Macromolecules 1991, *24*, 1955-1961

Relaxation Processes in a Poly(cyclohexyl methacrylate)/Additive System As Studied by Photon Correlation, Dielectric Relaxation, and Mechanical Relaxation Spectroscopy

G. Floudas and G. Fytas*

Research Center of Crete, P.O. Box 1527, 711 10 Heraklion, Crete, Greece

E. W. Fischer

Max-Planck-Institut für Polymerforschung, P.O. Box 3148, 6500 Mainz, F.R.G.

Received June 4, 1990; Revised Manuscript Received September 4, 1990

ABSTRACT: Dynamic light scattering (PCS), mechanical relaxation (MR), and dielectric (DR) relaxation techniques are employed to examine the effect of the additive di(2-ethylhexyl) phthalate (DOP) on the primary and secondary relaxations of high molecular weight poly(cyclohexyl methacrylate) (PCHMA) in the glassy and rubbery states within the temperature range 133-430 K and with DOP content up to 15%. The results indicate that the primary (α) glass-rubber relaxation is shifted to lower temperatures with increasing DOP content, and the width of the distribution of relaxation times is insensitive to composition variations. When the same data analysis is employed, an agreement between PCS and MR results is observed, whereas the interrelation of the primary relaxation times from PCS and DR measurements on plasticized PCHMA is subject to some uncertainties in the description of the dipole autocorrelation functions with increasing DOP composition. The average primary relaxation times exhibit a strong temperature dependence, and when the same data analysis is employed, we found a quantitative agreement between PCS and MR times, whereas the agreement between PCS and DR times was rather semiquantitative. Sub-T_g or β-relaxation was enchanced with additive content in contrast to the γ-relaxation associated with the chair-to-chair inversion of the cyclohexyl ring. The latter relaxation times exhibit an Arrhenius temperature dependence with activation parameters independent of the additive content and of the technique used. The secondary (γ) intensity suppression effect, reported in some polymer/additive systems, was not observed in the PCHMA/DOP system.

Introduction

Different techniques have been used to study the dynamics of relaxation processes: dielectric relaxation (DR),[1] mechanical relaxation (MR),[2] ultrasonic relaxation (US),[3] NMR,[4] time-resolved optical spectroscopy,[5] and dynamic light scattering techniques.[6] Although dielectric relaxation and mechanical relaxation have long been used to study the dynamics of glassy polymers, photon correlation spectroscopy (PCS) has only recently been utilized to investigate the glassy state.[7] For weakly anisotropic scatterers, such as segments of poly(cyclohexyl methacrylate) (PCHMA), the dominant contribution to the light scattering intensity arises from density fluctuations. Fully relaxed density correlation functions below and above T_g have been obtained for PCHMA.[7] In a recent publication[8] we have reported PCS measurements on the density and concentration fluctuations of plasticized PCHMA samples in the temperature range from near T_g to T_g + 150 K. It is tempting to continue this study at low temperatures.

PCHMA was studied earlier mostly by mechanical,[9] dielectric,[10,11] and, more recently, NMR[12] techniques. It shows three relaxation processes below the α-relaxation originating at the T_g: a hindered β-relaxation, a well-defined (and well separated from the α-relaxation) γ-relaxation with a reported temperature-independent activation energy of 11.3 ± 0.2 kcal/mol associated with the chair-to-chair inversion of the cyclohexyl ring, and finally a δ-relaxation at low temperatures.

It is well-known that secondary relaxations determine the physical properties of bulk polymers, and the occurrence of these relaxations has been associated with an intrinsic property of the glassy state.[13] It is also known that additives can suppress the secondary relaxations of a class of polymers.[14] The secondary suppression effect has been studied in a number of polymers and additives mainly by MR[14] and pulsed ^{2}H NMR.[14,15] Although its appearance was found in a class of polymers (i.e., bisphenol-A polycarbonate), its absence was reported in another class of polymers (i.e., poly(methyl methacrylate)). The main purpose of the present study is twofold: first, to investigate the effect of the additive di(2-ethylhexyl) phthalate (DOP) on the primary (α) and secondary relaxations (β and γ) of PCHMA and to account for the effect in terms of recent theoretical approaches, and second, to directly compare the relaxation times obtained from PCS, DR, and MR. In this context, earlier reports[16,17] argue that dynamic light scattering relaxation times cannot be directly compared with standard dielectric and mechanical relaxation data. Recently, a new method of data analysis has been proposed in the study of the dynamics of density fluctuations by DR and PCS in poly(phenylmethylsiloxane) (PPMS).[18] We will adopt this method for the present analysis.

Experimental Section

Samples. The amorphous PCHMA/DOP samples with 5%, 10%, and 15% DOP and a weight-averaged molecular weight $M_w \sim 2 \times 10^5$ were carefully prepared by thermal polymerization. The samples were kindly provided by Dr. M. Stickler (Röhm, Darmstadt). The glass transition temperature T_g, measured with a DSC (heating rate 10 K/min), amounts to 82, 72, and 64 °C for 5%, 10%, and 15% DOP, respectively. Alternatively, the value of T_g can be computed from the T_g's and the expansion coefficients of the bulk PCHMA and neat DOP in the functional form given in ref 19. The resulting values were at most 5 °C different, i.e., 86, 72, and 59 °C, respectively, for the plasticized PCHMA with 5%, 10%, and 15% DOP.

