Photon Correlation Study of the Relaxation Processes in Bulk Poly(*n*-butyl methacrylate)

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ABSTRACT: We report a photon correlation study of bulk poly(*n*-butyl methacrylate) over the temperature range 35.8–70.6 °C. It is shown that the most appropriate analysis of the data involves two distinct relaxation processes. An analysis using only one single-relaxation process, apart from the systematic errors it displays, fails, as it yields an unexpected temperature-dependent distribution parameter $\dot{\beta}$. In contrast to this, with the present analysis both distribution functions $\dot{\beta}_1$ and $\dot{\beta}_2$ turn out to be temperature independent. The relaxation time of the fast process agrees well with published dielectric relaxation data, while the somewhat less accurate values of the relaxation time of the slow process agree with mechanical relaxation data of the α-process. A correlation function obtained at 1 kbar supports this kind of analysis.

1. Introduction

The dynamics of bulk polymers have been recently studied quite extensively by photon correlation spectroscopy.[1-11] The results obtained up to now show that this method constitutes a useful tool in this field and that the results are in good agreement with dielectric and mechanical data.[5,7,10] The main drawback common both to dielectric and to light scattering methods is the lack of an adequate theoretical model of the underlying process, which compels us to use an empirical distribution function to fit the experimental correlation functions and to obtain properly defined relaxation times. The Williams–Watts (WW) distribution function was thus shown to yield excellent fits to photon correlation data. Generally, we obtain values of the width parameter $\dot{\beta}$ equal to or larger than 0.35. However, the few cases[5,12] of very low values of $\dot{\beta}$ such as $\dot{\beta} \sim 0.2$ give rise to the suspicion that the fit does not represent the real situation since such large distributions probably do not have the same physical basis as the cases with larger $\dot{\beta}$.

In order to elucidate somewhat this situation, it is worthwhile to perform very careful experiments on such polymers where we apparently observe wide distribution functions. In such experiments we have to be very careful with the probe preparation, and, above all, the data analysis should avoid the many pitfalls connected with the fitting procedure, especially when the correlation function has not decayed to the real base line.

It is well-known, mainly from dielectric measurements, that bulk polymers may exhibit more than one relaxation process.[13,14] We generally have to deal with a fast β-motion and a slow α-motion, which in some cases have been resolved unambiguously.[13,15] This is the case for alkyl methacrylate polymers, where two relaxation processes have been observed in dielectric and mechanical measurements.[13,14] In particular, the dielectric relaxation method emphasizes more the fact β-mode, probably due to the fact that the dipole moment is located in the side group. Alternatively, the mechanical relaxation data for poly(ethyl methacrylate) (PEMA)[14] and poly(*n*-butyl methacrylate (PBMA)[16] show besides the α-mode strong evidence for the β-process, which affects more strongly the real compliance $\mathcal{J}'$. In not yet well-defined manner further slower entanglement dynamics might contribute to $\mathcal{J}''$.[16] In the case of PEMA[5] and poly(methyl methacrylate) (PMMA)[12] Patterson et al. have reported photon correlation functions represented by a single WW equation, but with a distribution parameter $\dot{\beta}$ changing significantly with temperature, in contrast to the usual situation.[3,4,7,10,11]

One could fit a very broad distribution with two less distributed functions; however, the solution should be unique, and physically meaningful results should be obtained. Significant contributions to this problem can be achieved by selecting suitable experimental conditions by using a sample with a low Landau–Placzek ratio and by performing temperature- and pressure-dependent measurements. In this paper we continue the effort to define the appropriate data analysis and hence to characterize as reliably as possible, within the present experimental constraints, the two relaxation modes in bulk PBMA by means of photon correlation spectroscopy.

2. Experimental Section

(a) Light Scattering Experiment. Photon correlation functions at different temperatures (35–70 °C) at ambient pressure were taken at a scattering angle $\theta = 90°$ with the apparatus described elsewhere.[17] The light source was an argon ion laser operating at $\lambda_0 = 514.5$ nm and power up to 300 mW. The incident beam was polarized perpendicular to the scattering plane, and since there was very little depolarized intensity, no polarizer was used in the scattered light. In order to establish refractive index matching conditions, low molecular weight silicone oil was filtered into the high-pressure light scattering cell up to the top of the sample cell.[10] The single-clipped photocount autocorrelation function was measured by means of a 96-channel Malvern correlator.

