Dynamic light scattering study of poly(di-n-butyl itaconate) in the glass transition region

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Dynamic light scattering (DLS) studies of several polymers were carried out in the bulk state at temperatures just above the glass transition using a multi-tau correlator. The principal focus was to characterize the viscoelastic relaxation spectrum of poly(di-n-butyl itaconate) (PdnBI), a thermorheologically complex polymer with a pronounced secondary relaxation process due to motions of the alkyl side chains. These data were compared with corresponding observations of two thermorheologically simple polymers, polystyrene (PS), and poly(vinyl acetate) (PVAc) whose DLS properties have been previously investigated. The complete DLS spectra of PS and PVAc can be obtained in a single multi-tau record and are reasonably consistent with earlier literature data, provided appropriate scaling to the glass transition temperature is made. The DLS spectrum of PdnBI requires splicing of two multi-tau records and thus exhibits a wider distribution of relaxation times than those of PS and PVAc. The shape of the PdnBI spectrum appears to be independent of temperature suggesting that there is a strong coupling of the side- and main-chain motions in the glass transition region.

(Keywords: dynamic light scattering; glass transition; viscoelastic relaxation)

INTRODUCTION

Photon correlation spectroscopy (p.c.s.) has found useful application in probing the dynamical behaviour of amorphous polymer materials in the temperature range close to and above the glass transition temperature, T_g[1–17]. The technique measures the normalized intensity autocorrelation function,

$$C(t) = \frac{\langle n(0)n(t)\rangle}{\langle n\rangle^2} - 1 \qquad (1)$$

where n is the measured intensity per sample interval, and the angular brackets denote the time-average of the enclosed quantity. The correlation function is related to the relaxation function $\Phi(t)$ for fluctuations in the dielectric tensor

$$C(t) = f\Phi^2(t) \qquad (2)$$

where

$$\Phi(t) = \langle \Delta\varepsilon(t)\Delta\varepsilon(0)\rangle / \langle \Delta\varepsilon^2\rangle \qquad (3)$$

and $\Delta\varepsilon(t)$ is the magnitude of the dielectric tensor fluctuation of the appropriate symmetry and f is a constant. Experiments may be performed in either VV geometry, with both the incident and detected radiation vertically polarized, or in VH geometry where the incident light is vertically polarized and the detected light horizontally polarized. The VV intensity is a superposition of the isotropic scattering contribution from the symmetric components $\Delta\varepsilon_{ii}$, and the anisotropic scattering from the off-diagonal components $\Delta\varepsilon_{ij}$, of the dielectric tensor. The VH scattering arises only from the latter dielectric anisotropy fluctuations, $\Delta\varepsilon_{ij}$.

The isotropic scattering can be shown to be related to the relaxation function of the density fluctuations:

$$C_{\mathrm{iso}}(t) = f\phi^2_{\mathrm{iso}}(t) \qquad (4)$$

where

$$\phi_{\mathrm{iso}}(t) = \langle \delta\rho(q,t)\delta\rho(q,0)\rangle / \langle \delta\rho(q,0)^2\rangle \qquad (5)$$

and

$$\delta\rho(q,t) = \int e^{iq\cdot r}[\rho(r,t) - \rho_0]\,\mathrm{d}^3r \qquad (6)$$

is the qth Fourier component of the density fluctuations with $|q| = (4\pi n/\lambda)\sin\theta/2$ the scattering vector. The anisotropic scattering is related to the relaxation function for fluctuations in the polarizability anisotropy:

$$C_{\mathrm{VH}}(t) = f''\phi^2_{\mathrm{VH}}(t) \qquad (7)$$

with

$$\phi_{\mathrm{aniso}}(t) = \langle \delta\gamma_0(0)\delta\gamma_0(t)\rangle \qquad (8)$$

where γ_0 is the mean anisotropy of polarizability per monomer. In each case, the correlation function of light scattered by amorphous polymers in the glass transition regime covers a relatively wide time scale and can often be described quite accurately[1–17] by a stretched exponential function

$$\phi(t) = \exp(-t/\tau)^\beta \qquad (9)$$

where the exponent β, $0 < \beta < 1$, is a measure of the width of the relaxation spectrum of the dissipative viscoelastic process which determines the dynamics of the fluctuations in $\Delta\varepsilon$.

