed in ref 1, although this is a necessary step in dealing with amorphous polymers, great accuracy must be obtained when measuring each section in order to be able to obtain an accurate composite time correlation function for subsequent data analysis.

We have fitted $\bar{\tau}$ values are various temperatures to the WLF equation[13]

$$\log \bar{\tau} = \log \bar{\tau}_g - \frac{C_1(T - T_g)}{C_2 + (T - T_g)} \tag{4}$$

where $\bar{\tau}_g$ is the mean relaxation time of PVAc at the glass transition temperature and C_1 and C_2 are the parameters.

To determine the C_1 and C_2 values, it would be useful to plot $(T - T_g)/\log(\bar{\tau}/\bar{\tau}_g)$ vs. $T - T_g$ and then to derive the parameters C_1 and C_2 from the slope and the intercept of the plot. Unfortunately, $\bar{\tau}_g$ is too long to be determined experimentally. Furthermore (as shown in Table I), $\bar{\tau}$ changes by more than 5 orders of magnitude in a fairly narrow temperature range (about 33 °C). It is difficult to determine with accuracy the parameters C_1 and C_2 with the usual technique, which involves using several trial $\bar{\tau}_g$ values until a linear plot of $(T - T_g)/\log(\bar{\tau}-/\tau_g)$ vs. $T - T_g$ is accomplished.[8] However, considering the fact[2,4] that above T_g the time correlation function $g(t)$ essentially reflects the time dependence of the bulk compliance $B(t)$, we taken C_2 = 52 K, as deduced from the mechanical shift factor reported in ref 6; and we then obtain, from the presently determined temperature-dependent $\bar{\tau}$ data, log $\bar{\tau}_g$(s) = 4.6 and C_1 = 18.8 K. This gives the product of C_1 and C_2 to be equal to 977.6.

From the above $\bar{\tau}_g$, C_1, and C_2 values we obtain the Vogel–Fulcher–Tammann (VFT) equation for $\bar{\tau}$ as

$$\bar{\tau} = \bar{\tau}_0 \exp\{B/(T - T_0)\} \tag{5}$$

where $B = 2.303C_1C_2$ = 2252 K, T_0 = 238 K, and $\bar{\tau}_0 = 6.4 \times 10^{-15}$ s.

The VFT equation may be interpreted in terms of the free volume theory of Cohen and Turnbull.[14] In this theory, T_0 is the fictitious temperature at which the free volume for molecular motion disappears, and in the free volume theory, the parameter B given in eq 5 is equal to $\gamma v^*/\alpha \bar{v}_m$, where $\bar{v}_m$ is the mean volume of the polymer segment responsible for the relaxation, α is the thermal expansion coefficient, and v^* is the minimum required volume of the void. Taking $\alpha = 5.8 \times 10^{-4}$ K^{-1}, we obtain $\gamma v^*/\bar{v}_m \simeq 1.31$ using B = 2252 K. This would be contrasted to $\gamma v^*/\bar{v}_m = 0.95$, obtained from a dielectric relaxation study.[8] Since the free volume for molecular motion is equal to $\alpha \bar{v}_m(T - T_0)$, it suggests that the free volume needed for density fluctuations is considerably less than that for dielectric relaxation, a result that might have been intuitively expected.

It is useful to compare the light scattering data with the mechanical and dielectric results. On the basis of reduced variables for the dynamic compressibility data, the WLF parameters C_1 and C_2 have been found to be equal to 17.5 and 52 K, respectively.[6] This is in good agreement with our light scattering data, indicating that both techniques above T_g practically measure the same dynamic quantity and suggesting that the shear modulus makes only a negligible contribution.

The principle of reduced variables has been applied to the shear compliance data and higher molecular weight PVAc (T_g = 31.8 °C).[3] The WLF parameters obtained[3] from the shear compliance data are C_1 = 15.4 K and C_2 = 46.8 K. These values give B = 1660 K, in contrast to B = 2096 K found from the dynamic compressibility data. Thus, the free volume required for shear relaxation is also larger than that needed for density fluctuations. The WLF parameters obtained from the dielectric relaxation[8] data of high molecular weight PVAc (T_g = 30 °C) are C_1 = 17.9 K and C_2 = 43.7 K, yielding B = 1810 K.

Although the physical processes that give rise to the mechanical and dielectric relaxation may be different, the closeness in the values of the parameters suggests that these methods apparently probe similar types of molecular motion, with only differences of detail as reflected by the amount of free volume needed in each case.

In descriptions of the viscoelastic data of the amorphous polymer, the dynamic modulus is often expressed in terms of the relaxation spectrum $H(\ln \tau)$. Here τ is the relaxation time. As shown in ref 2 and 4, normalized time correlation functions of density fluctuations $g(t)$ probed in the photon correlation spectroscopic experiment are related to the creep longitudinal compliance $D(t)$ by

$$D(t) = D_0 - (D_0 - D_\infty)g(t) \tag{6}$$

where D_0 and D_∞ are the zero- and high-frequency compliance, respectively. For amorphous polymers above T_g, we can replace the longitudinal compliance by the bulk compliance B, because the shear modulus is small.

