Longitudinal viscoelastic relaxation in amorphous polybutadiene by dynamic light scattering and ultrasonic absorption*

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We report polarized photon correlation measurements of amorphous bulk polybutadiene ($M_w = 13\,000$, $T_g = 222$ K) in the temperature range 230–246 K and complementary temperature- (160–360 K) and frequency- (0.1–63 MHz) dependent ultrasonic relaxation measurements on an identical sample. The light scattering and ultrasonic data on the longitudinal density fluctuations over nine decades of time conform to a single WLF equation. The strong temperature dependence of the average relaxation time was found to be different from that of the viscosity. The coupling model of relaxation can account for this difference. At temperatures higher than T_g, photon correlation spectroscopy detects slower relaxation modes, which are active in the ultrasonic experiment. From the latter, these modes are related to subchain motions and entanglement effects.

(Keywords: polybutadiene; longitudinal viscoelastic functions; photon correlation; ultrasound; segmental relaxation; slow chain motions)

INTRODUCTION

The dynamic behaviour of polymers includes a variety of motional modes. There are fast segmental motions and slow chain modes, e.g. 'Rouse'- and 'reptation'-like motions depending on the chain length. Because of this complexity, the application of various experimental methods is useful for the investigation of the time- and temperature-dependent properties of polymeric systems. Dynamic light scattering and ultrasonic relaxation have proved to be potential methods for the study of bulk polymer dynamics near and above the glass transition temperature (T_g). Both methods reflect the dynamic mechanical properties of the systems studied.

The dynamics of the thermodynamic fluctuations in the density and optical anisotropy over the time range 10^{-6}–10^{2} s can be investigated by photon correlation spectroscopy (p.s.c.)[1]. For weakly anisotropic scatterers, such as the segments of polybutadiene, the dominant contribution to the light scattering intensity arises from density fluctuations. The corresponding time correlation function $c(t)$, which has a highly non-exponential shape, is dominated by the so-called primary (α) glass–rubber relaxation for all the studied polymers except poly(alkyl methacrylates)[1–3]. The mean relaxation time τ exhibits strong temperature and pressure dependence but is independent of chain length and the probing wavelength[4] q, where q^{-1} is the scattering vector. These findings suggest that localized segmental motions of the polymer chain grossly affect the slow density fluctuations in undiluted polymers near T_g.

Recently, the density time correlation function has been associated[5] with the time-dependent longitudinal compliance $D(t)$, which otherwise cannot be easily obtained. Two p.c.s. experiments with poly(vinyl acetate) (PVAc)[6] and polypropylene (PP)[7] were subsequently carried out to test this prediction. The retardation spectrum $L(\log \tau)$ obtained from an inverse Laplace transform analysis of the experimental $c(t)$ was compared with the compressional L_B and shear compliance L_J retardation spectrum. In PVAc[6], the shape of $L(\log \tau)$ and its maximum resembles that of L while the first peak of L_J (due to the segmental motion) has its maximum at much longer times. For a full comparison, however, between experimental p.c.s. and mechanical data, the relevant viscoelastic function is the complex longitudinal modulus (M^*).

Ultrasonic investigations are based on mechanical perturbation of the system in a frequency range from a few kilohertz up to gigahertz. In the case of longitudinal wave propagations, the real M' and imaginary M'' parts of the modulus M^* can be determined from the sound velocity and the absorption coefficient. A large number of ultrasonic relaxation measurements in polymer solutions have been reported[8,9], but there are fewer studies in polymer melts[8,10–13]. Those studies of ultrasonic absorption in polymer melts have indicated that, besides local segmental motions, coherent subchain motions ('Rouse'-like chain modes) and the effects of chain entanglements can also contribute to the loss component $M''(\omega)$.

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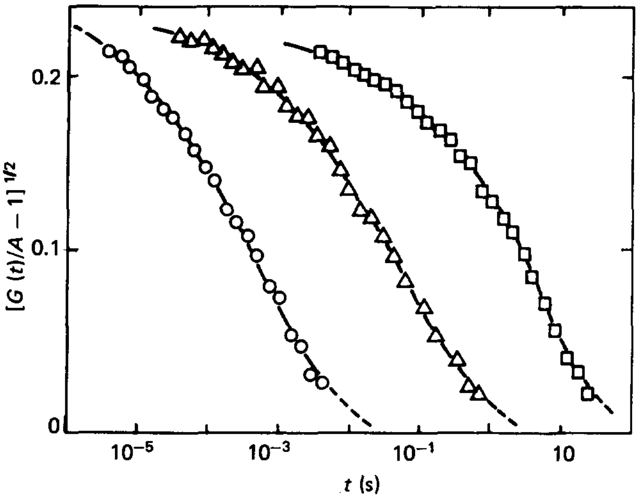