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Previous dynamic light scattering (DLS) studies of polymer may be divided into those which deal with thermorheologically simple polymers, i.e. polymers whose relaxational behaviour near T_g is dominated by the main-chain dynamics associated with the glass transition, and thermorheologically complex polymers whose viscoelastic behaviour near T_g is influenced by multiple relaxation processes. Examples of the former include polymers like poly(vinyl acetate) (PVAc)[10,13], polypropylene[15]and polybutadiene[16]. For these species, anisotropic scattering is negligible in comparison to the isotropic scattering from density fluctuations. The correlation functions for VV scattering are fitted satisfactorily by equation (8) with $\beta = 0.3 - 0.4$. For polypropylene glycol (PPG) and polystyrene (PS), two other thermorheologically simple polymers, both VV and VH scattering have been studied. For each polymer, the VV scattering fits equation (1) with $\beta = 0.3$ (PS)[2] and $\beta = 0.5$ (PPG)[6]. Likewise, the VH scattering fits equation (1) with $\beta = 0.4$ (PS)[1] and $\beta = 0.5$ (PPG)[6]. The exponent is essentially constant over the temperature range accessible to study, $T_g + 5°\text{C} < T < T_g + 60°\text{C}$ consistent with the expectation that the width of the relaxation spectrum for these materials should be independent of temperature.

Several thermorheologically complex polymers have been studied. These generally represent polymers with flexible alkyl side chains whose motions have a relaxation spectrum which overlaps that of the backbone motions in the T_g range. Examples include members of the n-alkyl methacrylates for which the scattering is dominated by the density fluctuations. The VV scattering from these polymers can also be fit reasonably well by equation (9) with, however, a smaller exponent which apparently shows significant temperature dependence, e.g. for poly(methyl methacrylate)[9,14,17], $\beta = 0.15$–0.31 in the range $T_g + 15°\text{C} < T < T_g + 40°\text{C}$. Similar behaviour has been reported for the ethyl[7] and n-butyl[11] derivatives. The small, temperature-dependent exponent observed in these studies is consistent with the expectation that there are two broad relaxation spectra which overlap and have different activation energies. Indeed, for the methyl[14,17], ethyl[7] and n-butyl methacrylate[11] polymers, evidence for the coexistence of two relaxation processes has been presented, either via fits of the correlation function to the bimodal expression

$$\phi(t) = \alpha \exp(-t/\tau_1)^{\beta}1 + (1-\alpha)\exp(-t/\tau_2)^{\beta}2 + b \qquad (10)$$

where b is a baseline correction of the order 10^{-3}, or by numerical inversion of the correlation function to obtain the distribution function, $G(\tau)$

$$G(t) = \int_0^{\infty} \phi(t)\,\mathrm{e}^{-t/\tau}\,\mathrm{d}\tau \qquad (11)$$

In these analyses, the temperature dependence of the calculated spectra are consistent with the identification of the fast and slow relaxation modes as, respectively, the side-chain motion and the glass transition process, associated with backbone motion.

Several theoretical discussions have attempted to connect the relaxation spectra for isotropic and anisotropic scattering to the appropriate viscoelastic spectra. An early heuristic discussion by Lee *et al.*[4], suggested that the dynamic scattering from density fluctuations is related to the retardation spectrum of the bulk (voluminal) compliance. Subsequently, following the molecular theory of scattering from fluids of Rytov[18], Patterson[19] has proposed that the isotropic scattering is determined by the relaxation spectrum associated with the longitudinal modulus. Finally, Wang and Fischer[20] presented a detailed theoretical analysis which produced a relationship between the isotropic scattering spectrum and the distribution of retardation times for the longitudinal compliance. In confirmation of this theory, DLS data on PVAc were found[13] to have a relaxation spectrum with a shape and average relaxation time comparable (though not identical) to that of the retardation spectrum for the longitudinal compliance as measured by McKinney and Belcher[21]. The connection between the depolarized light scattering spectrum and the viscoelastic properties has also been discussed. Patterson[19] and Wang[22] have suggested a relationship with the relaxational part of the shear modulus.

EXPERIMENTAL

Optically clear prisms of PS, PVAc and poly(di-n-butyl itaconate) (PdnBI) were synthesized by bulk polymerization of ultra-filtered monomer using procedures described elsewhere[3,10,12]. Vinyl acetate monomer (Aldrich Chemical Co.) and di-n-butyl itaconate monomer (Polysciences Inc.) were purified by several slow, careful distillation steps, filtered several times through a 0.5 μm Millipore filter, and finally filtered directly into a sample cell suitable for light scattering experiments. The monomer in the sample cell was cycled through a freeze/thaw procedure under vacuum (1.33×10^{-2} Pa) to remove dissolved gases until no air bubble was visible during the thaw period. The monomer was then frozen and sealed at 1.33×10^{-2} Pa. To effect polymerization, the samples were irradiated with ultraviolet (u.v.) radiation at 35°C for ~48 h. The resulting samples were annealed at 80°C for 1 week, and then at 90°C for 1 week. Subsequently, the samples were stored at 60°C. Styrene monomer (Aldrich Chemical Co.) was purified by vacuum distillation several times, and mixed with 0.05% w/v of azobisisobutyronitrile initiator (previously recrystallized from methanol). The mixture was filtered through a 0.5 μm filter into the sample cell and placed under vacuum (1.33×10^{-2} Pa) for 30 min and then sealed under vacuum. To effect polymerization, the mixture was maintained, sequentially, at 80°C for 3 days, 90°C for 5 days, 100°C for 1 week and 120°C for 1 week. The sample was stored at 110°C.