For bulk polymers in the melt of glassy state, the shape of $g(t)$ is complicated. Previously we approximate it as a

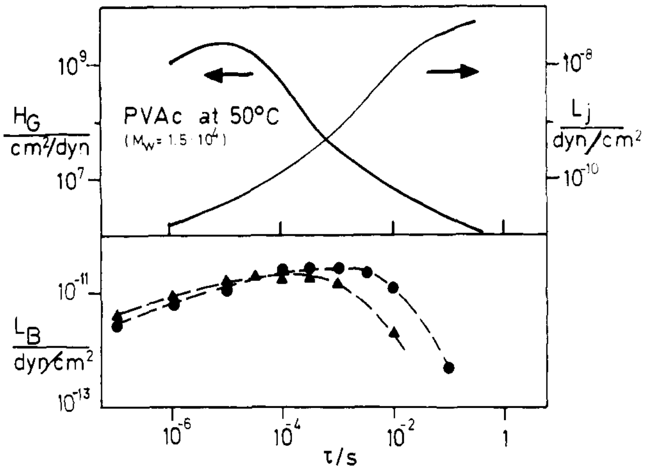

Figure 4. Comparison of the retardation spectrum obtained from light scattering data (circles) and dynamic compliance data (triangles). The retardation spectrum and relaxation spectrum constructed from the shear mechanical data reduced to 50 °C are also plotted.

fraction exponential. It is theoretically more appealing to express it as an integral sum of exponential decays taken over a distribution of relaxation times

$$g(t) = \int_0^\infty d\tau \; \rho(\tau) e^{-t/\tau} \tag{7}$$

where $\rho(\tau)$ is a normalized distribution function.

The mean relaxation time $\bar{\tau}$ is thus equal to the first moment of the distribution function.

$$\bar{\tau} = \int_0^\infty dt \; g(t) = \int_0^\infty d\tau \; \tau\rho(\tau) \tag{8}$$

Because $\rho(\tau)$ is normalized, we can rewrite eq 6 as

$$D(t) = D_\infty + (D_\infty - D_0)\int_0^\infty d\tau \; (1 - e^{-t/\tau})\rho(\tau) \tag{9}$$

Introducing the retardation spectrum $L(\ln \tau)$, we rewrite eq 9 as

$$D(t) = D_\infty + (D_\infty - D_0)\int_0^\infty d \ln \tau \; L(\ln \tau)(1 - e^{-t/\tau}) \tag{10}$$

where $L(\ln \tau) = \tau\rho(\tau)$.

The relaxation time that is determined from the photon correlation spectroscopic experiment thus represents the area of the retardation spectrum $L(\ln \tau)$, or the zeroth moment of $L(\ln \tau)$ integrating over the linear scale.

One can obtain more information from the retardation spectrum itself; unfortunately, this cannot be carried out exactly at present. However, approximated methods for obtaining $L(\ln \tau)$ exist in the literature. We use the method of Schwarzl and Staverman[3] to approximate $L(\ln \tau)$ as

$$L(\ln \tau) = \left[\frac{dB(t)}{d \ln t} - \frac{d^2B(t)}{d(\ln \tau)^2}\right]_{t=2\tau} \tag{11}$$

where $B(t)$ is given by eq 10 (with $D(t)$ replaced by $B(t)$).

The retardation spectrum calculated by using this method for PVAc at 50 °C has been described elsewhere[4] and is reproduced here for comparison in the lower part of Figure 4 as indicated by L_B. The retardation spectrum calculated by using the dynamic compressibility data of ref 6 is included in Figure 4 for comparison. Except for the portion at long relaxation times ($\tau > 5 \times 10^{-3}$ s), the agreement between the dynamic light scattering and the dynamic compressibility techniques is quite good. The deviation at long relaxation times is probably due in part to the presence of plasticizer in the sample of ref 6 and in part to the neglect of the shear modulus, which may affect the long-time result.

The retardation spectrum constructed from the shear compliance[15] reduced to 50 °C (indicated by L_j) is shown in the upper part of Figure 4. In reducing the shear compliance data we have taken into account the low T_g value of the present sample. Note that the value of L_j not only is greater than L_B by nearly 3 orders of magnitude, but also changes by several powers of 10 over the relaxation time range of 10^{-6}–10^{-1} s, in contrast to the behavior of L_B which is quite flat. Since the maximum shear compliance decreases with an increasing number of polymer molecules per unit volume, vis., L_j is an increasing function of the molecular weight,[3] it is not unexpected to see that L_j and L_B for PVAc behave differently. As a matter of fact, it is now known that localized segmental motion is responsible for the relaxation of the bulk compliance; the bulk retardation spectrum L_B is insensitive to changes in the long-range molecular configuration or contour shape. We expect no striking difference between polymers at low and high molecular weights in L_B.

