Effect of Pressure on the Dielectric Relaxation of Poly-n-Butyl Methacrylate

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The dielectric properties of poly-n-butyl methacrylate have been studied over a range of frequency, temperature and pressure. The data shows that the relaxation process is ($\alpha\,\beta$) at low pressures, and resolves into components at high pressures. The behaviour of the ($\alpha\,\beta$) and resolved β relaxations is discussed, and mechanisms are proposed for these processes.

Many studies have been made of the dielectric relaxation of poly-n-alkyl methacrylates.[1-6] Two relaxation regions (α and β) are observed in polymethyl methacrylate and polyethyl methacrylate. In poly-n-butyl, poly-iso-butyl and poly-n-nonyl methacrylates only one relaxation region is observed in the frequency range $10-10^6$ c/sec over a wide range of temperature.[6] Brouckère and Offergeld [3] considered that the relaxation observed in these polymers is a β relaxation, and is attributed to the motions of the ester side groups. Ishida and Yamafuji [6] consider that this relaxation is an α relaxation and is due to the microbrownian motions of the polymer chain.

In view of the large effect of a hydrostatic pressure on the α relaxation,[7-9] and the small effect of pressure on the β relaxation in linear amorphous polymers,[9] it should be possible to determine the mechanism of the relaxation in the higher n-alkyl methacrylates using the hydrostatic pressure variable in addition to temperature variation.

EXPERIMENTAL

Poly-n-butyl methacrylate was prepared by the bulk polymerization of purified monomer, using benzoyl peroxide as catalyst. The crude polymer was reprecipitated from acetone solution several times using water as the precipitant, and was freeze-dried from benzene solution.

The dielectric measurements were made using a WTW modified Schering Bridge, in conjunction with a high-pressure dielectric cell operated in the range 1-3000 atm in the manner previously described.[7] The pressure transmitting medium was silicone oil. Samples were compression-moulded at 100°C into 2·54 cm diam., 0·1 cm thick discs.

RESULTS

Preliminary measurements were made over a frequency-temperature-applied pressure range on differing samples, in order to investigate the reproducibility of our measurements. The agreement from sample to sample was poor, and was due to traces of benzene in the samples. This acted as a plasticizer to the molecular motions, and the primary loss peak locations differed by up to 0·4 decade of frequency over the samples studied. This difficulty was overcome by heating the samples

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under vacuum prior to measurement. The results then agreed at 1 atm applied pressure with those of Ishida and Yamafuji.[6]

Owing to the wide range of frequency, temperature and pressure studied, it was found necessary to make measurements on a given sample in a limited pressure range. The agreement between measurements made on different samples was judged in the region of overlap in the pressure ranges studied, and was found to be satisfactory. Fig. 1 shows a plot of dielectric loss factor ε'' as a function of frequency for given temperatures, where the pressure was varied at the given temperature. At 60·5°C the loss peak decreases rapidly with increased pressure and there is an unusual change of shape at 1000 atm. The frequency of maximum loss is hardly changed on going from 1500 to 2500 atm. For an α relaxation, we would expect [7-9]
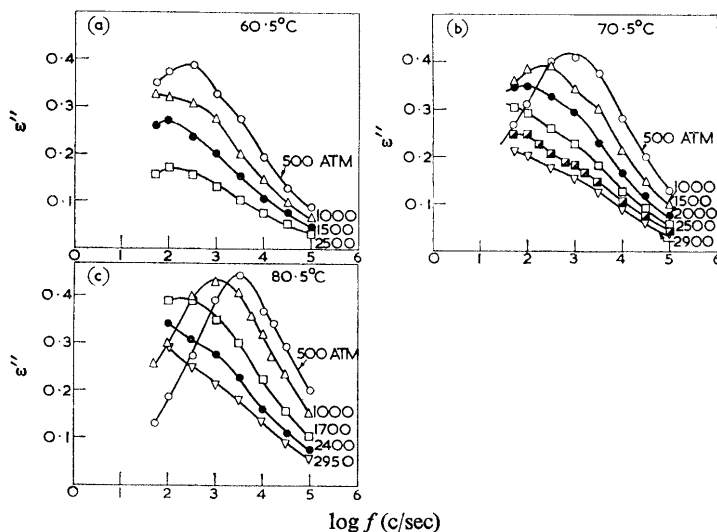

FIG. 1.—Dielectric loss factor ε'' as a function of frequency for given temperatures and applied hydrostatic pressures.

the loss curve to move continuously to lower frequencies, increasing slightly in height, keeping its shape at all pressures. This is certainly not the case for the data at 60·5°C. Also $(\partial \log f_{max}/\partial P)_T = x_T$, is found to be in the range -1 to -3×10^{-3} atm^{-1} for a normal α relaxation, which is far larger than the shift observed in fig. 1a. We conclude that the relaxation in poly-n-butyl methacrylate (PBMA) is not a normal α relaxation at 60·5°C. Hence it is not due to the co-operative microbrownian motions of the dipole units along the chain, at 60·5° at any pressure.