The apparent glass transition of each sample was measured by differential scanning calorimetry (d.s.c.) at several heating and cooling rates. The T_g was determined by double extrapolation to zero heating/cooling rate, as shown in *Figure 1*. We obtained T_g (PS) = 100.5°C, T_g (PdnBI) = −5°C and T_g (PVAc) = 33°C.

The light scattering instrument comprised an argon ion laser source (Coherent Radiation) providing 300 mW of power at 514 nm, an ITT FW 130 photomultiplier tube, and a 256-channel multi-tau digital correlator (Brookhaven BI 2030 AT). Complete dynamical characterization of the light scattered by the PS and PVAc samples could be achieved in a single multi-tau record, with appropriately spaced sampling rates. For the PdnBI sample, the correlation function encompassed a considerably wider range of decay times, and it was necessary to splice together two multi-tau records. Minor

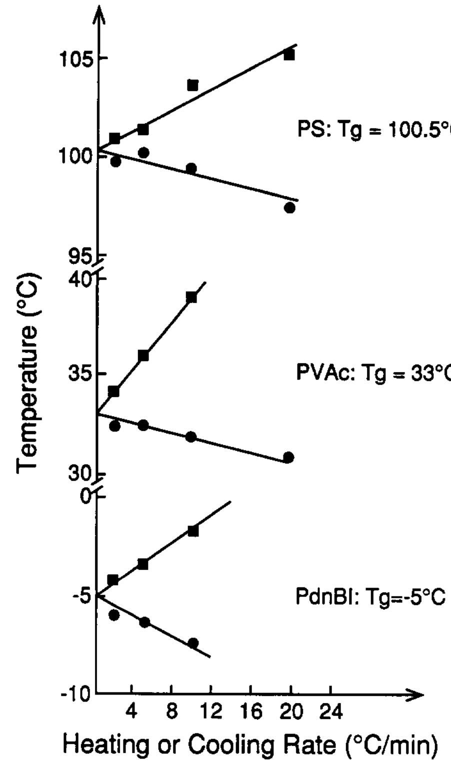

Figure 1 Determination of T_g by extrapolation of apparent transition temperatures in d.s.c. scans at variable heating (■) and cooling (●) rates

vertical adjustments were necessary to join the overlapping segments smoothly.

The correlation functions, normalized according to equation (1) by the experimental baseline, $\langle n \rangle^2$, were fitted to an equation of the stretched exponential form

$$\phi(t) = \exp(-t/\tau_0)^{\beta} + b \qquad (12)$$

where τ, β and b are adjustable parameters determined by a non-linear least squares program that minimized the residuals. The parameter b is a small adjustment to the baseline (of the order 10^{-3}) which arises from several sources:

1. slow variations in laser intensity over the long times required for data collection;
2. light scattering from slow processes which relax on time scales comparable to the collection time scale;
3. slight misnormalizations in the correlation function.

RESULTS AND DISCUSSION

Experimental studies of PS, PVAc and PdnBI were carried out primarily for the purpose of comparison with earlier investigations. In *Figure 2* we show representative correlation functions for VH scattering from PS at 110.5°C, VV scattering from PVAc at 60°C and VV scattering from PdnBI at 15°C. The first two data sets represent single multi-tau records; the third corresponds to two multi-tau records spliced together. Also shown in *Figure 2* are the least-squares fits to equation (12). Results of such fits for each polymer at several temperatures are summarized in *Tables 1–3*, together with values of the mean relaxation time, $\langle \tau \rangle$, calculated from[1–3]