Figure 1 Measured net correlation functions for amorphous polybutadiene at three different temperatures: □, 229.6 K; △, 236.2 K; ○, 243.5 K

In the present paper, we have conducted p.c.s. and ultrasonic measurements on the same amorphous polybutadiene sample. The density correlation function $c(t)$ obtained over the temperature range 229.7 to 245.7 K was analysed in terms of a single continuous spectrum of retardation times $L(\log \tau)$ affected only by local segmental motions.

The segmental relaxation times obtained from the maximum in the frequency or temperature dependence of M'' are compared with the p.c.s. relaxation times. The resulting single set of WLF constants are different from those determined from the temperature dependence of steady-state viscosity and the parameters reported for the temperature dependence of the frequency-scale shifts for the dynamic shear modulus G^* in the terminal region[14]. This finding is similar to that recently reported for PP[7], indicating a lack of thermorheological simplicity. Furthermore, the large dispersion in $M''(\omega)$ at megahertz frequencies is contributed to by additional slower relaxation processes. We have attempted to detect those processes by p.c.s., too.

EXPERIMENTAL

The correlation functions $G(t)$ of the polarized light scattered intensity at different temperatures (230 to 246 K) were measured at a scattering angle of $\theta = 90°$. The light source was an argon-ion laser (Spectra Physics 2020) operating at 488.0 nm with a power of 200 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 of time were measured with a 28-channel logarithmic-linear (Malvern K7027) single clipped correlator in one run. In homodyne detection the desired normalized density time correlation function $c(t)$ associated with the thermal density fluctuations is related to $G(t)$ by:

$$G(t) = A[1 + b|c(t)|^2] \qquad (1)$$

A is the baseline measured at long delay times and the amplitude b is considered as a fitting parameter.

The ultrasonic absorption measurements were performed over a frequency range from 0.1 to 63 MHz using the statistical reverberation method[15,16], the resonator method[17] and several pulse methods[18,19]. The temperature dependence of the ultrasonic absorption and velocity have been measured at 1 and 5 MHz by modified pulse methods. The velocity at 1 MHz was also determined by an interferometer method.

The amorphous polybutadiene (PB) has a weight- and number-average molar mass of 1.3×10^4 and 8.6×10^3, respectively. Its chemical microstructure consists of 71% 1,2 (vinyl), 20% 1,4-*trans* and 9%, 1,4-*cis*. The glass temperature T_g determined in a Perkin–Elmer DSC-2C at a scan rate of $+8$ K min^{-1} amounts to 222 K. This agrees with the T_g value of 228 K reported for a similar sample[14]. No crystallization effects could be detected. The temperature dependence of the static shear viscosity was measured by using a Couette-type viscometer (Rheotest 2, MLW Medigen).

DATA ANALYSIS

Time correlation functions

The net experimental correlation function $[G(t)/A - 1]$ with fixed baseline was used to process the data. The Kohlrausch–William–Watts (KWW) fractional exponential decay function for $c(t)$[20]:

$$c(t) = \exp[-(t/\tau_0)^\beta] \qquad 0 < \beta \leqslant 1 \qquad (2)$$

fits the experimental functions well, treating b, τ_0 and β as adjustable parameters. The net functions $[G(t)/A - 1]^{1/2}$ are plotted *versus* $\log t$ in *Figure 1* for three different temperatures. Like the situation in polypropylene (PP), the value of the shape parameter is equal to 0.36 ± 0.03 and is virtually independent of temperature. As shown in refs. 5 and 6, the density correlation function $c(t)$ is related to $D(t)$ by:

$$c(t) = [D_0 - D(t)]/(D_0 - D_\infty) \qquad (3)$$

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

$$D(t) = D_\infty + \int_{-\infty}^{\infty} L(\ln \tau)(1 - e^{-t/\tau})\, d \ln \tau \qquad (4)$$

then:

$$c(t) = \int_{-\infty}^{\infty} \tilde{L}(\ln \tau)\, e^{-t/\tau}\, d \ln \tau \qquad (5)$$

where:

$$\tilde{L}(\ln \tau) = L(\ln \tau)/(D_0 - D_\infty)$$

An algorithm developed by Provencher is used to calculate $b^{1/2}\tilde{L}(\ln \tau)$ from equation (5) with $b^{1/2}c(t)$ obtained experimentally (equation (1)). This constrained inverse Laplace transform (*ILT*) has been modified to yield $L(\ln \tau)$ of viscoelastic systems[21]. When the functions $c(t)$ are well represented by a single KWW decay (equation