Measurements. The correlation functions $G(t)$ of the polarized light scattered intensity were taken at a scattering angle of 90° at different temperatures (213-398 K). The light source was an argon ion laser (Spectra Physics Model 2020) operating

0024-9297/91/2224-1955$02.50/0

in the single mode at 488 nm with a stabilized power of 200 mW. The single-clipped intensity autocorrelation function $G(t)$ over 4.3 decades in time was measured in one run with a 28-channel Malvern log-lin correlator (K-2027). The desired normalized relaxation function $g(t)$ associated with the density fluctuations is computed from $G(t)$ through the equation

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

where A is the baseline measured at long delay times t, f is the instrumental factor, and α is the fraction of the total scattered intensity associated with the slow density fluctuations. The PCHMA and PCHMA/DOP samples used in this study seem to display homodyne scattering as indicated from the low value of the Landau-Placzek Rayleigh-Brillouin intensity ratio.[20] The latter attains the value 4 and 5 for PCHMA and PCHMA/DOP-(15%), respectively, at 20 °C.

The real and imaginary parts of the complex dielectric permitivity, ϵ' and ϵ'', were measured with a frequency-response analyzer (Solartron Schlumberger 1254, frequency range from 10^{-4} to $\sim 10^5$ Hz). The frequency-response analyzer employed a high-impedance buffer amplifier of variable gain. The sample capacitor was made of two gold-plated stainless steel electrodes, with a separation of 200 μm being maintained by three small fused-silica spacers. The capacitor was placed in a custom-made cryostat described elsewhere.[21] The sample temperature was controlled by a stream of temperature-controlled nitrogen gas in the temperature range 212-430 K, with a stability better than ±0.02 K.

The dynamic mechanical results were obtained with a Rheometrics RMS 800 spectrometer. The apparatus directly yields the storage modulus (G'), loss modulus (G''), and tan δ values. The measurements were carried out in the temperature range 133-423 K and for ten frequencies between 0.1 and 100 rad/s.

Data Analysis

The Kohlrausch-Williams-Watts (KWW) decay function

$$g(t) = \exp(-(t/\tau^*)^\beta) \tag{2}$$

is commonly used to represent the experimental $[(G(t)/A) - 1]^{1/2}$ (eq 1), treating α, τ^*, and β as adjustable parameters. The value of β is a measure of the width of the distribution of relaxation times implied by the nonexponential character of the relaxation function. The average relaxation time is then given by

$$\langle\tau\rangle = (\tau^*/\beta)\Gamma(1/\beta) \tag{3}$$

where $\Gamma(1/\beta)$ is the gamma function. It is also possible to describe the experimental data using the Laplace transformation of a distribution of retardation times $L(\ln \tau)$

$$g(t) = \int_{-\infty}^{+\infty} \mathrm{d} \ln \tau \, L(\ln \tau) e^{-t/\tau} \tag{4}$$

An algorithm developed by Provencer[22] is used to extract $L(\ln \tau)$ from the experimental $\alpha g(t)$. Using $L(\log \tau)$ to describe the distribution of retardation times, we write the average $\langle \log \tau \rangle$ as the first moment of $L(\log \tau)$:

$$\langle \log \tau \rangle = \int_{-\infty}^{+\infty} \log \tau \, L(\log \tau) \, \mathrm{d} \log \tau \Big/ \int_{-\infty}^{+\infty} L(\log \tau) \, \mathrm{d} \log \tau \tag{5}$$

The $\langle \log \tau \rangle$ values are plotted in Figure 1 for the PCHMA and PCHMA/DOP mixtures versus $1/T$ in the temperature range 213-483 K.

The dielectric relaxation results have been fitted to the empirical model of Havriliak and Negami[23] (HN):

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{[1 + (i\omega\tau)^\alpha]^\gamma} \qquad (0 < \alpha, \gamma \le 1) \tag{6}$$

where ϵ_∞ and ϵ_0 are the values of the complex dielectric function on the high- and low-frequency side of the relaxation process, τ is the mean relaxation time, and the parameters α and γ describe the broadening and asymmetry of the relaxation time distribution, respectively.

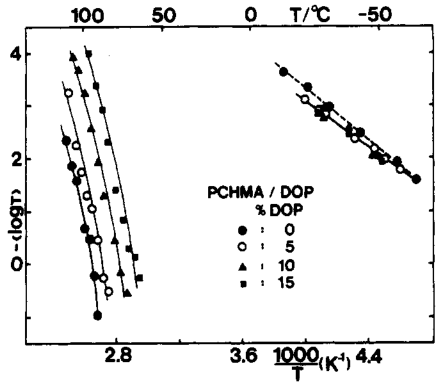

Figure 1. Temperature dependence of the average time $-\langle\log \tau\rangle$ (eq 5) for the primary (α-) and secondary (γ-) relaxations in bulk and plasticized PCHMA investigated by photon correlation spectroscopy (PCS).

In order to compare the data measured with dielectric spectroscopy in the frequency domain with the results of PCS measured in the time domain, we have transformed the dielectric data in the time domain. This procedure mirrors the work by Boese et al.[18] in a comparison between PCS and DR results of poly(phenylmethylsiloxane) (PPMS). The normalized relaxation function $\varphi(t)$ is related to $\epsilon''(\omega)$ by the well-known Kramers-Kronig relation

$$\varphi(t) = \frac{2}{\pi} \int_0^\infty \frac{\epsilon''(\omega)}{\epsilon_0 - \epsilon_\infty} \frac{\cos(\omega t)}{\omega} \, \mathrm{d}\omega \tag{7}$$

The time-dependent function $\varphi(t)$ is directly related to the dipole moment time correlation function which describes the randomization of the dipole moment vector in time due to molecular motion. Thus[24]

$$\varphi(t) = \sum_{i,j}^{N} \langle \mu_i(0) \, \mu_j(t) \rangle \Big/ \sum_{i,j}^{N} \langle \mu_i(0) \, \mu_j(0) \rangle \tag{8}$$

where $\mu_j(t)$ denotes the elementary dipole moment in the chain at time t. The analytical form of $\epsilon''(\omega)$ given in ref 23 is used to calculate numerically the autocorrelation function $\varphi(t)$ for different temperatures. The resulting correlation function $\varphi(t)$ is very well represented by the KWW equation. Now a direct comparison between PCS and DR relaxation times can be made.