$$\langle \tau \rangle = (\tau_0/\beta)\Gamma(1/\beta) \qquad (13)$$

The experimental data for PS are consistent with previous

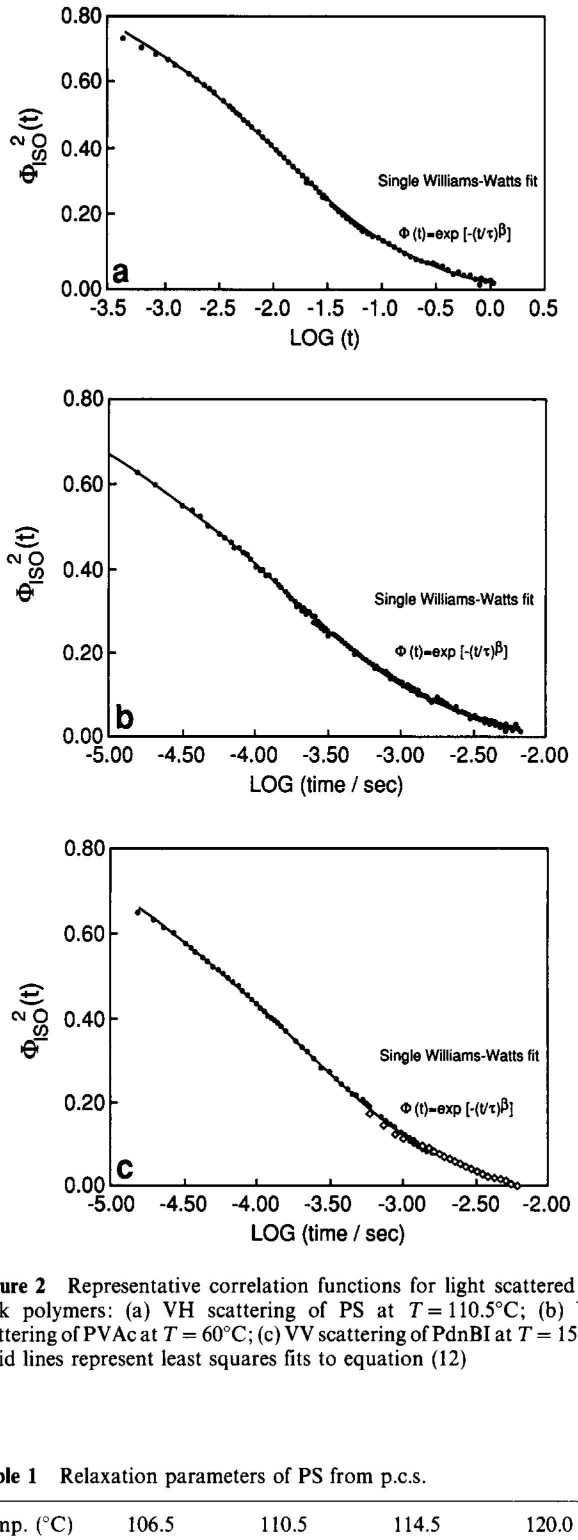

Figure 2 Representative correlation functions for light scattered by bulk polymers: (a) VH scattering of PS at $T = 110.5$°C; (b) VV scattering of PVAc at $T = 60$°C; (c) VV scattering of PdnBI at $T = 15$°C. Solid lines represent least squares fits to equation (12)

Table 1 Relaxation parameters of PS from p.c.s.

Temp. (°C)	106.5	110.5	114.5	120.0
τ_0 (s)	1.630	0.084	0.013	0.006
β	0.370	0.360	0.366	0.380
b	0.0008	0.0018	0.0040	0.0009
$\langle \tau \rangle$ (s)	6.710	0.380	0.060	0.025

Table 2 Relaxation parameters of PVAc from p.c.s.

Temp. (°C)	45	50	55	60
τ_0 (s)	0.4970	0.0647	0.0066	0.0009
β	0.37	0.34	0.35	0.36
b	0.0010	0.0015	0.0007	0.0011
$\langle \tau \rangle$ (s)	2.0200	0.3750	0.0340	0.0042

Table 3 Relaxation parameters of PdnBI from p.c.s. (single KWW fit)

Temp. (°C)	10	15	20	30
τ_0 (s)	1.3500	0.2500	0.1200	0.0084
β	0.25	0.23	0.24	0.24
b	0.0015	0.0018	0.0005	0.0056
$\langle\tau\rangle$ (s)	31.90	12.05	4.19	0.24

results[1-3]. Thus the relaxational exponent β determined in this work is temperature independent and has a value 0.37 ± 0.01 consistent with that determined by fits to equation (12) in previous work[2]. Likewise, values of $\langle\tau\rangle$ determined here are numerically similar to those obtained in earlier work[1-3].