At 70·5°C, the loss peak decreases in height with increasing pressure, a pronounced shoulder is seen near 10^3 c/sec at high pressures, and there is a remarkable change of shape with further increase in pressure. The same pattern of behaviour is observed it 80·5°C, the main difference being that the breakdown of the shape of the curve now occurs at a higher pressure at 80·5°C than that at 70·5°C. Measurements made on a different sample to that shown in fig. 1, at 90·6°C gave loss curves whose shape was relatively independent of pressure up to about 1500 atm, but increased pressure up to 2800 atm revealed a complete breakdown of shape, and a high frequency shoulder appeared at $10^{3·5}$ c/sec at 2500 and 2800 atm.

The explanation for the unusual loss curves of fig. 1 is clear. At low temperatures and 1 atm, α and β relaxations occur in PBMA but the locations of the

separated peaks occur at inaccessibly low frequencies. As the temperature is increased at 1 atm, the α peak moves more rapidly to higher frequencies than the β peak, and at some temperature, the α and β regions overlap. At still higher temperatures, at 1 atm, the α and β peaks merge and in this condition a single process ($\alpha\beta$) is observed. On a molecular level, at low temperatures, the backbone motions (α process) and side group motions (β process) are well separated. In a critical temperature region at 1 atm, the relaxation times of backbone and side group motions become comparable and the α and β regions overlap. At higher temperatures at 1 atm, the α and β processes become indistinguishable (resulting in a single peak), since the backbone motion and side group motion both involve the composite dipole of the ester group. The dipole moment of this group can be resolved into one component μ_α directly attached to the motions of the chain backbone, and another component μ_β associated only with the independent motions of the side group. This may be represented as

$$\mu_\alpha \quad \begin{array}{c} \nearrow \quad O \\ C \!\!-\!\!-\!\!-\!\! C \\ \diagup \quad \diagdown \\ CH_3 \qquad OC_4H_9 \end{array} \quad \mu_\beta$$
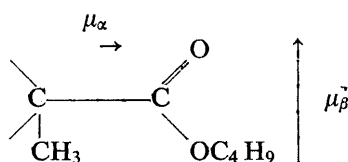
At high temperatures the backbone and side group motions become indistinguishable. Ishida and Yamafuji [6] have given a theory based on the site model for relaxation, which shows that the α and β processes will resolve at low temperatures, and become indistinguishable at high temperatures. The merged ($\alpha\ \beta$) absorption will have the character of an α absorption, particularly if the β absorption intensity is smaller than the α absorption intensity.

Two difficulties prevent a detailed analysis of the data for PBMA in terms of the site model. Ishida and Yamafuji [6] treat the motion of the backbone unit and side group unit in a single plane. In reality, the barrier opposing the backbone motion occurs in a plane perpendicular to the barrier opposing the side group motion. Thus the correct site model must be considered in three dimensions. Also these authors consider only the relaxation of a single monomer unit of the chain (their " one body approximation "), and the coupling of the motions between adjacent monomer units is not considered due to the immense mathematical difficulties of such a problem. Their theory in principle is nevertheless a considerable advance in the understanding of coupled relaxations within a single monomer unit.

The effect of pressure on relaxations coupled according to the model described above is as follows. At high temperatures and 1 atm applied pressure, the ($\alpha\ \beta$) merged relaxation is observed. Increase of pressure moves the ($\alpha\beta$) along uniformly to lower frequencies initially, but due to the effect of pressure on the α (backbone) relaxation, a splitting will occur at some high pressure which is analogous to the 1 atm critical temperature for the merging of α and β processes. At still higher pressures the α relaxation will be separated from the β relaxation and the β relaxation should be observed in our frequency range. Inspection of fig. 1 shows that this is the case experimentally. At 60·5°C, the 500 atm curve corresponds to the ($\alpha\ \beta$) relaxation at a temperature only a little higher than the coalescence condition. At 1000 atm the α peak is resolving out, at 1500 atm the β peak is left, and at 2500 atm the same β peak is observed, only its intensity has decreased with increased pressure.

At 70·5°C the 500 atm peak is a little broader than the 1 atm peak at this temperature,[6] the α splits out at 1000 atm, giving a shoulder at $10^{3·5}$ c/sec which is a manifestation of the β process. Further increase in pressure moves the α peak away, and the shoulder due to the β peak is seen at all higher pressures. The intensity of the β peak decreased with increased pressure in view of the 60·5°C data, and also from recent measurements we have made on the well-resolved β peak in polyethyl methacrylate [10] at high pressures. As a result we do not observe the actual resolved β peak at 70·5°C. The pattern at 80·5°C is similar, with the exception that 1700 atm is required to split the (α β) peak into its structure. Our measurements on a different sample at 90·6°C are similar to those at 80·5, only now 2000 atm is required to break down the (α β) peak into its structure).
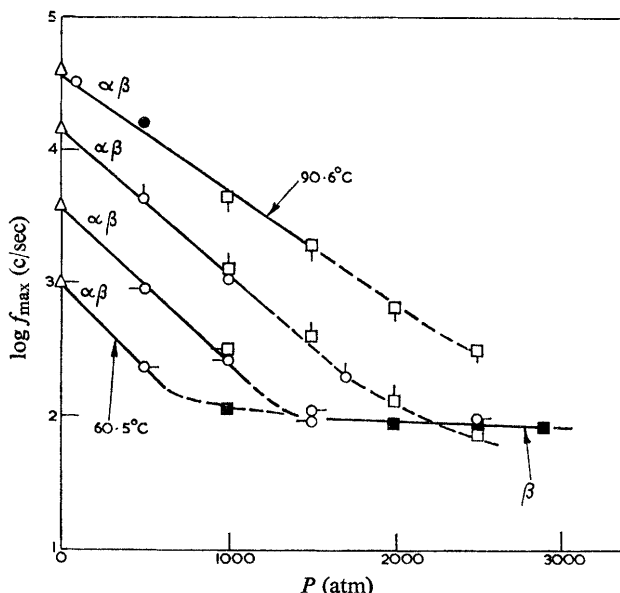