Before we compare our dynamic mechanical results with the PCS results, we note that the maximum loss ($G''_{\max}$) occurs at a frequency higher than $\langle\tau\rangle^{-1}$ for values of β typical for polymers. We have corrected our $\langle\tau\rangle$ measured by mechanical relaxation (MR), using the distribution parameter obtained from PCS and the table of ref 17. The above procedure is valid only if the distribution of relaxation times is the same for both PCS and MR.

Results and Discussion

α- and β-Relaxations. We have used eqs 1 and 2 to represent the experimental correlation functions (ref 8, Figure 3) at temperatures near T_g. The fraction α of the dynamic light scattering which contributes to the relaxation function at times longer than 10^{-6} s is about 0.5 for the plasticized polymer and higher (0.6) for the unplasticized polymer, the difference being due to the presence of concentration fluctuations in the former. The distribution parameter β amounts to 0.37, 0.40, 0.38, and 0.36

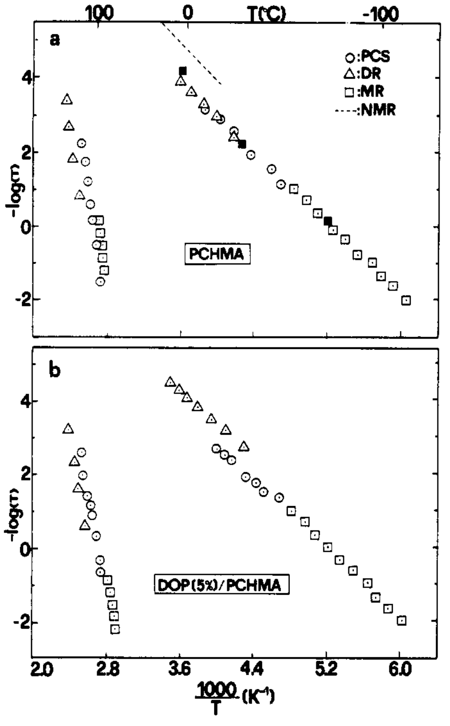

Figure 2. (a) Temperature dependence of $-\log\langle\tau\rangle$ for the α- and γ-relaxations in bulk PCHMA investigated by PCS, dielectric relaxation (DR) and Mechanical relaxation (MR): symbols are for some of the mechanical results of Heijboer; (- - -) NMR results. (b) Temperature dependence of $-\log\langle\tau\rangle$ for the 5% plasticized PCHMA.

for the 0%, 5%, 10%, and 15% DOP/PCHMA mixtures and is insensitive to temperature variations. The average relaxation time $\langle\tau\rangle$ (eq 3) is q-independent[8] as expected for local density fluctuations when examined with light scattering q's. In contrast the decay rate of the concentration time correlation function in plasticized PCHMA/DOP systems clearly exhibits a q^2 dependence.[8]

Figure 2 shows the temperature dependence of the log $\langle\tau\rangle$ (which is different from the $\langle\log\tau\rangle$ plotted in Figure 1) for the primary (α) and secondary (γ) relaxations of PCHMA and DOP(5%)/PCHMA. If we choose an Arrhenius temperature dependence to describe our primary relaxation times, we obtain an unrealistically high activation energy of ~70 ± 10 kcal/mol for both unplasticized and plasticized samples. On the other hand, it is known that the Vogel–Fulcher–Tammann–Hesse (VFTH) equation

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

represents well the experimental relaxation times near T_g. In the VFTH equation $\log\langle\tau\rangle_0$, $B = c_1c_2$, and $T_0 = T_g - c_2$ are characteristic parametes and c_1 and c_2 are the WLF coefficients. To determine these parameters from our experimental PCS data over a narrow temperature range, we have used a fixed $c_2 = 90$ K.[7] Using this value for c_2 and the calculated T_g's, we obtain $B = 1360 \pm 120$ K and $\log\langle\tau\rangle_0 = -12.5 \pm 1$ (τ in seconds) independent of DOP composition. We should note here that the calculated T_g values were used to construct a plot of the average primary relaxation times at temperatures equidistant from their T_g's (ref 8, Figure 6).

