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# Relaxation Processes in Amorphous Poly(cyclohexyl methacrylate) in the Rubbery and Glassy State Studied by Photon Correlation Spectroscopy

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ABSTRACT: Photon correlation functions of the polarized component of the scattered light from a high molecular weight amorphous poly(cyclohexyl methacrylate) (PCHMA, $T_g$ = 374 K) have been studied above and well below $T_g$ in the temperature range 213–398 K. Near and above $T_g$ the major part (~60%) of the total light-scattered intensity is due to the slow density fluctuations associated mainly with the primary glass–rubber relaxation. Well below $T_g$, although the segmental relaxation times are too long to be observed by photon correlation, there is significant (~30%) dynamic light scattering from glassy PCHMA. The relaxation functions for the density fluctuations from secondary relaxations are analyzed quantitatively for the first time. The computed retardation spectrum is moderately broader than a single-valued spectrum and exhibits an Arrhenius temperature dependence. These quantities agree very well with the results of dynamic mechanical and NMR measurements on glassy PCHMA, which undergoes a narrow secondary relaxation associated with the chair–chair inversion of the cyclohexyl ring.

## Introduction

Photon correlation spectroscopy (PCS) has been proved to be a potential dynamic light scattering technique for the study of bulk polymer dynamics near and above the glass transition temperature ($T_g$).[1] For weakly anisotropic scatterers, such as segments of poly(cyclohexyl methacrylate), the dominant contribution to the light-scattering intensity arises from density fluctuations.

The density time correlation $g(t)$, which has been mainly measured near and above $T_g$, is directly related with the time-dependent longitudinal compliance $D(t)$.[2-4] Although the latter has been represented as a spectrum $L(\log \tau)$ of retardation times, there is no evidence that the nonexponential $g(t)$ has to be interpreted as actually caused by a distribution of relaxation times. The $L(\log \tau)$ representation of $D(t)$ (see eq 5) should be considered formal at this time. The distribution of retardation times $L(\log \tau)$ displays a single maximum associated with the so-called primary glass–rubber relaxation for all polymers studied so far except poly(alkyl methacrylates).[5-7] The mean relaxation time exhibits a strong pressure dependence and a non-Arrhenius temperature dependence but is independent of chain length and the probing wavelength ($q^{-1}$).[8] It is generally accepted that localized segmental motions grossly affect the slow density fluctuations in undiluted polymers near $T_g$. Poly(methyl methacrylate) (PMMA) is so far the first polymer whose retardation spectrum $L(\log \tau)$ clearly reveals an additional short-time peak assigned to the secondary $\beta$-relaxation.[9,10]

PMMA was the first bulk polymer examined by PCS in the glassy state.[11-13] These earlier papers failed to report consistent results, probably because of the poor quality of the samples used as well as the much restricted time range over which the broad correlation functions were recorded. In amorphous polymers in the glassy state the retardation times associated with the primary glass–ruber relaxation are too long to be observed by PCS. Thus, the presence of dynamic light scattering from polystyrene (PS) in the glassy state was ascribed to the secondary relaxation.[14,15] However, due to the very broad relaxation function $g(t)$ it was not possible to analyze the data quantitatively.[15] To obtain meaningful results we should consider a secondary relaxation with a moderate distribution of relaxation times. In this case, the $g(t)$ can reach both the baseline and the short–time intercept in the time window of the log correlator available to date.

In this paper, we report for the first time to our knowledge fully relaxed density correlation functions in the glassy poly(cyclohexyl methacrylate) (PCHMA) ($T_g$ = 374 K). It is known primarily from mechanical relaxation measurements that this polymer undergoes a narrow secondary relaxation associated with the cyclohexyl ring motions.[16-18] The correlation functions of the density fluctuations were measured above and below $T_g$ in the temperature range 213–398 K and analyzed formally in terms of a continuous spectrum of retardation times, $L(\log \tau)$, by using an inverse Laplace transform technique.[19,20] Above $T_g$ the major part of the total light-scattering intensity is due to the slow density fluctuations associated with the primary glass–rubber relaxation. The time correlation functions well below $T_g$ show a distinct decay, and the corresponding spectrum $L(\log \tau)$ is narrower than that of the parimary relaxation.