(b) Sample Preparation. The preparation of a clear, optically homogeneous, dust-free sample that is also free of strains is a very crucial point for a correct photon correlation study. We have prepared amorphous PBMA by employing two different procedures.

(a) The PBMA polymer purchased from Polysciences had a molecular mass of 250 000 daltons. The polymer was precipitated from a ~15 wt % acetone solution with water, and after it was washed several times with methanol, it was dried under vacuum for a few days. The PBMA thus obtained was dissolved in benzene and was then filtered through a 0.45-μm Millipore filter into a dust-free flask (100 mL) sealed to the light scattering cell (10-mm o.d.) After a few days of freeze-drying, the polymer was melted at 120 °C, filling up the light scattering cell. The glass transition temperature determined from DTA data (Mettler DTA 2000 B) at a scan rate of 10 °C/min amounts to 25 °C.

A strong confirmation of the suitability of the bulk PBMA sample for photon correlation measurements was provided by the low value of the Landau–Plazcek intensity ratio $I_C/2I_B$ of the central Rayleigh to the Brillouin doublet. We computed this ratio by recording the polarized Rayleigh–Brillouin spectrum of PBMA by means of Fabry–Perot interferometry.[18] Such a spectrum of PBMA at 60 °C is shown in Figure 1. The intensity ratio $I_C/2I_B$ amounts to 7.2, in very good agreement with a reported value for PBMA.[19] At sufficiently low temperatures above T_g, slow motions have no effect on the Brillouin intensity but they do strongly contribute to the central Rayleigh line.[18] The intensity of the pure Rayleigh line associated with thermal diffusion is relatively small ($(\gamma - 1)/\gamma, \gamma = C_p/C_v$, the specific heat ratio). On the other hand, the fraction of the central Rayleigh intensity due to slowly

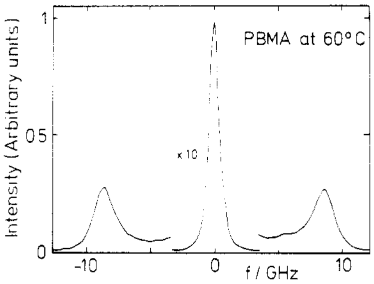

Figure 1. Polarized Rayleigh–Brillouin spectrum of bulk PBMA at 60 °C.

relaxing density fluctuations in PBMA can be roughly estimated from the value of the measured Landau–Placzek ratio and the thermodynamic value of the specific heat ratio $\gamma = 1.4$ to account for about 81% of the total polarized scattered intensity, which seems to be reasonable at low temperature. The slow motions in bulk polymers can be ascribed to the structural relaxation (α- and β-mode) and for high molecular weight polymers to entanglement dynamics.

(b) Another PBMA sample was prepared by thermal polymerization at 90 °C of the monomer butyl methacrylate purchased from Merck. The clean, dry monomer, after vacuum distillation and addition of 0.1 wt % 2,2-azobis(isobutyronitrile) as initiator, was filtered through a 0.22-μm Millipore filter into the dust-free light scattering cell (10-mm o.d.), and after the cell was degassed, it was flame sealed under vacuum. This monomer sample was polymerized at 90 °C for nearly 10 months. The PBMA polymer thus obtained yielded a Landau–Plazcek ratio twice as large as that of the sample prepared from the freeze-dried polymer. The polarized scattered intensity from the latter sample is assumed to arise only from inherent density fluctuations. The photon correlation function of the scattered light from the two bulk PBMA samples will be discussed below. In both procedures we found that pressurizing (500–1000 bar) the sample for a few days at 60 °C and then releasing the pressure after cooling slowly at room temperature led to good-quality samples for photon correlation study; i.e., a further decrease of the Landau–Plazcek ratio was observed.

3. Data Analysis

The measured single-clipped autocorrelation function $G_k^{(2)}(t) = N\langle n_k(0)n(t)\rangle$ in a homodyne beating experiment has the form

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

where $g^{(1)}(t)$ is the desired normalized correlation function of the scattered electric field, k is the clipping level, $\langle n_k\rangle$ and $\langle n\rangle$ are respectively the mean clipped and unclipped counts per sample time $\Delta\tau$, N is the total number of samples, and t ($=I\Delta\tau$) is the delay time, I being the channel number. The amplitude b is an unknown parameter used in the data-fitting procedure depending mainly on the clipping level, the coherence area, the sample time, and the relaxation strength, i.e., the fraction of the scattered intensity associated with the slowly relaxing fluctuations. The base line can be computed ($A = N\langle n_k\rangle\langle n\rangle$) or measured at long delay times.