With regards to PVAc, two earlier PCS studies exist in the literature[10,13]. The relaxational exponent we obtain here is again found to be temperature independent with a value of $\beta = 0.34 \pm 0.015$ similar to that reported by Fytas *et al.*[13] on a low molecular weight sample ($T_g = 17$°C) and significantly smaller than that ($\beta = 0.46$) obtained in earlier experiments on a sample with $T_g = 35$°C in our laboratory, using a single-tau correlator and multiple record splicing. The average relaxation times $\langle\tau\rangle$ obtained here are numerically comparable, but not identical, to those reported in the earlier studies, provided appropriate scaling is made for variations in T_g between the various samples. The average relaxation times determined in our experiments are systematically smaller by ~30% than those of Fytas *et al.*[13] at comparable temperature distances from T_g. As discussed below, these discrepancies are probably due to errors in the precise location of T_g for one or more of the PVAc samples utilized in the different p.c.s. studies.

To see this, it is instructive to compare the viscoelastic functions computed from the p.c.s. data. We adopt the theoretical arguments developed by Wang and Fischer[20] that the scattering from density fluctuations is equivalent to a measurement of the relaxational component of the longitudinal compliance, $D(t)$:

$$D(t) = D_0 - (D_0 - D_\infty)\phi(t) \tag{14}$$

where D_0 and D_∞ are the zero- and high-frequency compliance, respectively. For amorphous polymers, above T_g, we can replace $D(t)$ by the bulk compliance $B(t)$, since the shear modulus, $G(t)$, is numerically small compared to $B(t)$:

$$B(t) = B_0 - (B_0 - B_\infty)\phi(t) \tag{15}$$

Note that it follows from equation (13) that the correlation function $\phi(t)$ is a direct measure of the distribution of retardation times, $L(\ln\tau)$, since by definition[23]

$$B(t) = B_0 - (B_0 - B_\infty)\int_{-\infty}^{\infty} L(\ln\tau)\,\mathrm{e}^{-t/\tau}\,\mathrm{d}\ln\tau \tag{16}$$

The retardation spectrum can be obtained[13] using the Schwarzl and Staverman approximation[24]

$$L(\ln\tau) = \frac{1}{B_0 - B_\infty}\left[\frac{\mathrm{d}B(t)}{\mathrm{d}\ln t} - \frac{\mathrm{d}^2B(t)}{\mathrm{d}(\ln t)^2}\right]_{t=2\tau} \tag{17}$$

Substituting equations (8) and (14) into (16), we obtain

$$L(\ln\tau) = \beta(2\tau/\tau_0)^\beta \exp[-(2\tau/\tau_0)^\beta \,|\, 1 + \beta(2\tau/\tau_0)^\beta - \beta] \tag{18}$$

This approach to extract $L(\ln\tau)$ has been successfully tested on several polymers[13].

In addition, the storage and loss components of the dynamic compliance, $B'(\omega)$ and $B''(\omega)$, can be computed from $L(\ln\tau)$ since it can be shown that[25]

$$B'(\omega) = B_\infty + (B_0 - B_\infty)\int_{-\infty}^{\infty} \frac{L(\ln\tau)}{1+\omega^2\tau^2}\,\mathrm{d}\ln\tau \tag{19}$$

$$B''(\omega) = (B_0 - B_\infty)\int_{-\infty}^{\infty} \frac{L(\ln\tau)\omega\tau}{1+\omega^2\tau^2}\,\mathrm{d}\ln\tau \tag{20}$$

In *Figures 3* and *4*, we show $B'(\omega)$ and $B''(\omega)$ computed from our experimental data using equations (16)–(20), and compare the results with the corresponding functions calculated from the experimental data of Fytas *et al.*[13], and with the mechanical relaxation data of McKinney and Belcher[21]. To make this comparison, we need to compensate for the difference in T_g of our PVAc sample ($T_g = 33$°C) from those used in the other two studies ($T_g = 17$°C in each case). We compute the DLS relaxation time, τ_0, at 66°C by using the WLF equation which fits our data:

$$\langle\tau(T)\rangle = \langle\tau(T_g)\rangle \exp\left[\frac{-2.303C_{1g}(T - T_g)}{C_{2g} + T - T_g}\right]$$

with $C_{1g} = 15.9$, $C_{2g} = 47.1$ and $\langle\tau(T_g)\rangle = 10^{3.6}$ s. The

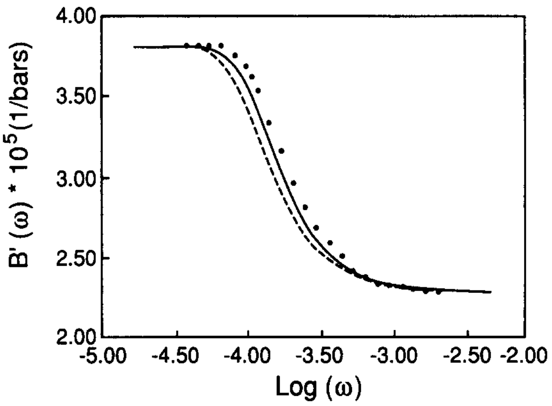

Figure 3 Storage bulk compliance $B'(\omega)$ of PVAc *versus* log frequency: (———) calculated from light scattering data (this work) scaled to 66°C ($T_g = 33$°C); (---) calculated from light scattering data[13] scaled to 50°C ($T_g = 17$°C); (●) mechanical relaxation data[21] at 50°C ($T_g = 17$°C)