## Experimental Section

The correlation functions $G(t)$ of the polarized light-scattered intensity at different temperatures (213–398 K) were measured at a scattering angle $\theta$ = 90°. The light source was an argon ion laser (Spectra Physics 2020) operating at 488.0 nm with a power of 300 mW. The incident beam was polarized vertically with respect to the scattering plane, and no polarizer was used for the scattered light. The correlation functions $G(t)$ over 4.3 decades in time were measured with a 28-channel log lin (Malvern K 7027) single clipped correlator in one run. For amorphous polymers which display homodyne scattering above $T_g$ the desired normalized density time correlations function $g(t)$ is related to $G(t)$ by

$$G(t) = A(1 + f|\alpha g(t)|^2) \qquad (1)$$

where $A$ is the base line measured at long delay times, $f$ the instrumental factor, and $\alpha$ the fraction of the total scattered intensity associated with the slow density fluctuations.[8] The PCHMA sample used in this study seems to fullfil the homodyne condition because of the low value of the absolute Rayleigh ratio, $R_{VV}$. At 25 °C, $\theta$ = 90°, and $\lambda$ = 488.0 nm, this quantity amounts to $1.2 \times 10^{-5}$ cm$^{-1}$. Homodyne and heterodyne net correlation functions measured at 388 K are shown in Figure 1. For heterodyne beating we used the two-beam spectrometer described elsewhere.[21] In heterodyne detection the density correlation function $g(t)$ is directly related to $G(t)$ by

$$G(t) = A'(1 + bg(t)) \qquad (2)$$

where the base line $A'$ is proportional to $I_0^2$, the intensity of the local oscillator that beats with the scattered intensity $I_s$, and $b \sim I_s/I_0$. The correlation functions of Figure 1 plotted according

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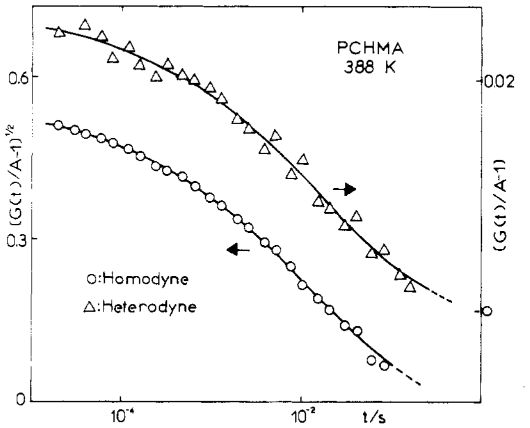

**Figure 1.** Measured net correlation functions for amorphous poly(cyclohexyl methacrylate) ($T_g$ = 374 K) at 388 K under homodyne (eq 1) and heterodyne (eq 2) conditions.

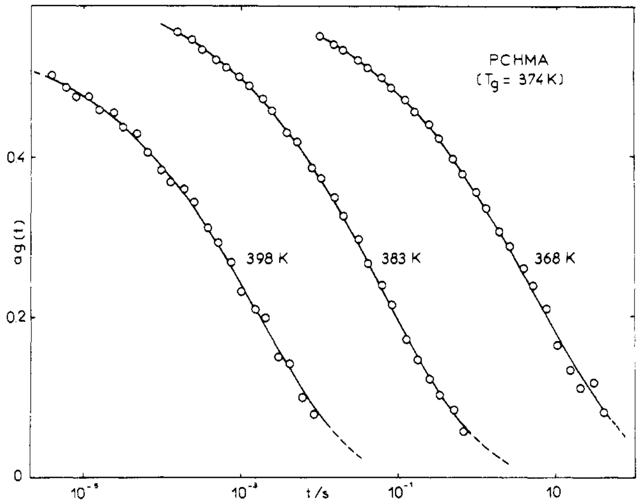

**Figure 2.** Measured time correlation functions for the density fluctuations in amorphous PCHMA at three different temperatures.

to equation 1 and 2 are very similar, and hence the values of the relaxational parameters for the two experiments are very close. The low-contrast $b$ under heterodyne condition was verified to be inversely proportional to the intensity of the local oscillator.

The amorphous poly(cyclohexyl methacrylate) (PCHMA) sample with a weight-averaged molecular weight $M_W \sim 2 \times 10^5$ was carefully prepared by thermal polymerization and kindly provided by Dr. W. Wunderlich (Röhm, Darmstadt). The measured glass transition temperature $T_g$ amounts to 374 K.