The fitting of the time correlation functions should proceed in terms of the net unnormalized intensity correlation $(G_k^{(2)}(t) - A)/A$, using a fixed base line A in order to reduce the number of unknown parameters. Fits with a floating base line, especially for broad distributions, can seriously affect the true shape of the $g(t)$, and the results often become unreliable.[7,20] It is well-known for glass-forming systems that the time correlation functions do not conform to a single-exponential scheme, but they can be well represented by the widely used empirical Williams–Watts function:[21]

$$g^{(1)}(t) = \exp(-t/\tau_0)^{\beta} \tag{2}$$

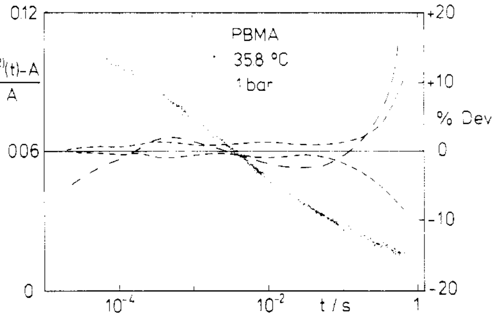

Figure 2. Measured composite correlation function $(G_k^{(2)}(t) - A)/A$ (dots) at 35.8 °C for bulk PBMA. The quality of the fit represented by percent deviation for fixed base line single-WW (eq 4, $a = 0$) (–·–) and for double-WW functions (eq 5) (– – –) is also given.

where β ($0 < \beta \leq 1$) is a measure of the width of the distribution of the delay times. The mean relaxation time $\bar{\tau}$ is given by

$$\bar{\tau} = \frac{\tau_0}{\beta}\Gamma(\beta^{-1}) \tag{3}$$

where $\Gamma(\beta^{-1})$ is the Gamma function.

The highly nonexponential time correlation functions require more than 2 decades of delay time, depending on the value of the β parameter. For a linearly spaced delay time correlator with a limited number of channels, the desired composite correlation function can be formed by splicing together sections with different $\Delta\tau$. In the case of PBMA we started the matching procedure from the section with the largest delay time $\Delta\tau$ using the computed base line A. In the case of bulk polymers, where a single-relaxation process has been observed, the equation

$$(G_k^{(2)}(t) - A)/A = a + b\exp[-2(t/\tau_0)^{\beta}] \tag{4}$$

has been successfully fitted to the combined correlation functions, where a is a small number (10^{-3}–10^{-4}) which is often introduced to account for a small base line correction. For β values larger than 0.35 we have found that the value of $\bar{\tau}$ is not significantly affected by setting $a = 0$.[7] Thus the fit of eq 4 to the experimental composite correlation functions for polystyrene (PS),[3,4,11] poly(propylene glycol) (PPG),[7] poly(ethyl acrylate) (PEA),[10] and poly(methyl acrylate) (PMA)[22] yields physically meaningful values of mean relaxation times that compare favorably with dielectric and mechanical relaxation results and β values in the range of 0.35–0.4 that are temperature and pressure independent. Since we do not yet have a theoretical model describing the measured correlation functions of bulk polymers above T_g, the agreement with other methods is valuable and constitutes a support of the data analysis.

Figure 2 shows the measured correlation function $(G_k^{(2)}(t) - A)/A$ at 35.8 °C and atmospheric pressure for PBMA. A systematic deviation from the fit according to eq 4 with $a = 0$ is evident. As a consequence we obtain for the parameter β for this fit a value as small as 0.15. Fitting eq 4 with a floating base line ($a \neq 0$), we obtained $\beta = 0.22$ and a mean relaxation time (eq 3) shorter by a factor of 20, but the deviation plot still showed a large systematic error. The base line correction in this case amounts to 6×10^{-3}, which is significantly larger than the experimental error. The parameter β is an increasing function of temperature and reaches the value 0.44 at 70.6 °C. This temperature dependence is in contrast to the light scattering findings for the above-mentioned polymers, where a single-relaxation process with a constant value of β has been observed. This could indicate that for PBMA