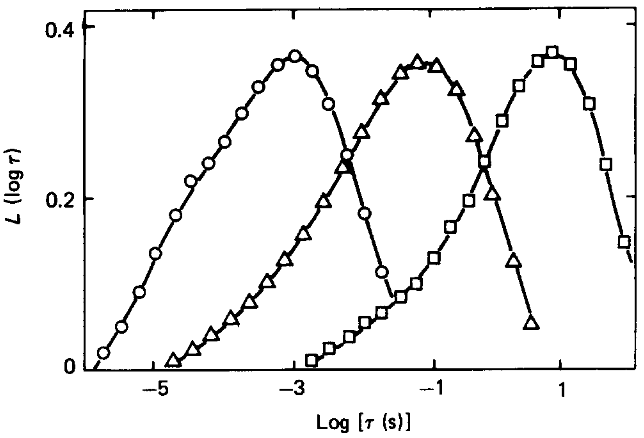

Figure 2 Retardation time spectra ($b^{1/2}\tilde{L}(\log\tau)$) plotted *versus* log τ for PB at three temperatures obtained from the inverse Laplace transform analysis of the experimental correlation functions: □, 229.6 K; △, 236.2 K; ○, 243.5 K

(2)), the numerical technique used to compute the $L(\ln\tau)$ gives an experimentally identical result with Provencher's *ILT* technique[21]. For poly(methyl methacrylate), however, the *ILT* analysis seems to reveal more clearly the underlying double structure of the $c(t)$[1].

Figure 2 shows the *ILT* results of the experimental $b^{1/2}c(t)$ for *PB* at three temperatures above T_g. Actually, we have plotted $b^{1/2}L(\log\tau)$ *versus* $\log\tau$. As expected from the nearly constant β and b values, the shape of $L(\log\tau)$ is insensitive to temperature variations within the considered range.

Ultrasonic spectra

In the ultrasonic (u.s.) experiment the attenuation α of longitudinal waves is related to the loss component M'' of the longitudinal modulus M^* by:

$$M'' = 2\rho v^2\alpha/\omega \qquad (6)$$

where ρ is the density and v is the sound velocity. Acoustic results are usually expressed as α/f^2, since for the case of non-relaxing liquids α is proportional to ω^2 ($\omega = 2\pi f$). The frequency dependences of α/f^2 and M'' are shown in *Figure 3*[22,23]. It should be noticed that for calculating $M''(\omega)$ the velocity value at 1 MHz was used for all frequencies, because it is difficult to carry out frequency-dependent measurements of the velocity. Nevertheless, this approximation would only lead to small deviations at the high-frequency limit of the range studied.

The frequency dependence of the absorption coefficient α/f^2 shows evidence of three different relaxation regions, as follows:

(i) The dispersion at high frequences can be ascribed to local segmental motions of the polymer backbone, which affect the relaxation function $c(t)$ (equation (1)) measured at lower temperatures with the photon correlation technique. Usually this type of relaxation can be represented by one relaxation time or by a distribution of relaxation times. Because of the difficulties of spectral decomposition, the high-frequency tail of the spectrum has been fitted by a single relaxation:

$$\alpha/f^2 = A/(1+\omega^2\tau^2) \qquad (7)$$

where A is the relaxation amplitude and τ is the minimum relaxation time of the spectrum. The mechanical loss $M''(\omega)$ then reaches its maximum value at $\omega = 1/\tau$.

(ii) In the region 1–20 MHz, the attenuation is related to subchain motions between entanglements generally described by 'Rouse'-like motion given by the dependence $(\alpha/f^2) \sim f^{-n}$. The exponent was determined to be $n = 0.3$.

(iii) In the range below 1 MHz, the slope of the α/f^2 curve changes. Based on the concentration dependence of the dynamic shear modulus and ultrasonic absorption in the same system[22,23], the low-frequency part of the absorption spectrum (*Figure 3*) is probably due to entanglement effects. A more detailed discussion of the ultrasonic spectra will be published in a separate paper[22].