## Data Analysis

The measured intensity autocorrelation functions near and above $T_g$ were treated in the homodyne limit (eq 1). The Kohlrausch-William-Watts (KWW) decay function

$$g(t) = \exp(-(t/\tau^*)^\beta) \tag{3}$$

fits well the experimental $(G(t)/(A-1))^{1/2}$ treating $\alpha$, $\tau^*$, and $\beta$ as adjustable parameters. Figure 2 shows relaxation functions $\alpha g(t)$ for PCHMA at three different temperatures above $T_g$. The distribution parameter $\beta$ is equal to 0.37 ± 0.02 and is virtually independent of temperature in contrast to the situation in other poly(alkyl methacrylates).[6,10] Alternatively, the present behavior is similar to that reported for most bulk polymers.[1,3,22]

The relaxation function $g(t)$ probed in the PCS experiment is related to the time-dependent longitudinal compliance $D(t)$[2,4] by

$$\alpha g(t) = (D_0 - D(t))/D_\infty \tag{4}$$

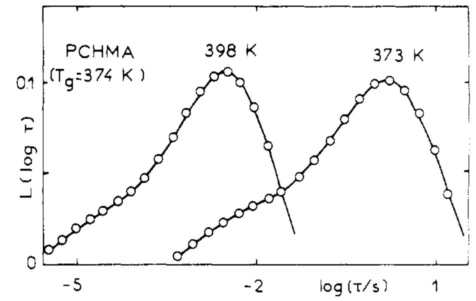

**Figure 3.** Retardation time spectra for PCHMA at two temperatures above $T_g$ obtained from the inverse Laplace transform analysis (eq 1 and 6) of the experimental correlation functions.

where $D_0$ and $D_\infty$ are, respectively, the limiting longitudinal compliances at low and high frequencies. If $D(t)$ is written in terms of the retardation spectrum $L(\ln \tau)$[17] as

$$D(t) = D_\infty + (D_0 - D_\infty)\int_{-\infty}^{\infty} L(\ln \tau)(1 - e^{-t/\tau})\, d \ln \tau \tag{5}$$

then

$$g(t) = \int_{-\infty}^{\infty} d \ln \tau \, L(\ln \tau) e^{-t/\tau} \tag{6}$$

where

$$\alpha = (D_0 - D_\infty)/D_\infty \tag{7}$$

An algorithm developed by Provencer[19] is used to extract $L(\ln \tau)$ from the experimental $\alpha g(t)$. This constrained inverse Laplace transform (ILT), has been modified to yield $L(\log \tau)$ of viscoelastic systems.[20] For amorphous poly(vinyl acetate),[4] polypropylene,[19] and polybutadiene,[22] where the correlation functions are well represented by a single KWW decay (eq 3), the numerical technique[23,24] used to compute $L(\log \tau)$ gives a result experimentally identical with the result of the ILT analysis. The latter, however, seems to reveal more clearly the double feature of the $g(t)$ in PMMA.[9,10]

Figure 3 shows the ILT results of the experimental $\alpha g(t)$ for PCHMA at two temperatures above $T_g$. As expected from the nearly constant $\beta$ and $\alpha$ values (eq 3 and 6), the shape of the $L(\log \tau)$ is rather insensitive to temperature variations. This finding, however, is in contrast to the two peak structures clearly evident in the $L(\log \tau)$ spectrum of PMMA near and above $T_g$.[9,10]

## Results and Discussion

**Primary Glass-Rubber Relaxation.** The relaxation functions $\alpha g(t)$ for the slow density fluctuations in PCHMA at a number of temperatures above $T_g$ are plotted vs log $t$ in Figure 2. The fraction of $\alpha$ of the dynamic light scattering which contributes to the relaxation function at times longer than $\sim 10^{-6}$ s is about 0.62. This light-scattering value might be compared (eq 7) with longitudinal or at least compressional compliance data which, however, are quite rare (ref 17, chapter 18). For PVAc[25] above $T_g$ the quantity $(D_0 - D_\infty)/D_\infty$, approximated by the compressional compliance, is equal to 0.69. A combination of ultrasonic and hypersonic Brillouin data can also be used to estimate $D_0$ and $D_\infty$, respectively, under adiabatic conditions.[22]