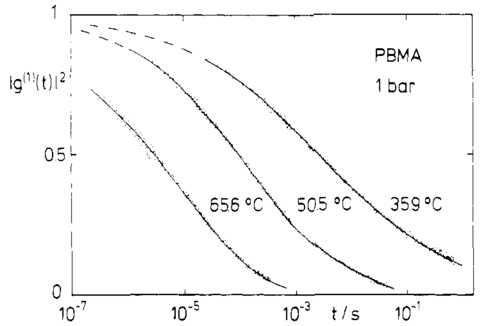

Figure 3. Measured normalized composite correlation functions $(G_k^{(2)}(t) - A)/(Ab)$ (dots) at three temperatures for bulk PBMA at 1 bar. The solid lines represent fits of eq 5 and eq 4 with $a = 0$ to the measured correlation functions at 35.8 and 50.5 °C and at 65.6 °C, respectively.

the physics behind the WW equation does not apply and hence the calculated values of β do not describe the situation. This situation is visualized in Figure 3, where the correlation function $(G_k^{(2)}(t) - A)/(Ab)$ is shown for three temperatures. It is apparent that, while the 3 decades in time are sufficient to analyze the measured correlation function at 65.6 °C, the delay of $g^{(1)}(t)$ spreads over more than 5 decades at 35.8 °C. At this temperature the correlation function remains far above the base line at $t \sim 1$ s. The present results mirror those obtained for PMMA[12] and indicate the presence of at least two relaxation processes, as is the case for PEMA.[5] Furthermore, we know from dielectric and mechanical studies of poly(alkyl methacrylate) that two relaxation modes contribute to the loss tangent (ϵ'') and compliance (ζ''), respectively, and that the location of the two maxima in ϵ'' are closer in PBMA than in PEMA.[13,14]

For the foregoing reasons we think that an adequate procedure is to fit a composite correlation function for PBMA of the form

$$[(G_k(t) - A)/A]^{1/2} = b_1 \exp(-t/\tau_1)^{\beta_1} + b_2 \exp(-t/\tau_2)^{\beta_2} \tag{5}$$

to the data. b_1 and b_2 are the amplitudes and τ_1 and τ_2 are the relaxation time distribution parameters of the fast and slow component, respectively. The mean relaxation times $\bar{\tau}_1$ and $\bar{\tau}_2$ were computed from the parameters τ_1,β_1 and τ_2,β_2 by using eq 3. The form of eq 5 represents a fixed base line, six-parameter double Williams–Watts fit, where the small base line correction a (eq 4) can be omitted. Alternatively, we observed that a seven-parameter double Williams–Watts fit with a floating base line ($a \neq 0$) affects only the parameters of the slow-relaxation process. A further support of the two-relaxation distribution feature of the experimental correlation functions for PBMA is provided by the composite correlation function at 98 °C and 1500 bar shown in Figure 4. We observe again that the two processes are better resolved at high temperatures by applying hydrostatic pressure.

4. Results and Discussion

(a) Single-Relaxation Process Approach. First, we consider the results of the four-parameter single Williams–Watts fit (eq 4) to the measured composite correlation functions for reasons of comparison, as this type of analysis is currently being performed by investigators in this field. However, it should be mentioned again that one must be aware of the uncertainties in the determination of the mean relaxation time $\bar{\tau}$, especially for a broad distribution ($\beta \sim 0.2$). In this case the fit of eq 4 with a floating base line causes a shift of the relaxation process to shorter times as compared to the fixed base line fit ($a = 0$), mainly due to the increase of the β parameter. In Figure 5 is shown the temperature dependence of the relaxation time $\langle\tau\rangle$ obtained from the fit of eq 4 to the experimental correlation functions in the temperature range 35–75 °C at 1 bar. An Arrhenius equation fit of the data in Figure 5 gives an apparent activation energy of 57 kcal/mol, similar to the high activation energy reported for the main glass–rubber relaxation (α) for PS,[3,4,11] PPG,[7] PEA,[10] and PMA.[22] Hence in these systems the temperature dependence of $\langle\tau\rangle$ can be described by the Williams–Landel–Ferry (WLF) equation, which is widely applied to the temperature–frequency superposition of the dynamic mechanical relaxation data:[14]

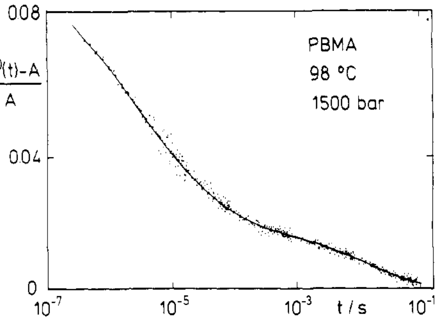

Figure 4. Measured composite correlation function $(G_k^{(2)}(t) - A)/A$ (dots) represented by a double-WW function (eq 5) (solid line) at a temperature of 98 °C and pressure of 1500 bar.