Figure 2 includes the primary relaxation times as measured by dynamic mechanical and dielectric techniques on the same samples used in the PCS study. The $\epsilon''(f)$ data (Figure 3) were described by a single HN (eq 6), which was then used to compute the dipole–dipole correlation function (eq 8). The latter is well described by the stretched exponential function (eq 2) with a temperature-independent distribution parameter, β, equal to 0.38 ± 0.02 for the unplasticized polymer, in excellent agreement with the β (=0.37 ± 0.002) value obtained from PCS. For the 5% plasticized polymer, $\beta = 0.32 \pm 0.03$ with a small temperature variation, whereas for the 10% and 15% DOP concentration the distribution parameter β changes drastically with temperature (from 0.45 at high temperatures to 0.22 at low temperatures), in contrast to the usual situation of nearly constant β (and about 0.35) reported for most bulk polymers examined by PCS.[6] Similar abnormal behavior has been observed with PCS in poly(alkyl methacrylates) and was interpreted to be due to the overlap of two relaxation processes.[25-27] Figure 3 demonstrates this effect for the 10% plasticized polymer. A distribution parameter as low as 0.27 is necessary to fit the constructed KWW at 110 °C, due to the high asymmetry of the $\epsilon''(f)$ curve at high frequencies. As discussed below (Figure 4), the observed broadening of the distribution of relaxation times (decrease of β) with increasing DOP concentration may be due to the enhancement of the β-relaxation in PCHMA. On the other hand, the observed decrease of the β value with descending temperature is consistent with the expected larger separation in the time scale of the α- and β-modes at low temperatures. Of course, on the grounds of an earlier polystyrene/DOP dielectric study[28] one cannot exclude the possibility that the additive contributes to the dielectric loss at the highest concentration used. However, the relative contribution due to the additive is expected to be rather small, at least for the 10% DOP plasticized PCHMA; the maximum $\epsilon''_{\max}$ due to the similar plasticizer di-n-butyl phthalate (DBP) in a 9.6% DBP/PS system[28] is about 0.003. Nevertheless, the use of an additive possessing lower dielectric loss could elucidate this point.

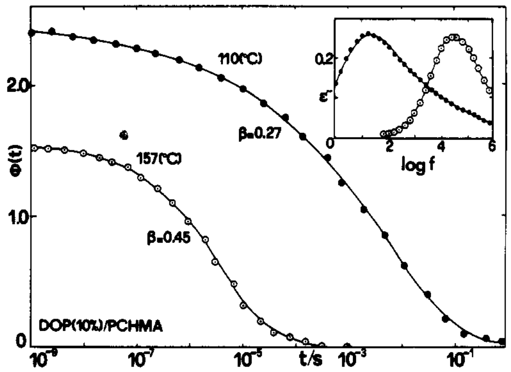

Figure 3. Dipole–dipole correlation function constructed from the HN parameters at 110 and 157 °C. The solid line denotes the fit of the KWW equation. The $\epsilon''(f)$ values versus log f are also shown.

Inspection of the primary PCS and DR relaxation times in Figure 2 shows that DR times are longer. Nice agreement between PCS and DR primary relaxation times has been reported so far in bulk PPMS,[18] for which the dipole moment lies in the chain backbone and only the primary α-relaxation was probed, resulting in a single $\epsilon''(f)$ peak. The agreement between the two methods led to the conclusion that the collective dynamics measured by light scattering and the molecular dynamics of reorienting dipoles are the same in polymer melts. In fact, one of the goals of the present study is to test this hypothesis/prediction for other polymers as well. Since PCHMA and PCHMA/DOP melts seem to deviate from the prediction above, we believe that more experimental work is needed

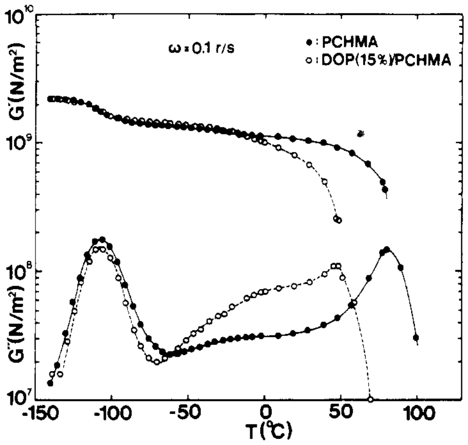

Figure 4. Storage G' and loss G'' moduli at 0.1 rad/s (0.016 Hz) as a function of temperature for bulk and plasticized PCHMA with 15% DOP.

in polymer melts to settle the matter. Based on eq 9, the finding that the α-relaxation times from the DR experiment are longer than the corresponding PCS values (Figure 2)—while exhibiting similar temperature dependences—can be rationalized if the reorienting side-chain dipoles of PCHMA (probed by DR) are "frozen in" at a temperature T_0 higher than the T_0 for the local segmental fluctuations (monitored by PCS). The latter observation implies a lower $c_2 = (T_g - T_0)$ value as determined by DR.

The mechanical primary relaxation times, determined by the frequency of maximum loss, corrected for the distribution of relaxation times, are also plotted in Figure 2. PCS and MR times are in good agreement for the 0% and 5% DOP samples. Figure 4 displays the storage G' and the loss G'' moduli at 0.1 rad/s as a function of temperature for PCHMA and DOP(15%)/PCHMA samples within the temperature range -150 to +120 °C. The main effect of the plasticizer in the T_g region is a decrease in the temperature of the α-relaxation at constant frequency due to the lower T_g value of the plasticizer[9,14] (T_g(DOP) = 184 K).[19] Additionally, it was found in plasticized polystyrene[29] with tricresyl phosphate (TCP) that the width of the retardation spectrum associated with the α-relaxation was insensitive to a variation in plasticizer content. This finding is in accordance with the virtually concentration-independent shape parameter β describing the density correlation functions and with the breadth ΔT of the conventional thermodynamic T_g, which was found surprisingly to be rather insensitive (within 5–10 K) in the plasticized PCHMA samples. An intriguing feature of Figure 4 is the existence of an additional relaxation below T_g, which is enhanced with the addition of DOP. This feature offers an explanation for the asymmetric broadening of the dielectric α-relaxation (Figure 3), which apparently does not seriously affect $G(t)$ above T_g.