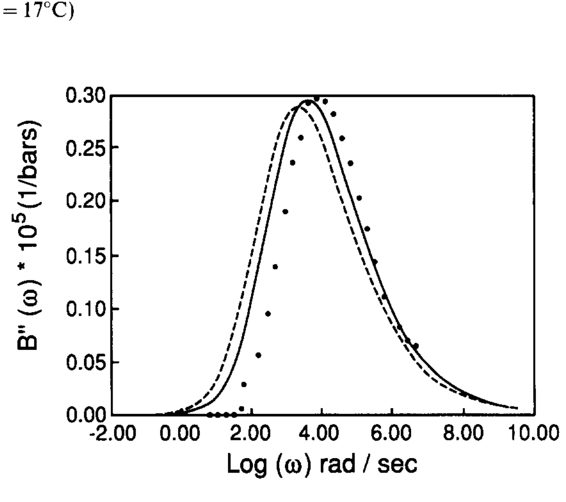

Figure 4 Loss bulk compliance $B''(\omega)$ of PVAc at $T = T_g + 33$°C. For symbols see *Figure 3*

latter values are in reasonable accord with literature data. We obtain $\tau_0(66°C) = 2.45 \times 10^{-4}$ s and utilized this value and $\beta = 0.36$ in equations (16)–(19). The corresponding values computed from the results of Fytas *et al.*[13] are $\tau_0(50°C) = 4.7 \times 10^{-4}$ s and $\beta = 0.35$. We computed B_0 and B_∞ values from the bulk moduli data of McKinney and Belcher[21], appropriately corrected for the difference in T_g of their sample:

$$B_0(T, P) \times 10^5 = 2.919 + 1.905 \times 10^{-2}(T - 16) - 0.95 \times 10^{-3}P - 1.011 \times 10^{-5}(T - 16)P$$

and

$$B_\infty(T, P) \times 10^5 = 1.865 + 0.836 \times 10^{-2}(T - 16) - 0.433 \times 10^{-3}P - 0.685 \times 10^{-5}(T - 16)P$$

We obtained $B_0 = 3.817 \times 10^{-10}$ and $B_\infty = 2.283 \times 10^{-10}$ Pa^{-1}.

Comparing our calculated results for $B'(\omega)$ and $B''(\omega)$ with those of Fytas *et al.*[13] and with the mechanical relaxation data of McKinney and Belcher[21], we find reasonable agreement. The discrepancy is almost certainly due to errors in defining the precise location of T_g. Note that our light scattering experiments were performed on an anhydrous PVAc sample sealed under vacuum, whereas our d.s.c. measurement of T_g was made on a piece of the sample in equilibrium with the atmosphere. It is well-established[26] that plasticization by atmospheric moisture significantly lowers the T_g of PVAc samples. If we utilized a higher $T_g = 36°C$ for our sample, our results would be in excellent agreement with the results of McKinney and Belcher[21].

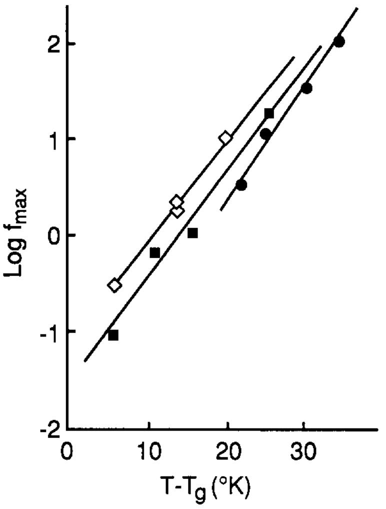

Figure 5 Comparison of frequencies of maximum loss for p.c.s. and mechanical spectroscopy of PdnBI: (■) f_{max} of $B''(\omega)$ calculated from DLS data, fitted to equation (12); (◇) f_{max} of $B''(\omega)$ calculated from DLS data[12]; (●) f_{max} of tan δ_E measured by Rheovibron[28]

Table 4 Relaxation parameters of PdnBI from p.c.s. (double KWW fit)