RESULTS AND DISCUSSION

Segmental relaxation times

If we use $L(\log\tau)$ for the distribution of retardation times probed by p.c.s., the average time $\langle\tau\rangle$ is given by the first moment of $L(\log\tau)$:

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

The results for $\langle\tau\rangle$ are shown in *Figure 4*. Over the temperature range of 229.7 to 245.7 K the mean $\langle\tau\rangle$ changes by more than four orders of magnitude with an unrealistic high Arrhenius activation energy of 66 kcal mol^{-1}. We have therefore fitted the Vogel–Fulcher–Tamman–Hesse (VFTH) equation:

$$\langle\tau\rangle = \langle\tau_0\rangle \exp[B/(T-T_0)] \qquad (9)$$

to the experimental $\langle\tau\rangle$ values. In the VFTH equation, which is an alternative form of the WLF equation, $\langle\tau_0\rangle$, $B = 2.303C_1C_2$ and $T_0 = T_g - C_2$ are characteristic parameters, where C_1 and C_2 are the WLF coefficients.

To determine these parameters, we extended the fairly narrow temperature range of the p.c.s. experiment by including the ultrasonic data from frequency- and temperature-dependent studies. We are certainly aware

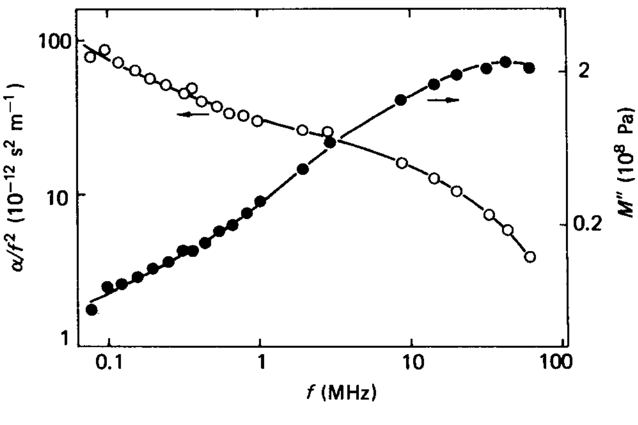

Figure 3 Ultrasonic attenuation α/f^2 (○) and dynamic longitudinal modulus M'' (●) *versus* frequency for PB at 20°C

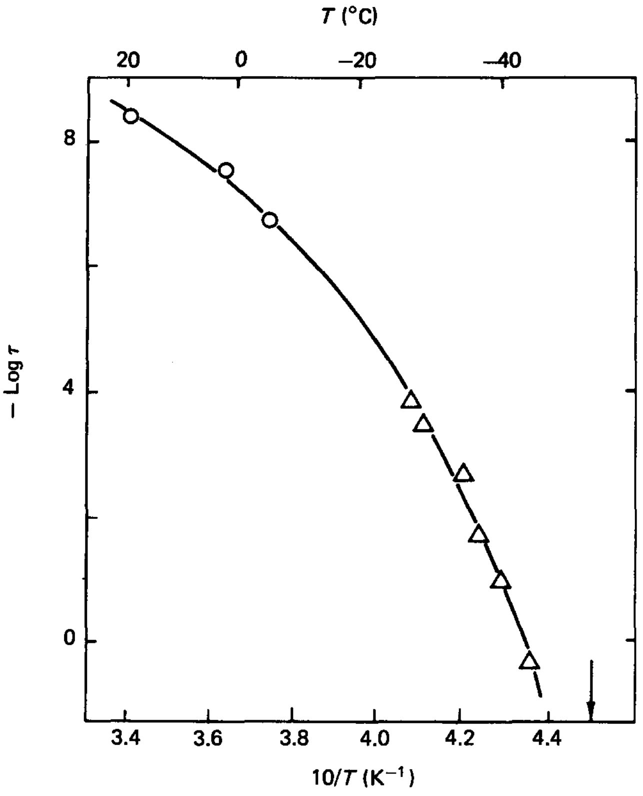

Figure 4 Temperature dependence of the segmental relaxation time from photon correlation spectroscopic (△) and ultrasonic absorption (○) measurements for PB. The full curve denotes the fit of the VFTH equation (9) to the experimental times. The glass transition temperature from d.s.c. is also indicated (arrow)

that the p.c.s. measures longitudinal compliance while ultrasonic dispersion measures longitudinal modulus. The dynamic modulus and the dynamic compliance are related by:

$$D'' = M''/[M')^2 + M'')^2] \qquad (10)$$

The real part M' is greater than M'' by at least one order of magnitude, and is assumed to have a negligible dispersion in the range investigated (0.1–63 MHz); at 20°C, $M' = 1.91 \times 10^9$ and $M'' = 0.23 \times 10^9$ Pa (*Figure 3*). These facts show that D'' and M'' reach their maximum value at virtually the same frequency ($1/\tau$). Moreover, if we ignore small differences between measurements under isothermal (p.c.s.) and adiabatic (u.s.) conditions[24], then the relaxation times obtained from the two techniques are very close. The fit of equation (9) to the experimental values of the relaxation time of *Figure 4* yields $\log[\langle\tau\rangle\,(s)] = -13.6 \pm 0.7$, $B = 1175 \pm 110$ K and $T = 193 \pm 5$ K. The WLF parameters C_1 and C_2 referred to T_g are 14.3 and 29 K, respectively. The two sets of data cover almost nine decades of time in the temperature range of T_g to $T_g + 65$°C and can be well represented by the VFTH equation.

The steady-state viscosity of the PB sample measured in the temperature range from 274 to 353 K were also fitted by the VFTH equation. The parameters thus obtained are $\eta_0 = 3.46 \times 10^{-3}$ Pa s, $B = 1345$ K and $T_0 = 176$ K. The shift factor as reported[14] for PB with similar microstructure in the temperature range of 25 to 125°C for G^* in the terminal region was found also to obey the WLF equation with $C_1 = 13.8$ and $C_2 = 29.8$ K. Hence the parameter B amounts to 1265 K, which is very close to the value of 1175 K obtained from light scattering and ultrasonic absorption. This finding resembles that of PP[7]: the local segmental dispersion has a different temperature dependence from that of the terminal dispersion, which is experimentally identical to that of the viscosity. This difference precludes thermorheological simplicity. The explanation given in ref. 7 is based on the extra prediction of the coupling model of relaxation[20]. It relates the shift factors to the different coupling parameter $(1-\beta)$ associated with the local segmental and slow chain modes.

The parameter B in equation (9) has so far been viewed through two apparently different approaches. In the simple three-state rotational isomerization model, B is related to the activation energy (E) of the rotation about the main-chain bonds, which incorporates the interaction of the polymer segments[25]. The energy E amounts to 9.8 kJ mol^{-1}, which is somewhat higher than the value for PP[7]. In the free-volume model, B is related to the free-volume expansion coefficient $\alpha_f = \gamma/B = 8.5 \times 10^{-4}$ K^{-1} (γ is a constant nearly equal to one)[26]. These physically meaningful values suggest that the segmental relaxation responsible for the ultrasonic absorption at high frequencies (*Figure 3*) is the same physical process expressed in $c(t)$. However, there are additional slower modes active in the ultrasonic experiment but so far inactive in the p.c.s. We next discuss this discrepancy in terms of the longitudinal compliance $D''(\omega)$ constructed from the u.s. and p.c.s. data.

Dynamic longitudinal compliance

The experimental $M''(\omega)$ shown in *Figure 3* was used to calculate $D''_{us}(\omega)$ (equation (10)) neglecting the small dispersion of $M'(\omega)$. The subscript 'us' indicates ultrasonic. Alternatively, $D''_l(\omega)$ was constructed from the relaxation function $c(t)$ according to:

$$D''_l(\omega) = (D_0 - D_\infty) \int_0^\infty \cos(\omega t) c(t)\,\mathrm{d}t \qquad (11)$$

The $c(t)$ was represented by the KWW equation (2) and a computer program employing numerical integration was used to obtain the values of $D''_l(\omega)/(D_0 - D_\infty)$ for the light scattering. The results of the calculations are plotted together with $D''_{us}(\omega)$ in *Figure 5* as a function of the logarithm of the reduced frequency $\alpha_T f$. The reference temperature was chosen as 20°C and the shift factor α_T for the light scattering time was computed from equation (9).

Some features of these results are as follows. The maximum of the quantity $D''_l(\omega)/D_0 - D_\infty)$ is an indication of the breadth of the retardation spectrum; it amounts to 0.5 for a single relaxation time. Here it has the value 0.195, indicating a broad distribution of retardation times characterized by $\beta = 0.35$ in equation (2). A similar value was reported for the bulk[6] and longitudinal compliance[27] in poly(vinyl acetate). Those measurements, however, were performed at temperatures equally removed from T_g. In the present case, D''_{us} was obtained at a higher temperature than D''_l, so that it is reasonable to assume a narrower distribution for the former[13,28]. The broken curve in *Figure 5* is computed from equation (11) with $\beta = 0.5$ for comparison. The obvious deviations at