Thermally stimulated depolarization current (TSDC) and thermally stimulated creep (TSC) techniques[30] have been applied to the study of sub glass transition temperature relaxation processes. The conclusion is that these sub-T_g relaxations (also called α'-relaxations) could be considered as some β-like precursor of the high-temperature α-relaxation. It is further predicted that these would be present in all kinds of glasses with a varying intensity. Internal friction measurements on metal glasses[31] revealed a sub-T_g relaxation occurring at a temperature of about 20 K below T_g. In contrast to the primary (α) glass–rubber relaxation, this sub-T_g relaxation is described by a very broad distribution of relaxation times and relatively low activation energies which probably arise from free-volume fluctuations in the glass. It is further suggested that the sub-T_g relaxation is a process distinctive from other secondary relaxations in that it appears at different temperatures and shows a strong decrease upon annealing at temperatures near T_g.

The above-mentioned sub-T_g relaxation is in agreement with the model of hierarchically constrained dynamics[32] in glassy materials. In this model, fast degrees of freedom successively constrain slower ones, generating the observed broad range of relaxation times. Dynamic Monte Carlo simulations of polymeric chains[33] support these ideas. It is suggested that local free-volume fluctuations act as the gating mechanism for long-distance diffusion of free volume, giving rise to longer distance motions associated with the glass transition. These phenomena can also be discussed in terms of recent theories[34,35] for the rheology of the glassy state, according to which the structure of a glass consists of randomly distributed regions of low- and high-density sites (called "defects"). Under the effect of mechanical stress these defects undergo shear deformation which leads to the nucleation of sheared microdomains and the appearance of a β-relaxation. During a long period of stress, these microdomains expand through hierarchically constrained motions and propagate at longer distances to yield the α-relaxation. These theories consider the β-relaxation as a precursor of the α-relaxation.

On the other hand, this β-relaxation could have a specific molecular origin, as was proposed by Heijboer.[9,36] In poly(methyl methacrylate) (PMMA) the molecular mechanism responsible for the β-relaxation was assigned partially to the rotation of the alkoxycarbonyl group and partially to main-chain motions[37] or movements of the neighboring side groups.[38] A weak short-time shoulder is also present in the bulk PCHMA and PCHMA/DOP samples as revealed by the inverse Laplace transformation (ILT) procedure on our PCS data, (ref 7, Figure 3, and ref 8, Figure 5). The well-defined β-peak in PMMA[36,39] is strongly depressed in PCHMA due to the bulkier cyclohexyl group.[7,11,36] Our β-maximum (Figure 4) at 0.1 rad/s is about 20% higher than in ref 9 at 6.3×10^{-4} rad/s. The effect of DOP on the intermolecular interactions in PCHMA is stronger than that of dibutyl phthalate (DBP) in PMMA.[9] The observed increase in magnitude with DOP content might be due to an enhanced mobility of the cyclohexylcarbonyl group (removal of complete blocking) as a result of an increased mobility of the main chain.[40]

γ-Relaxation. In a recent PCS study[7] it was shown that bulk PCHMA displays a significant amount of dynamic light scattering even at temperatures well below T_g. This also applies to the plasticized polymer as is evident from the experimental correlation functions in the temperature range -60 to -14 °C (Figure 5). Following the same data analysis employed for the correlation functions above T_g, the KWW fit to the experimental $G(t)$ yields $\beta = 0.5 \pm 0.05$ and $\alpha \sim 0.3$ for both unplasticized and plasticized samples. On the basis of the low intensity associated with the detected process and the relatively small Landau–Placzek intensity ratio displayed by the samples,[20] we have treated the experimental correlation functions, below T_g, in the homodyne limit (eq 1).[7]

Figure 5 shows experimental correlation functions for the unplasticized PCHMA and for the plasticized PCHMA with 5% and 15% DOP at 224 K along with the corresponding ILT results of the above correlation functions. A pertinent feature of Figure 5 is the insensitivity of the width of the distribution of retardation times to the

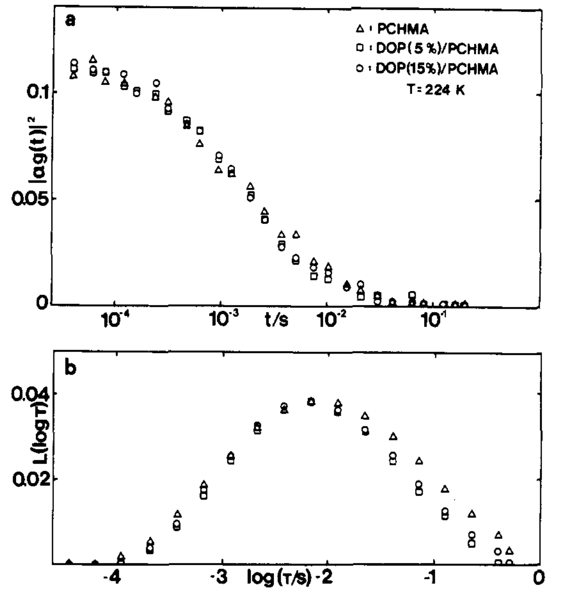

Figure 5. (a) Measured correlation functions for density fluctuations in bulk and plasticized PCHMA at 224 K. (b) The corresponding retardation time spectra $L(\log \tau)$ (eq 4) at 224 K.