Temp. (°C)	10	15	20	30
α	0.27	0.32	0.38	0.39
$(1 - \alpha)$	0.73	0.68	0.62	0.61
τ_1 (s)	0.0640	0.0120	0.0058	0.0012
β_1	0.35	0.33	0.31	0.27
τ_2 (s)	4.850	1.810	0.770	0.038
β_2	0.29	0.30	0.31	0.27
b	0.0015	0.0015	0.0004	0.0055
$\langle\tau_1\rangle$ (s)	0.310	0.075	0.047	0.020
$\langle\tau_2\rangle$ (s)	52.00	16.80	5.99	0.57
$\langle\tau\rangle$ (s)	38.00	11.45	3.73	0.36

The distribution of relaxation times associated with the light scattering properties of PdnBI is considerably broader than that of PVAc or PS, as evidenced by the smaller value of the relaxational exponent $\beta = 0.23 \pm 0.01$ (*Table 3*). This is consistent with the fact that in the temperature range of our study there are two overlapping mechanisms contributing to the relaxation of the density fluctuations, namely side-chain motions as well as the cooperative backbone motions which are principally associated with the glass transition. Our present results are in good, but not perfect, agreement with our earlier p.c.s. study of PdnBI[12], using a single-tau correlator. Thus, in *Figure 5*, we compare values of the frequency of maximum loss, f_{max}, estimated in our previous work, with values determined via computation of $B''(\omega)$ (equation (20)) in this study. The small systematic discrepancies are again most likely due to errors in defining the T_g (= 2°C) of our earlier sample, which was measured at a finite heating rate ($10°C\,min^{-1}$). A significant distinction is that in fitting our correlation functions to equation (12), we find an exponent β which is temperature independent, within experimental error. In our earlier analysis, we obtained[12], over a comparable temperature range, an exponent which was larger, and systematically increased with temperature ($0.32 < \beta < 0.46$). These differences may be due, again, to errors in the smoothing and splicing procedures used in our previous work to generate a composite correlation function. An additional factor, however, is that the relative separation of the side- and main-chain relaxation spectra is decreased in the present PdnBI sample which has a lower T_g. We also show in *Figure 5*, the temperature dependence of the maximum in $\tan \delta_E = E''/E'$ from tensile modulus data[28] on a PdnBI sample of $T_g = 12°C$. Again reasonable agreement is observed with the p.c.s. data.

The observation of a temperature-independent β parameter in PdnBI suggests we may be dealing with a hybrid process in which the side- and main-chain motions are coupled. Such behaviour has been suggested as occurring in the poly(n-alkyl methacrylates) over certain temperature–frequency ranges, and has been referred to as an $\alpha\beta$-process[27]. We note that the tan δ mechanical loss peak of PdnBI ($T_g = 12°C$) at a frequency of 1 Hz shows a single well-defined peak in the glass transition regime, with no sign of a low-temperature shoulder as observed in the other di-n-alkyl itaconates[28], and in the poly(n-alkyl methacrylates)[29]. To further illustrate this behaviour, we present, in *Table 4*, results of fits of the correlation function to a sum of two stretched exponential functions (equation (10)). Such double-function fits are of comparable quality to those based on equation (12). Contrasting these parameters with those derived by fitting to a single function in *Table 3*, we find that, as expected, the mean relaxation times of the former $\langle\tau\rangle = \alpha\langle\tau_1\rangle + (1 - \alpha)\langle\tau_2\rangle$ are numerically similar to the latter. The bi-functional fits yield two functions of comparable shape and width, as evidenced by the numerical similarity of $\beta_1 \sim \beta_2 \sim 0.3$. The temperature dependence of the average relaxation times of the fast and slow modes, $\langle\tau_1\rangle$ and $\langle\tau_2\rangle$, are consistent with the

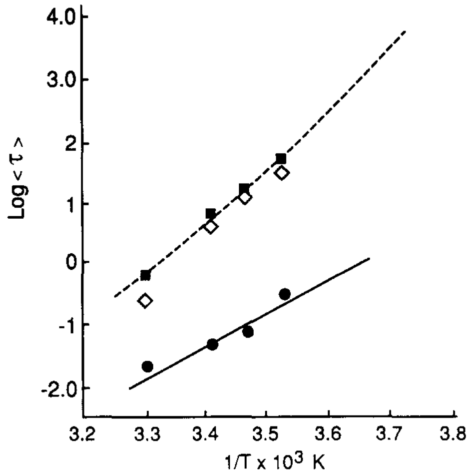

Figure 6 Arrhenius plot of relaxation times computed from DLS data of PdnBI; (◇) $\langle\tau\rangle$ values (*Table 3*); (■) $\langle\tau_1\rangle$ and (●) $\langle\tau_2\rangle$ values (*Table 4*); (---) Williams–Landel–Ferry fit with parameters $C_{1g} = 13.6$, $C_{2g} = 86.7$, $\langle\tau(T_g)\rangle = 5623$ s