Typical distributions $L(\log \tau)$ of retardation times for the primary relaxation are shown in Figure 3. The asymmetric distributions correspond to KWW distributions with $\beta \sim 0.37$. The weak short-time shoulder is probably related to the $\beta$-relaxation reported for poly(alkyl methacrylates). The pronounced $\beta$-peak in PMMA[16,10] is strongly depressed in PCHMA due to the bulkier cyclohexyl group.[16-26]

**Table I**
**Primary Relaxation Times**

| $T$, °C | $\log \tau^{*a}$ | $\langle\log \tau\rangle^{b}$ | $T$, °C | $\log \tau^{*a}$ | $\langle\log \tau\rangle^{b}$ |
|---|---|---|---|---|---|
| 125 | -2.8 | -3.0 | 105 | -0.8 | -1.1 |
| 120 | -2.3 | -2.6 | 100 | -0.1 | -0.4 |
| 115 | -1.8 | -2.1 | 95 | 0.7 | 0.5 |
| 110 | -1.2 | -1.4 | | | |

[a] Equation 3. [b] Equation 8.

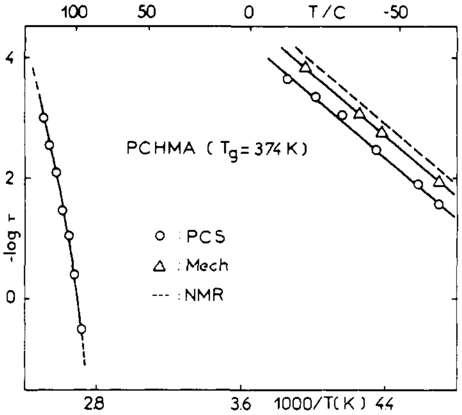

**Figure 4.** Temperature dependence of the primary and secondary relaxation time from photon correlation spectroscopic, mechanical,[16] dielectric,[26] (Δ) and NMR[33] measurements on PCHMA.

Using $L(\log \tau)$ to describe the distribution of retardation times, we write the average $\langle\log \tau\rangle$ as the first moment of $L(\log \tau)$.

$$\langle\log \tau\rangle = \int_{-\infty}^{\infty} \log \tau \, L(\log \tau) \, \mathrm{d} \log \tau \Big/ \int_{-\infty}^{\infty} L(\log \tau) \, \mathrm{d} \log \tau \tag{8}$$

The results for $\langle\log \tau\rangle$ are listed in Table I. Over the temperature range 95–125 °C the average $\langle\log \tau\rangle$ changes by 3.5 orders of magnitude with an unrealistic high Arrhenius activation energy of 77 kcal/mol. We have therefore fitted the Vogel–Fulcher–Tamman–Hesse (VFTH) equation[17]

$$\langle\log \tau\rangle = \langle\log \tau\rangle_0 + B/(T - T_0) \tag{9}$$

to the experimental relaxation times. In the VFTH equation, which is an alternative form of the WLF equation, $\langle\log \tau\rangle_0$, $B = c_1 c_2$ and $T_0 = T_g - c_2$ are characteristic parameters, where $c_1$ and $c_2$ are the WLF coefficients.

To determine these parameters by using the PCS data obtained over a fairly narrow temperature range, we have used a fixed $c_2 = 90$ K similar to that found from mechanical measurements on poly($n$-hexyl methacrylate) over a larger temperature range.[27] Using this value for $c_2$ and $T_g = 374$ K, we obtain $\langle\log \tau\rangle_0 = -12.8$ ($\tau$ in s), $B = 1120 \pm 108$ K and $c_1 = 12.5 \pm 1$. Within experimental error linear plots of $\langle\log \tau\rangle$ vs $1/(T - T_0)$ are accomplished by using trial $c_2$ values in the range $90 \pm 15$ K. Figure 4 shows the temperature dependence of the average $\langle\log \tau\rangle$ for the primary relaxation represented well by eq 9. Equation 9 has been also used to fit the relaxation time $\tau_0^*$ (Table I) of the KWW equation (eq 3). Using again a fixed $c_2 = 90$ K, we obtain $\log \tau_0^* = -12.4$ and $B = 1112$ K. As expected from the nearly constant $\beta$, the activation parameter $B$ is experimentally the same for both representations of $g(t)$. The primary relaxation process in PCHMA has also been studied by dynamic mechanical[16,26] and dielectric[26,28] techniques. The temperature dependence of the relaxation time $\tau = (2\pi f_m)^{-1}$, where $f_m$ is the frequency at the loss permitivity maximum, yields values similar to the VFTH parameters, $\log \tau_0 = -12.4$ and $B = 1139$ K.[26,29]