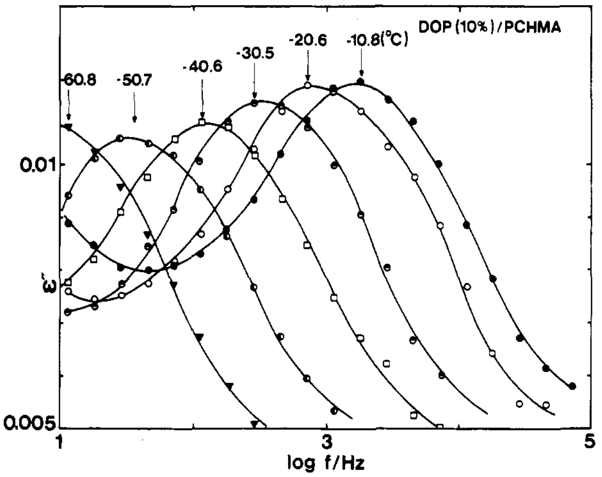

Figure 6. $\epsilon''(f)$ versus $\log f$ for DOP(10%)/PCHMA at different temperatures as indicated.

variation of additive concentration, as is expected from the nearly constant β-parameter of the KWW equation. The γ-relaxation times thus determined have been represented by the Arrhenius equation

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

with activation parameters $\log \langle \tau \rangle_0 = -12.8, -10.8, -11.1$, and -11.9 (τ in seconds) and $B = 11.3, 9.3, 9.7$, and 10.5 (in kcal/mol) for the 0%, 5%, 10%, and 15% samples, respectively. The Arrhenius relation is an appropriate description of the experimental times, and the exhibited weak temperature dependence is in contrast to that of the α-relaxation times (Figure 1).

The dielectric loss curves ϵ'' for the γ-relaxation have been described again by the HN model (eq 6) from which the dipole moment correlation function was constructed (eq 7). The subsequent KWW fit to these correlation functions yields $\beta = 0.35 \pm 0.02$ independent of temperature and additive content. Typical loss curves are shown for the DOP(10%)/PCHMA sample in Figure 6. The average relaxation times obtained from the correlation functions can be represented by an Arrhenius dependence (eq 10). The activation parameters were $\log \langle \tau \rangle_0 = -12.2 \pm 1$ and $B = 10.8 \pm 0.5$ kcal/mol for all samples. An alternative way of fitting the dielectric loss curves below T_g is to use two HN equations due to the asymmetry at low frequencies (Figure 6). This procedure results in $\beta = 0.4 \pm 0.05$ with corresponding activation parameters $\log \langle \tau \rangle_0 = -11.9 \pm 1$ and $B = 10.9 \pm 0.5$ kcal/mol. Evidently, the activation energy is insensitive to the fitting procedure, the only discrepancy appearing in the shape parameter, which is within the experimental error.

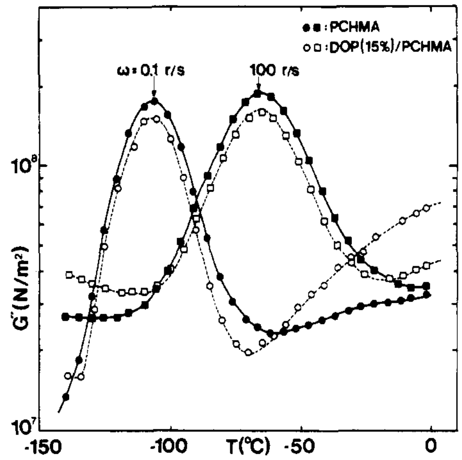

Figure 7. Loss modulus G'' versus temperature for the γ-relaxation of PCHMA and DOP(15%)/PCHMA at two frequencies (0.1 and 100 rad/s).

Figure 4 shows that the γ-relaxation differs from the α-relaxation with regard to its dependence on the DOP composition; T_{max}, the temperature at which G'' attains its maximum value, is insensitive to the variation of DOP concentration, while the decrease in the amplitude of the γ-relaxation with diminishing polymer concentration is mainly due to the decrease of the concentration of cyclohexyl groups which participate in the motion. This dilution effect was found for the γ-maximum of the cyclohexyl group,[9] with the only exception of diphenyl phthalate (DPP), for which a significant antiplasticization effect is observed. In Figure 7 a comparison is made between the low-temperature relaxations of PCHMA and DOP(15%)/PCHMA. At the highest frequency used and at the lowest temperature, a new relaxation is observed only in the plasticized polymer. This relaxation should be related to a motion within the plasticizer molecule itself.[40] Therefore, there is no indication of interference between the relaxation of DOP and the damping of the cyclohexyl region in the present system. A master curve for this γ-relaxation can now be drawn by application of the time–temperature superposition principle since the height of G''_{max} does not change appreciably with frequency. Figure 8 shows the result of shifting the G'' curves with one at −80 °C as a reference curve for the DOP(15%)/PCHMA mixture. As in the case of unplasticized PCHMA, the master curve for the 15% plasticized polymer gives a rather sharp peak with a width only about twice the width of a single-valued spectrum. Furthermore, it is shown[7] that by constructing the normalized dynamic longitudinal compliance $D''(\omega)/D''_{max}$ from the PCS relaxation function $g(t)$, using numerical integration, the dynamic mechanical and PCS curves for PCHMA are identical, implying that both techniques "sense" the same shape parameter β for this sharp secondary maximum.

Mechanical relaxation times were obtained from the frequency of maximum loss, corrected for the distribution of relaxation times as discussed in the data analysis. The relaxation times $\log \langle \tau \rangle$ exhibit an Arrhenius temperature dependence (eq 10) with $\log \langle \tau \rangle_0 = -12.8, -13.1, -12.9$, and -12.5 (τ in seconds) and $B = 11.2, 11.5, 11.4$, and 10.9 (in

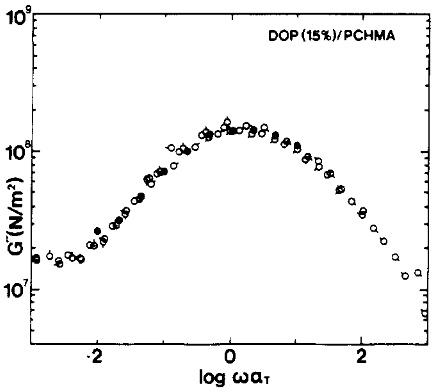

Figure 8. Reduced G'' data for DOP(15%)/PCHMA. The reference temperature is -80 °C. Filled circles represent direct measurements at this temperature, while unfilled symbols are for different temperatures and frequencies.