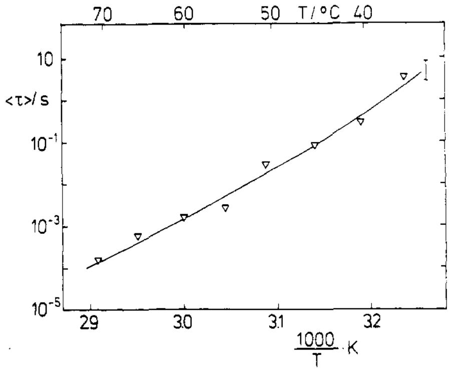

Figure 5. Temperature dependence of the mean relaxation time $\langle\tau\rangle$ obtained from the fit of eq 4 to the measured correlation function of the scattered intensity by PBMA. The solid line represents a fit of the WLF (eq 6) function to the values of $\langle\tau\rangle$. The β-parameter increases from 0.22 at 35 °C to 0.44 at 75 °C.

$$\log \langle\tau\rangle = \log \langle\tau_g\rangle - \frac{C_1(T - T_g)}{C_2 + T - T_g} \tag{6}$$

where C_1 and C_2 are the WLF constants and $\langle\tau_g\rangle$ is the mean relaxation time at T_g.

The WLF constants C_1 and C_2 are usually obtained by fitting extensive compliance data over a larger temperature range. In the case of PBMA the reported values are $C_1 = 17$ and $C_2 = 96.6$ K for $T_g = 300$ K,[16] which is in agreement with the value of the glass transition temperature of the PBMA sample used in the present study. Using these values for C_2 and T_g, we obtain $\langle\tau_g\rangle = 72$ s and $C_1 = 18.2$ from the fit of eq 6 to the times of Figure 5. The agreement between the two values of C_1 obtained from the two methods is very good. Concerning now the absolute value of $\langle\tau_g\rangle$, one has to consider the correction for the difference between $\langle\tau\rangle$ and $1/f_{\max}$ (frequency at maximum loss),[23] as well as the different weighting of the observed relaxation process by the two methods. Apart from the reservations we mentioned in the previous section for the

Table I
Relaxation Parameters $\bar{\tau}_1$, $\bar{\tau}_2$, $\dot{\beta}_1$, and $\dot{\beta}_2$ and Amplitude Ratio $b_1/(b_1 + b_2)$ Obtained from the Fit of Eq 5 and $\bar{\tau}$ and $\dot{\beta}$ from the Fit of Eq 4 with $a = 0$ to the Composite Correlation Functions for PBMA at 1 bar and in the Temperature Range 35.8-70.6 °C

T/°C	$\dot{\beta}_1$	$\bar{\tau}_1$/s	$\dot{\beta}_2$	$\bar{\tau}_2$/s	$b_1/(b_1 + b_2)$	$\dot{\beta}$	$\bar{\tau}$/s
35.8	0.34	0.017	0.38	14	0.33		
40.2	0.35	0.011	0.5	1	0.65		
45.1	0.37	3.7×10^{-3}	0.52	0.4	0.60		
50.5	0.40	1.3×10^{-3}	0.53	0.08	0.54		
55.2						0.27	9.4×10^{-3}
60.1						0.28	5.9×10^{-3}
65.6						0.31	7.3×10^{-4}
70.6						0.34	3.8×10^{-4}

single-process analysis (see Figure 2), additionally the $\dot{\beta}$ parameter increases significantly with increasing temperature ($\dot{\beta} = 0.22$ at 35 °C to $\dot{\beta} = 0.44$ at 75 °C). A similar temperature dependence has been reported for PMMA[12] and PEMA,[5] but the present results are not compatible with the α-relaxation data in PS,[3,4,11] PPG,[7] PEA,[10] and PMA.[22]

However, we still need to explain why the fit of eq 4 to the composite correlation functions gives a relaxation time $\langle \tau \rangle$ comparable to the α-relaxation mechanical data, despite the obvious limitations of this fit (Figure 2). Patterson[12] observed that the value of $\langle \tau \rangle$ in the Williams–Watts representation (eq 4) is dominated by the longest relaxation time associated with the primary (α) relaxation process. On the other hand, he claimed that the secondary (β) relaxation dominates the correlation function of the light scattered by PMMA and PEMA. This situation is discussed and, to our mind, somewhat clarified in the next section.