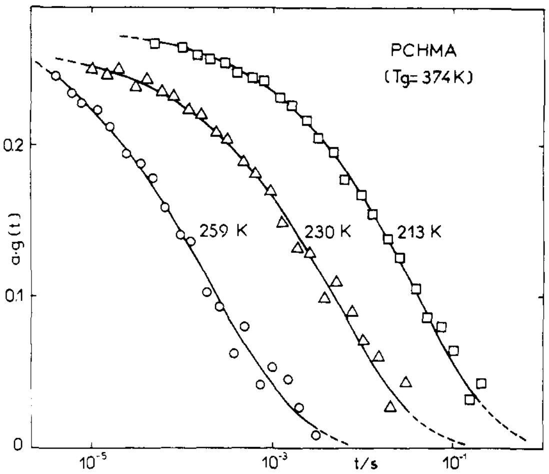

**Figure 5.** Measured time correlation functions for the density fluctuations in glassy PCHMA at three temperatures.

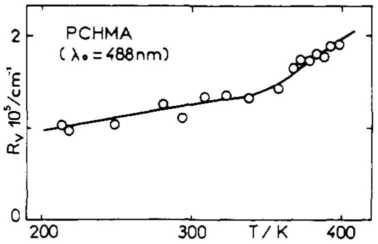

**Figure 6.** The absolute light-scattering intensity $R_V$ at $\theta = 90°$ as a function of temperature.

The activation parameter $B$ in eq 9 has so far been viewed through apparently different theoretical approaches. In the simple three-state rotational isomerization model[30] $B$ is related to the activation energy of the rotation about the main chain bonds, with $E = 2.303RB$ ($R$ being the gas constant). The energy $E$, which incorporates interactions between polymer segments,[30] amounts to 5.1 kcal/mol and is somewhat higher than the value for PMMA.[10] In the free volume model, $B$ is related to the free volume expansion coefficient $\alpha_f = \gamma/(2.303B) \approx 3.9 \times 10^{-4}$ K$^{-1}$ ($\gamma$ is a constant nearly equal to 1).[17]

**Secondary Relaxation in the Glassy State.** Although well below $T_g$ the primary relaxation times are too slow to be observed by PCS, there is significant dynamic light scattering from the glassy PCHMA. Figure 5 shows experimental correlation functions treated in the homodyne limit (eq 1). Several important features emerge from these relaxation functions. They show strong evidence of a leveling off at short times, a narrower shape, and a smaller fraction than the primary relaxation functions of Figure 2. If we follow the same data analysis pursued for the correlation functions above $T_g$, the KWW fit (eq 1 and 3) to the experimental $G(t)$ in the range -60 to -14 °C yields $\beta = 0.49 \pm 0.03$ and $\alpha = 0.29 \pm 0.02$. The latter value is probably underestimated due to partial heterodyning of the signal by quasi-static density fluctuations, which also lead to slower relaxation times.

To provide a crude estimate of the scattering intensity arising from the "static" fluctuations in the glassy state, we have measured the total absolute Rayleigh ratio $R_V$ at $\theta = 90°$ and temperatures above and below $T_g$. The temperature dependence of $R_V$, which is proportional to the mean-square density fluctuations, is displayed in Figure 6. The two different temperature ranges in the vicinity of $T_g$ present a general behavior of amorphous polymers and have been discussed elsewhere.[31,32] The difference between intensities measured and extrapolated into the

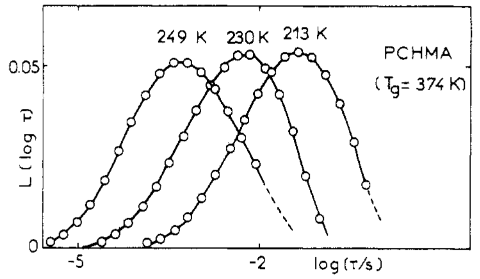

**Figure 7.** Retardation spectra for the glassy PCHMA at three temperatures obtained from the ILT analysis (eq 1 and 6) of the experimental correlation functions.