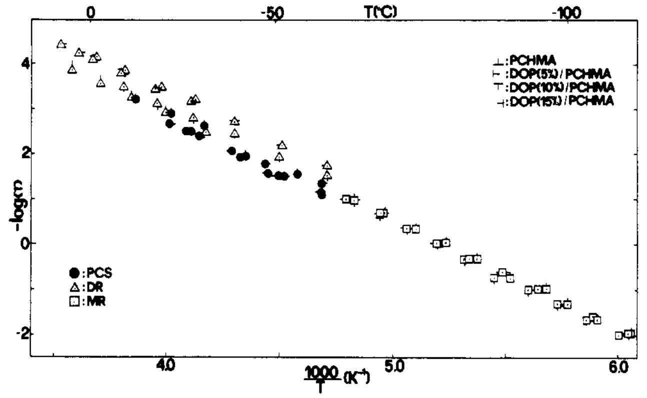

Figure 9. Arrhenius plot of the $-\log \langle \tau \rangle$ times for the γ-relaxation in bulk and plasticized PCHMA as investigated by PCS (●), DR (△), and MR (□).

kcal/mol) for the 0%, 5%, 10%, and 15% samples, respectively. This latter observation raises the question of how the cyclohexyl ring can relax between the two chair conformers independent of the environment and yet be mechanically active. Mechanical activity can only be understood if there exists strong coupling between the cyclohexyl group and its environment. A two-potential-well model which includes this coupling can explain qualitatively the "paradoxial" situation of strong coupling together with activation parameters which hardly depend on the environment.[41]

Mechanical activity of secondary relaxations can also be viewed in terms of the free-volume fluctuation model.[14] According to this model, local density or volume fluctuations δV are assumed to have a Gaussian distribution and mechanical activity requires a free-volume fluctuation δV exceeding a critical value δV^*. The form of the distribution $P(\delta f)$, where δf is the relative volume fluctuation ($\delta f = \delta V / \langle V \rangle$), and the corresponding critical value δf^* depend on the polymer involved. Thus, high δf^* values and narrow distributions can lead to a suppression of the secondary relaxation, whereas low δf^* values or broad distributions may explain the lack of secondary suppression. As the distribution of relaxation times (Figures 5 and 8) associated with the γ-relaxation in PCHMA is rather narrow and moreover insensitive to DOP content, the lack of secondary suppression may suggest low δf^* requirements. Pulsed ^{2}H NMR line shapes revealed the presence of suppression of secondary relaxation in polycarbonate (PC)/additive mixtures.[15] The π-flip which is associated with the secondary relaxation of PC is hindered by additives. Furthermore, additives were found not only to shift the mean value of the distribution of correlation times to higher values but also to increase the width of the distribution. Clearly, this is not the case with PCHMA. We found no evidence of γ-suppression from the MR and PCS results, and, moreover, the relaxation parameters were found to be independent of the additive content.

Figure 9 shows an Arrhenius plot of all γ-relaxation times obtained from PCS, DR, and MR. The γ-relaxation probed by dielectric relaxation, mechanical relaxation, and light scattering appears in the same frequency zone and has very similar activation parameters for the unplasticized and plasticized polymers. We can thus conclude that the three techniques, having different physical origins, probe the same molecular process below T_g, namely, the inversion of the cyclohexyl ring from a chair to another chair conformer as was proposed by the extensive mechanical studies of Heijboer[9,36] and recently confirmed by dielectric[11] and NMR[12] studies. Subtle differences between PCS and DR results with regard to the values of β are due to the constrained fit of the asymmetric ϵ'' peak (Figure 6).

Conclusions

In this paper we have examined the effect of the additive DOP on the primary and secondary relaxations of PCHMA using dynamic light scattering (PCS), dielectric relaxation (DR), and mechanical relaxation (MR) on the same polymer samples. The effect of additives on the primary relaxation of PCHMA is a strong decrease in the temperature—the well-known plasticizer effect. Sub-T_g relaxation or β-relaxation was found to be enhanced with the addition of DOP, and this was attributed to an increased mobility of the cyclohexylcarbonyl group facilitated by the main chain. The low-temperature γ-relaxation is found to be insensitive to the presence of additive as was expected from the extensive mechanical studies of Heijboer.

Primary relaxation times exhibiting a strong temperature dependence were fitted to the VFTH free-volume equation. The distribution of retardation times reliably extracted from the density time correlation functions is experimentally the same in the bulk and plasticized PCHMA. Quantitative agreement between PCS and MR times is observed when the same definition of $\langle \tau \rangle$ is used. On the other hand, possible additional contributions to the dielectric loss data for the plasticized PCHMA renders the interrelation of the DR and PCS results rather semiquantitative. Data on secondary relaxation were analyzed similarly and the relaxation times obtained were fitted to an Arrhenius temperature dependence. The activation parameters were nearly the same for both plasticized and unplasticized polymer and independent of the technique used, in accordance with the intramolecular nature of the γ-relaxation associated with the chair-to-chair transition of the cyclohexyl ring. The reported secondary suppression effect in other systems (e.g., PC/additive) was not observed in PCHMA/DOP.