(b) Double-Relaxation Process. The measured composite correlation function $(G_k^{(2)}(t) - A)/A$ of the polarized scattered intensity by PBMA at three different temperatures (35, 50, and 65 °C) is shown in Figure 3. Up to about 55 °C the deviation plot of the fit to eq 4 with $a = 0$ shows a systematic error, and the correlation functions have consequently been fitted to eq 5. At higher temperatures and at a pressure of 1 bar the relaxation times of the slow process are close to the relaxation times of the fast mode, so that eq 4 with $a = 0$ fits well to the measured correlation functions. The values of $\bar{\tau}_1$,$\bar{\tau}_2$, $\dot{\beta}_1$, and $\dot{\beta}_2$ from the fit of eq 5 and the values of $\bar{\tau}$ and $\dot{\beta}$ from the fit of eq 4 with $a = 0$ to the experimental correlation functions are given in Table I. Again the parameters $\bar{\tau}_2$ and $\dot{\beta}_2$ characterizing the slow process are sensitive to the uncertainty of the base line. As shown in the data analysis section, it is obvious that two relaxation modes contribute to the time correlation functions for PBMA, at least in the temperature range 35–55 °C. Each of these processes, however, consists of a relatively broad distribution of relaxation times. The separation of these two broad relaxation modes by fitting eq 5 to the data becomes more reliable if one adjusts their time range to the accessible time window (about 6 orders of magnitude from 10^{-6} to 1 s) of the linearly spaced delay time correlator by choosing appropriate temperatures and pressures (see Figure 4). This result at 98 °C and 1500 bar gives further support to the present type of data analysis at 1 bar.

Figure 6 shows the temperature dependence of the mean relaxation times $\bar{\tau}_1$, $\bar{\tau}_2$, and $\bar{\tau}$ obtained from the fit of eq 5 and 4 (with $a = 0$) to the experimental correlation functions. By fitting the experimental relaxation times $\bar{\tau}_1$ of the fast process to an Arrhenius temperature dependence, we obtain an activation energy of 35 kcal/mol for the fast mode.

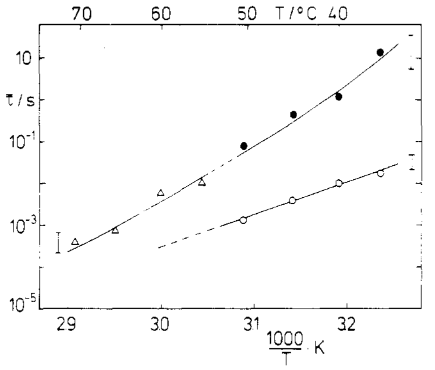

Figure 6. Temperature dependence of the mean relaxation time of the slow process $\bar{\tau}_2$ (●), the fast process $\bar{\tau}_1$ (○), and the time $\bar{\tau}$ (△) obtained from the fit of eq 5 and 4 (with $a = 0$) to the experimental correlation functions of PBMA.

Dielectric relaxation measurements of PBMA have been performed by several investigations in this field.[13,15] As in the case of PEMA the dielectric relaxation loss absorption emphasizes more the fast (β) relaxation process, obviously due to the fact that PBMA has a dipole moment in the side group ($COOC_4H_9$). At low temperatures (25–39 °C) a slow (α) process appears as a low-frequency shoulder on the main β-peak. The agreement of the β-dielectric relaxation times with the present light scattering fast process is very good. The reported activation energy assuming an Arrhenius temperature dependence for the β-dielectric times lies in the range 24–30 kcal/mol[13] and compares favorably with the value of 35 kcal/mol.