The relaxation spectrum H_G for the shear modulus of PVAc is also included in Figure 4. Note the maximum in H_G occurs at shorter times than that in L_j. This is consistent with the comparison of the maximum position of the loss longitudinal modulus and loss longitudinal compliance recently calculated by Wang and Stuhn[16] from photon correlation data for poly(propylene glycol).[1] It may be pointed out that Saito has observed a similarity between his dielectric data and the viscoelastic data of amorphous polymers presented in terms of the dynamic modulus.[8] Since the frequency at which the loss compliance is maximum is lower than the frequency of maximum modulus, the dielectric relaxation time is expected to be shorter than the light scattering relaxation time or the mechanical retardation time when compared at the same temperature. This observation is consistent with what has been found in PVAc, in poly(propylene glycol),[1] and in nonpolymeric glass-forming liquids such as o-terphenyl.[17] In all these systems, the dielectric relaxation times are found to be shorter than the light scattering relaxation times, in contrast to prediction based on the Debye model. These results simply indicate that the free volume required for density fluctuations is smaller than that needed for dielectric relaxation, rather than a wide distribution of relaxation times associated with the relaxation function, as incorrectly suggested by Patterson.[18]

In summary, we have investigated the photon correlation spectrum of poly(vinyl acetate) at different temperatures above T_g. We have compared the light scattering data with the mechanical and dielectrical relaxation data. We have shown that similar types of localized segmental motion are probed by those techniques, with detailed difference reflected by the required free volume for the motion. The process of density fluctuations requires the least amount of free volume and is manifested by the shortest mean relaxation time when compared to the data obtained by various techniques at the same temperature. Good agreement is obtained when comparing the dynamic compliance and the light scattering data.

Acknowledgment. C.H.W. acknowledges the Polymer Program (DMR 82-16221) of the National Science Foundation for partial financial support. He also thanks the Alexander von Humboldt Foundation of West Germany for a U.S. Senior Scientist Prize. G.F. thanks MPI for a fellowship.

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

References and Notes

(1) C. H. Wang, G. Fytas, D. Lilge, and Th. Dorfmüller, *Macromolecules*, **14**, 1363 (1981).

(2) C. H. Wang and E. W. Fischer, *J. Chem. Phys*, in press.

(3) J. D. Ferry, "Viscoelastic Properties of Polymers", Wiley, New York, 1980.

(4) C. H. Wang, G. Gytas, and E. W. Fischer, *J. Chem. Phys.*, in press.

(5) J. Hargenau, G. Meirer, G. Fytas, E. W. Fischer, and C. H. Wang, to be submitted for publication.

(6) J. E. McKinney and H. V. Belcher, *J. Res. Natl. Bur. Stand., Sect. A*, **67A**, 43 (1963).

(7) J. Tribone, A. M. Jamieson, and R. Simha, *J. Polym. Sci., Polym. Symp.*, **71**, 231 (1984).

(8) S. Saito, *Kolloid-Z*, **189**, 116 (1963); H. Sasabe and C. T. Maynihan, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 1447 (1978).

(9) The T_g value is consistent with that given by R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, **11**, 221 (1956) for PVAc with $\bar{M}_v = 1.5 \times 10^4$.

(10) G. Meier, G. Fytas, and Th. Dorfmüller, *Macromolecules*, **17**, 457 (1984).

(11) G. Fytas, "Physical Optics of Dynamic Phenomena and Processes in Macromolecular Systems", B. Sedlacek, Ed., 27th IUPAC Prague Microsymposium, Walter de Gruyter and Co., West Berlin, 1984.

(12) J. A. Bucaro, M. D. Dardy, and R. D. Corsaro, *J. Appl. Phys.*, **46**, 741 (1975).

(13) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.*, **77**, 3701 (1955).

(14) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1954).

(15) N. G. McCrum, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids", Wiley, New York, 1967.

(16) C. H. Wang and B. Stuhn, "Physical Optics of Dynamic Phenomena and Processes in Macromolecular Systems", B. Sedlacek, Ed., 27th IUPAC Prague Symposium, Walter de Gruyter and Co., West Berlin, 1984.

(17) G. Fytas, C. H. Wang, D. Lilge, and Th. Dorfmüller, *J. Chem. Phys.*, **75**, 4247 (1981).

(18) G. D. Patterson and C. P. Lindsey, *Macromolecules*, **14**, 83 (1981).

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

Shigeo Kato, Nobuhiko Yamauchi, Hiroyasu Nomura,* and Yutaka Miyahara

Department of Chemical Engineering, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya-shi, 464 Japan. *Received September 25, 1984*

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-