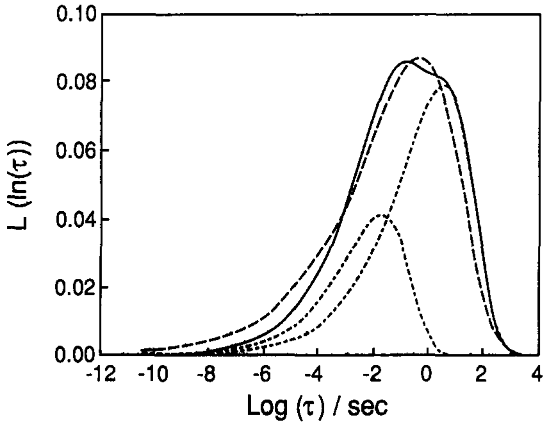

Figure 7 Normalized retardation spectra computed from DLS data of PdnBI at 15°C: (---) equation (17), single relaxation process; (———) equation (17), sum of two relaxation processes; (·–·–) equation (17), fast and slow relaxation components of double relaxation fit

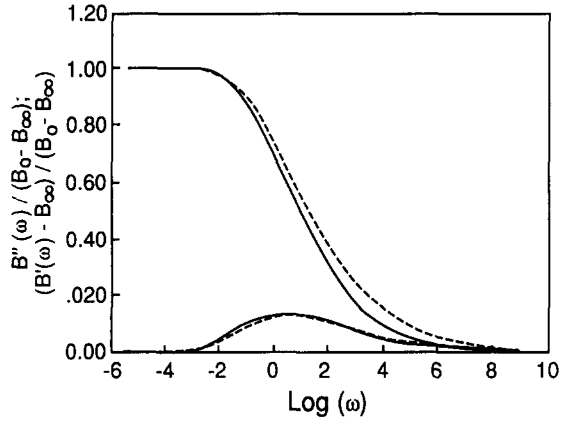

Figure 8 Comparison of normalized storage and loss bulk compliance of PdnBI, computed based on fits of DLS data to a single (---) and double (———) relaxation process at $T = 15$°C

assignment of the former to the side-chain motion, and the latter to the main-chain motion, as shown in *Figure 6*. The apparent activation energy of the slow mode is $E_{a_2} = 163\,\mathrm{kJ\,mol^{-1}}$, comparable to that ($E_a = 201\,\mathrm{kJ\,mol^{-1}}$) reported for the temperature dependence of $\tan\delta_E$. Note that E_a of $\langle\tau\rangle$ estimated from fits to a single stretched exponential (*Table 3*) is $176\,\mathrm{kJ\,mol^{-1}}$, consistent with the fact, evident from *Table 4*, that the average relaxation time is dominated by contributions from the slow mode. On the other hand, the activation energy of the fast mode in *Figure 6*, $E_{a_1} = 92\,\mathrm{kJ\,mol^{-1}}$, is similar to literature values for the side-chain motion of the poly(alkyl itaconates)[30] and the poly(alkyl methacrylates)[31].

An interesting feature of the bi-functional fits evident in *Table 4*, is that the relative amplitude of the two relaxation modes shows significant temperature dependence, with the slow mode decreasing in intensity with increasing temperature. This effect is illustrated in *Figure 7* where we compare the retardation spectra calculated via equation (17) for single and bi-functional fits. Since each fit is of a comparable accuracy, *Figure 7* also exemplifies the relative insensitivity of $\phi(t)$ to the precise details of $L(\ln\tau)$ when the α and β processes overlap. At lower temperatures, a shoulder is clearly seen in the spectra calculated for the bi-functional fits which is not present in the single fits. Note, that the computed viscoelastic quantities $B'(\omega)$ and $B''(\omega)$ are similarly insensitive to the precise form of $L(\ln t)$, as shown in *Figure 8*, in which we compare these functions for single and bi-functional fits at $T = 10$°C. Even for the latter fit, for which $L(\ln\tau)$ has a pronounced shoulder (*Figure 8*), $B''(\omega)$ shows a single peak. We recall here that $\tan\delta_E$ and log decrement shear studies of PdnBI likewise show a single loss peak at frequencies in the range 1–110 Hz. In dielectric and mechanical relaxation studies of poly(n-alkyl methacrylates), where separation of the side- and main-chain contributions has been attempted[30,31], an analogous decrease in the relative amplitude of the latter is found with increasing temperature[32]. This effect has been interpreted as a manifestation of coupling or exchange of energy between the two processes[33].

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