Dynamic mechanical compliance (J' and J'') measurements have also been reported for PBMA.[16] The observed deviation from the usual superposition with reduced variables for J' has been attributed to the β-process with an activation energy of 24 kcal/mol. A second deviation for J'' at higher temperatures has been ascribed to the chain entanglement. If we now assign the fast relaxation process to the hindered rotation of the $COOC_4H_9$ group around the C–C bond linking it to the main chain, the relaxation time $\bar{\tau}_1$ can be discussed in terms of the Kramer rate constant theory at low friction.[24] From the preexponential term and the activation energy for $\bar{\tau}_1$ we compute a value of $I = 10^{-47}$ g·cm^2 for the moment of inertia of the side group. However, this value is too small compared with the theoretically expected value of $\log I = -40$.[24] This discrepancy indicates that the assumption of low friction in the motion of $COOC_4H_9$ is probably not valid. Structural relaxation of the butyl part of the side group and the steric hindrance of the α-methyl group may also play a role in the dynamics of the polymer above T_g.

We consider now the temperature dependence of the slow relaxation times $\bar{\tau}_2$ (up to 55 °C) in Figure 6, which is discussed in terms of the WLF eq 6. Again using $C_2 = 96.6$ K and $T_g = 300$ K from ref 16, we obtain $C_1 = 19.1$ and $\bar{\tau}_g = 436$. The agreement between the values of C_1 obtained from light scattering and mechanical relaxation data, within the experimental errors of $\bar{\tau}_2$, is very good. Furthermore, the present double feature of the measured correlation functions (eq 5) leads to reliable unique relaxation times $\bar{\tau}_1$ for the fast process and gives us, although less precisely, the value of the slow relaxation time $\bar{\tau}_2$, which is strongly temperature dependent, characteristic for the α-process. Finally, a comparison between the values of the relaxation times $\langle \tau \rangle$ in Figure 5 and $\bar{\tau}_2$ in Figure 6 supports Patterson's suggestion that the single Williams–Watts fit (eq 4) gives the relaxation time $\langle \tau \rangle$ associated with the α-process, even though the β-mode dominates the time correlation function for the alkyl methacrylate polymers.[12]

(c) Probe Quality. As mentioned above a second PBMA sample (II) prepared by thermal polymerization of *n*-butyl methacrylate has been studied by photon correlation spectroscopy at the temperatures 45, 50, and 55 °C. We have chosen these temperatures to reexamine a peculiar change of the profile of the composite time correlation function of PBMA over a narrow temperature interval at 50 °C.[8] First, sample II shows twice as much total scattered intensity as sample I, prepared by the freeze-drying procedure, which yields only inherent intensity arising mainly from density fluctuations (Figure 1). The contrast $(b_1 + b_2)^2$ (eq 6) of sample II, as expected, was by a factor of 3 lower than in sample I. However, no change in the dynamics of the two processes was observed. On the other hand, the amplitude ratio of the fast to the slow process b_1/b_2 was found to be lower by 75% for sample II; i.e., an improvement of the sample quality has led to a better resolution of the two processes. Thus the very small amplitude of the fast relaxation process and hence the value $\beta_1 = 1$ reported for bulk PBMA polymer can be presumably attributed to the sample quality and arbitrary base line correction.[8] Finally, it is worth mentioning that both samples show as reported a distinct decrease of the total intensity by a factor of 2 at 50 °C "related with the glass transition".[19] This conforms to the observation of Stevens et al.,[19] who report a similar change in the Rayleigh–Brillouin spectrum. Since we have not noticed any dynamic change in this temperature region, we presume that the observed intensity change cannot be attributed to the slow thermal fluctuations in PBMA.

5. Conclusion

The time correlation functions of the polarized scattered intensity by bulk PBMA at different temperatures and pressures have been analyzed by assuming two distinct relaxation processes (eq 5). The mean relaxation time for the fast process compares favorably with the dielectric relaxation time of the β-process whereas the mean relaxation time of the slow process yields a strong temperature dependence described by the WLF equation (eq 6), in agreement with the mechanical data. It appears that the representation of the measured correlation functions with a single Williams–Watts equation (eq 4) gives fits which at low temperatures deviate significantly from the experimental data and leads to relaxation times very close to those of the slow process. From the analysis outlined above we see that the interactive way we had to proceed in chosing the experimental conditions and the theoretical equation has led to an adequate description of the dynamics of density fluctuations monitored by the light scattering experiment.

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