**Table II**
**Secondary Relaxation Times**

| $T$, °C | ⟨log $\tau$⟩ | $T$, °C | ⟨log $\tau$⟩ |
|---|---|---|---|
| -14 | -3.6 | -43.2 | -2.4 |
| -24.2 | -3.3 | -55 | -1.9 |
| -33 | -3.1 | -60 | -1.6 |

glassy region represents the contribution of the frozen-in fluctuations, which can act as a source of heterodyne scattering. In the temperature range 210–260 K the ratio of the dynamic to the static component of the total scattered intensity is at least one. Under these conditions the relaxation time $\tau^*_{ho}$ obtained from a correlation function, treated, however, as if it were in the pure homodyne limit, is 3 times larger than that obtained from the same correlation function correctly treated in the partially heterodyned limit (combination of eq 1 and 2).[15] Pure heterodyne detection (eq 2) and $\beta = 0.5$ (eq 3) would yield $\tau_{ho}/\tau_{he} = 4$. The effect of the beating conditions on the shape parameter $\beta$ is experimentally negligible. Nevertheless, since the fraction $\alpha$ is still comparable to that for the primary relaxation functions and the additional terms in eq 1 resulting from partial heterodyning are uncertain, we have treated the experimental correlation functions below $T_g$ in the pure homodyne limit. Alternatively, the low intensity in the glassy state precludes a full heterodyne experiment similar to that performed above $T_g$ (Figure 1).

Figure 7 shows the ILT results of the experimental correlation functions at three temperatures far below $T_g$. As expected from the nearly constant $\alpha$ and $\beta$ values (eq 1 and 3), the shape of the $L(\log \tau)$ is insensitive to temperature variations. Furthermore, due to the rather high $\beta$ value the distribution $L(\log \tau)$ is symmetric and quite narrow relative to the width and shape of the $L(\log \tau)$ (Figure 3) above $T_g$.

The values of the average ⟨log $\tau$⟩ computed from eq 8 are listed in Table II and are shown in the Arrhenius plot of Figure 4 along with the primary relaxation times. Whereas the latter (which are controlled by the average free volume) exhibit a VFTH temperature dependence (eq 9), the secondary relaxation times follow the Arrhenius equation

$$\langle \log \tau \rangle = \langle \log \tau \rangle_0 + H/(2.303RT) \qquad (10)$$

where $\langle \log \tau \rangle_0 = -13.4$ ($\tau$ in seconds) and $H = 11.5$ kcal/mol.

Extensive dynamic shear and tension measurements on PCHMA have been performed.[16,17,26] The maximum loss tangent (tan $\delta$) from shear and extension mechanical measurements and recent NMR correlation times[33] are shown in Figure 4 for comparison. The resulting activation energy of 11.3 ± 0.2 kcal/mol, which agrees very well with the light scattering value, was assigned to the energy required for the chair–chair inversion of the cyclohexyl ring in a two-potential-well model. This specific internal motion is mechanically active through the strong coupling of the group responsible for relaxation and its surrounding matrix. However, the relaxation parameters hardly depend on the environment.[34] The secondary light-scattering times of Figure 4 are insensitive to changes in free volume of the glassy PCHMA as produced by annealing procedures. These thermal treatments change only the average free volume whereas free volume fluctuations are not affected, as was shown in small-angle X-ray experiments.[35] If there exists a direct dependence of secondary relaxations on the mean-square free volume fluctuations as recently reported for plasticized PMMA and polycarbonate,[18] then changes in thermal history do not affect secondary relaxations. The difference (by a factor of 2) between the values of light scattering and mechanical relaxation times in Figure 4 may therefore be due to the presence of some "static" segmental fluctuations in the glassy sample, as discussed above.