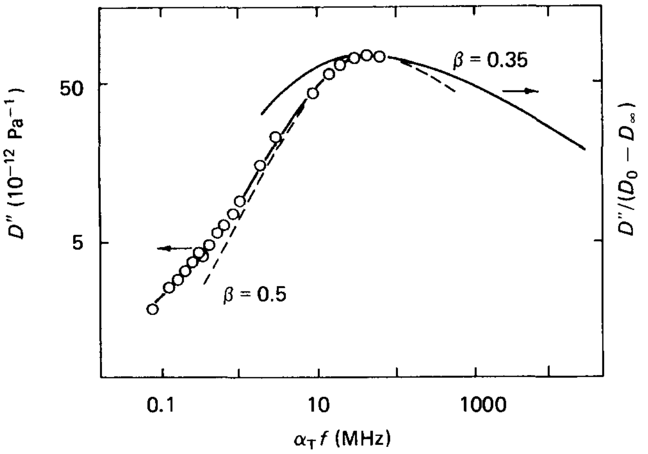

Figure 5 Dynamic longitudinal compliance D'' obtained from the ultrasonic data of *Figure 3* and the normalized $D''/(D_0 - D_\infty)$ computed from equation (11) using the relaxation function $c(t)$ *versus* the reduced frequency. Full and broken curves denote calculations using $\beta = 0.35$ and 0.5, respectively

lower frequencies are probably due to the contribution of cooperative chain modes in D''_{us}.

The ultrasonic data of *Figure 3* still show significant dispersion at frequencies lower than 1 MHz observed also by dynamic viscosity measurements[22,23]. This finding suggests that we should detect in the time window of the correlator dynamic light scattering from PB at 20°C. *Figure 6* shows for the first time, to our knowledge, a weak correlation from about 10^{-6} to 10^{-2} s, which cannot be confused with the tail of the segmental relaxation clearly observed at low temperatures; at 20°C it would be less than 10^{-7} for the KWW equation (2). Based on the comparison with the ultrasonic data, the correlation of *Figure 6* is probably contributed by slow chain modes. From the viewpoint of the ultrasonic spectra[22,23], these slow modes are connected to 'Rouse'-like normal modes and entanglement effects. The small amplitude of $c(t)$ in *Figure 6* suggests that $D_l''(\omega)$ is affected less by the viscoelastic normal modes, usually seen in shear compliance J^* (ref. 29), than by local modes. This is not surprising, because longitudinal deformation combines shear and compressional contributions[26]:

$$D^* = B^*J^*/(J^* + \tfrac{4}{3}B^*) \qquad (12)$$

In the terminal region far above T_g, since the shear J^* is much greater than the compressional compliance B, the longitudinal D^* is approximated by B^*. It is known that the localized segmental motion is mainly responsible for the relaxation of B[26,27]. Thus for soft polymers for which the factor B^*/J^* is very small at the frequency of measurements, D^* is nearly equivalent to B^*.

CONCLUSIONS

The combination of dynamic light scattering and ultrasonic relaxation studies provides a deeper understanding of the dynamic behaviour in polymers. The main advantage is that both methods probe the same mechanical properties over a wide frequency range. It has been shown that the segmental relaxation time obtained from the photon correlation spectroscopic and ultrasonic measurements on bulk PB over nine decades of time conform to a single WLF equation. At higher temperatures, photon correlation spectroscopy can also detect slower modes, which are active in the ultrasonic experiments. Based on ultrasonic relaxation results, these modes can be related to subchain motions and entanglement effects.

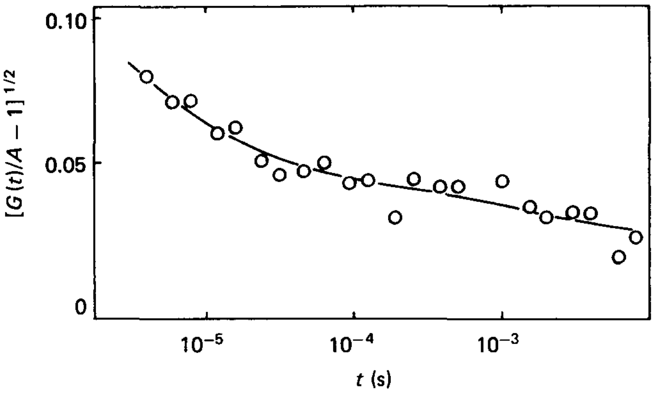

Figure 6 Measured net correlation function for PB at 20°C

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