Acknowledgment. Support by the Volkswagen Stiftung (No. I/62872), the RCC, and the Max-Planck Gesellschaft is gratefully acknowledged. G. Floudas thanks Dr. F. Kremer and Dr. T. Pakula for providing the dielectric and mechanical instruments and Dr. J. Heijboer for very helpful suggestions. We also thank Dr. M. Stickler of Röhm Darmstadt, F.R.G., for providing us with the plasticized PCHMA samples.

References and Notes

(1) See, for example: Boese, D.; Kremer, F. *Macromolecules* **1990**, *23*, 829 and references therein.

(2) Ferry, J. D. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.

(3) Bailey, R. T.; North, A. M.; Pethrich, R. A. *Molecular Motion in High Polymers*; Clarendon Press: Oxford, 1981.

(4) Spiess, H. W. *Adv. Polym. Sci.* **1985**, *66*, 23.

(5) For example: Hyde, P. P.; Ediger, M. D.; Kitano, T.; Ito, K. *Macromolecules* **1989**, *22*, 2253.

(6) Meier, G.; Fytas, G. In *Optical Techniques to Characterize Polymer Systems*; Bassler, H., Ed.; Elsevier: Amsterdam, 1989.

(7) Fytas, G. *Macromolecules* **1989**, *22*, 211.

(8) Fytas, G.; Floudas, G.; Ngai, K. L. *Macromolecules* **1990**, *23*, 1104.

(9) Heijboer, J. Mechanical properties of glassy polymers containing saturated rings. Ph.D. Thesis, University of Leiden, 1972.

(10) Ishida, Y.; Yamafuji, K. *Kolloid Z.* **1961**, *177*, 97.

(11) Ribes-Greus, A.; Gomez-Ribelles, J. L.; Diaz-Calleja, R. *Polymer* **1985**, *26*, 1849.

(12) Laupretre, F.; Virlet, J.; Bayle, J. P. *Macromolecules* **1985**, *18*, 1846.

(13) Johari, G. P.; Goldstein, M. *J. Chem. Phys.* **1970**, *53*, 2372.

(14) Fischer, E. W.; Hellmann, G. P.; Spiess, H. W.; Hörth, F. J.; Ecarius, U.; Wehrle, M. *Makromol. Chem., Suppl.* **1985**, *12*, 189.

(15) Wehrle, M.; Hellmann, G. P.; Spiess, H. W. *Colloid Polym. Sci.* **1987**, *265*, 815.

(16) Lindsey, C. P.; Patterson, G. D.; Stevens, J. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 1547.

(17) Patterson, G. D.; Lindsey, C. P. *Macromolecules* **1981**, *14*, 83.

(18) Boese, D.; Momper, B.; Meier, G.; Kremer, F.; Hagenah, J.-U.; Fischer, E. W. *Macromolecules* **1989**, *22*, 4416.

(19) Kalachandra, S.; Turner, D. T. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1971.

(20) Floudas, G.; Fytas, G.; Stickler, M., unpublished results.

(21) Kremer, F.; Boese, D.; Meier, G.; Fischer, E. W. *Colloid Polym. Sci.* **1989**, *80*, 129.

(22) Provencer, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

(23) Havriliak, S.; Negami, S. *Polymer* **1967**, *8*, 101.

(24) Williams, G.; Watts, D. C.; Dev, S. B.; North, A. M. *Trans. Faraday Soc.* **1971**, *67*, 1323.

(25) Patterson, G. D.; Carroll, D. J.; Stevens, J. R. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *17*, 613.

(26) Meier, G.; Fytas, G.; Dorfmüller, Th. *Macromolecules* **1984**, *17*, 957.

(27) Fytas, G.; Wang, C. H.; Fischer, E. W.; Mehler, K. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1859.

(28) Hains, P. J.; Williams, G. *Polymer* **1975**, *16*, 725.

(29) Plazek, D. J.; Riande, E.; Markovitz, H.; Raghupathi, N. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *17*, 2189.

(30) Colmenero, J.; Alegria, A.; Alberdi, J. M.; der Val, J. J.; Ucar, G. *Phys. Rev. B* **1987**, *35*, 3995.

(31) Chen, H. S.; Morito, N. *J. Non-Crystalline Solids* **1985**, *72*, 287.

(32) Palmer, R. G.; Stein, D. L.; Abrahams, E.; Anderson, P. W. *Phys. Rev. Lett.* **1984**, *53*, 958.

(33) Kolinski, A.; Skolnick, J.; Yaris, R. *J. Chem. Phys.* **1986**, *84*, 1922.

(34) Cavaille, J. Y.; Perez, J.; Johari, G. P. *Phys. Rev. B* **1989**, *39*, 2411.

(35) Perez, J. *Rev. Phys. Appl.* **1986**, *21*, 93.

(36) Heijboer, J. *Int. J. Polym. Mater.* **1977**, *6*, 11.

(37) Heijboer, J.; Baas, J. M. A.; van de Graaf, B.; Hoefnagel, M. A. *Polymer* **1987**, *28*, 509.

(38) Cowie, J. M. G.; Ferguson, R. *Polymer* **1987**, *28*, 503.

(39) Fytas, G.; Wang, C. H.; Fischer, E. W. *Macromolecules* **1988**, *21*, 2253.

(40) Heijboer, J., private communication.

(41) Struik, L. C. E. *Molecular Dynamics and Relaxation Phenomena in Glasses*; Springer-Verlag: Berlin, 1985.

Registry No. PCHMA, 25768-50-7; DOP, 117-81-7.