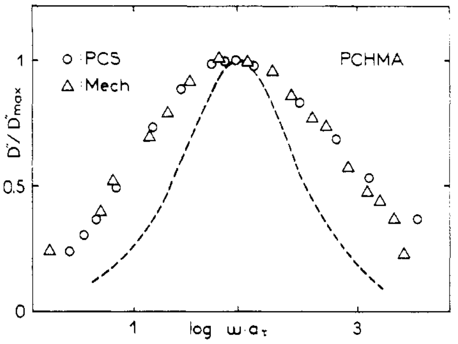

**Figure 8.** Normalized dynamic longitudinal compliance (○) computed from eq 11 by using the relaxation function $g(t)$ for the secondary relaxation in glassy PCHMA. Open triangles denote mechanical tan $\delta$ data[17] reduced to −60 °C. Dashed line is prediction from a single relaxation time spectrum.

We have chosen PCHMA for this investigation on account of its sharp tan $\delta$ peak measured as a function of temperatures at some frequencies.[11,17] The tan $\delta$ reduced at −60 °C is plotted versus reduced frequency ($\omega\alpha_T$) ($\alpha_T$ being the shift factor) in Figure 8. This normalized plot gives a rather sharp peak with a width only about twice the width of a single-valued spectrum, also drawn in Figure 8. Alternatively, the dynamic longitudinal compliance D'' ($\omega$) was constructed from the PCS relaxation function $g(t)$ according to

$$D''(\omega) = (D_0 - D_\infty)\omega \int_{-\infty}^{\infty} \cos \omega t \, g(t) \, dt \qquad (11)$$

The $g(t)$ was represented by the KWW equation (eq 3) with $\beta = 0.49$, and a computer program employing numerical integration was used to obtain the normalized values of $D''(\omega)/D''_{max}$. The results of the calculations are plotted in Figure 8 for comparison. Slight adjustments on the frequency scale are necessary (see Figure 4) to make the maxima coincide. Within experimental uncertainty the agreement between the two experimental curves for the secondary relaxation in glassy PCHMA is very good. Finally, it is worth noting that no time–temperature reduction is involved in the light-scattering experiment, which measures $D(t)$ isothermally over a broad dynamic range.

## Conclusions

This paper deals with a new application of photon correlation spectroscopy to the study of secondary relaxation in glassy polymers. It was shown that there is significant (~30%) dynamic light scattering from PCHMA below $T_g$ (=374 K) with decay times longer than $10^{-6}$ s. The correlation functions for the slow density fluctuations were analyzed quantitatively in the homodyne limit. The computed formal retardation spectrum and the Arrhenius activation energy agree very well with dynamic mechanical, dielectric, and NMR data associated with the chair–chair inversion of the cyclohexyl ring.

Above $T_g$ the major part ($\sim$60%) of the total light-scattering intensity is due to the slow density fluctuations, and the experimental relaxation functions are dominated by the primary glass–rubber relaxation. The retardation spectrum shows a single-peak structure and displays a strong temperature dependence representated by the VFTH free volume equation.

We may finally note that the use of a carefully prepared polymer sample which displays only intrinsic scattering is a crucial point.

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**Registry No.** PCHMA, 25768-50-7.

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# End-to-End Cyclization of a Pyrene End-Capped Poly(bisphenol A–diethylene glycol carbonate)[1a]

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ABSTRACT: The cyclization dynamics of pyrene end-capped bis(bisphenol A–diethylene glycol carbonate) in dilute solution was investigated through studies of intramolecular fluorescent excimer formation. Steady-state and fluorescence decay data were used to determine all the rate constants for the cyclization of three samples having different molecular weights. Measurements performed in acetone, acetonitrile, and toluene showed the influence of both viscosity and quality of the solvent. The behavior of this type of chain was found to be totally classical with respect to the results already known for polystyrene. However, a polycarbonate chain shows a greater extent of cyclization than a polystyrene chain having the same number of backbone bonds. This could be explained by the high flexibility of the diethylene glycol moiety and the angular structure of the bisphenol A unit.

End-to-end cyclization of polymer chains has been the focus of numerous investigations for many years.[3] These studies are prompted by new developments in the theory of diffusion-controlled reactions of polymers,[4] coupled with new photophysical tools[5] for measuring cyclization events. Particularly meaningful information can be obtained from fluorescence measurements on pyrene end-capped macromolecules where cyclization is detected by the formation of a fluorescent intramolecular excimer. Here one can combine steady-state and fluorescence decay measure-

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