FIG. 2.—Log f_{max} as a function of pressure for given temperatures. ⊖, ⊙ and ⊘ were obtained from data of fig. 1, at 60·5, 70·5 and 80·5°C respectively. ■, ⊟, ⊡, and ☐ were obtained using a different sample at 60·5, 70·5, 80·5 and 90·6°C respectively. ● was obtained on a further sample at 90·6°C. △ indicates 1 atm data (from ref. (6)). Dashed lines indicate region of decomposition of (α β) relaxation.

Hence our experimental data shows that the (α β) mixed peak retains its normal character up to quite high pressures for 90·6°C, but as the temperature is reduced, the pressure required for distortion of the (α β) peak is also reduced, and is about 500 atm at 60·5°C.

We have plotted the frequency of maximum loss as a function of pressure for given temperatures in fig. 2. Data are presented for several samples, and the internal agreement is good. The 1 atm values were taken from ref. (6). We measured a sample of PBMA at 59·5 and 70·2°C at 1 atm in a conventional (low-pressure) dielectric cell. The locations of the loss peak coincided exactly with the data of ref. (6).

At 60·5°C, fig. 2 shows the observed frequency location of the loss peak. The continuous line indicates the region we consider the relaxation to be essentially (α β). The dashed line indicates the region where the relaxation has seriously departed from (α β) character, and the points along the 60·5°C curve above 500 atm

actually trace out the location of the β relaxation which is resolved from the α relaxation. At 70·5°C, we are able to follow the $(\alpha\beta)$ relaxation up to about 1000 atm. The points on the dashed line refer to the observed loss peak (see fig. 1). The loss curve at these high pressures shows the β relaxation shoulder, but we cannot resolve the actual β peak without unjustifiable assumptions of superposition of α and β curves. The pattern at 80·5 and 90·6°C is similar to that at 70·5°C, and we see that the $(\alpha\beta)$ relaxation breaks down (indicated by dashed lines) at still higher pressures.

The data fall into two regions of interest: (a) the behaviour of the $(\alpha\beta)$ process with pressure; (b) the behaviour of the resolved β process with pressure.

The $(\alpha\beta)$ relaxation is extremely sensitive in location to change of applied pressure. We have evaluated x_T to be $-1\cdot3$, $-1\cdot2$, $-1\cdot2$ and $-1\cdot1_5$ in units of 10^{-3} atm^{-1} at 60·5, 70·5, 80·5 and 90·6°C respectively, with an uncertainty of $\pm0\cdot05\times10^{-3}$ atm^{-1} at each temperature. It was found [7] that $-x_T$ for the α relaxation in poly methyl acrylate varied from $2\cdot6\times10^{-3}$ atm^{-1} at 40°C to $1\cdot2\times10^{-3}$ atm^{-1} at 90°C, and the α relaxation in polypropylene oxide gave $1\cdot8\times10^{-3}$ atm^{-1} at -10°C up to $2\cdot7\times10^{-3}$ atm^{-1} at $-40\cdot7$°C. For PBMA, the $|\,x_T\,|$ values do decrease with increasing temperature in accord with the above work on normal α relaxations, but the variation is smaller. The actual values of x_T for PBMA are smaller than those obtained for the α relaxation, which may reflect the fact that we are studying a merged $(\alpha\beta)$ process and not a simple α process. We have evaluated the quantity $(\partial T/\partial P)_\tau$ from a cross plot of the data of fig. 2. It decreases with increasing pressure at a given $\tau = 2\pi f_{max})^{-1}$. Taking the slopes at low pressures we obtained $(\partial T/\partial P)_\tau$ equal to 17, 18, 18 and 19°C per 1000 atm at log f_{max} equal to 2·5, 3·0 3·5 and 4·0 respectively. Thus, $(\partial T/\partial P)_\tau$ increases with increasing relaxation frequency (decreasing relaxation time) as was found previously for the α relaxations.[7, 8] The values for $(\partial T/\partial P)_\tau$ are similar to those found for polymethyl acrylate [7] and for polypropylene oxide.[8] Hence the $(\alpha\beta)$ relaxation in PBMA has properties similar to the normal α relaxation in linear polymers.

The shape of the $(\alpha\beta)$ relaxation is essentially independent of temperatures at high temperatures.[6] We have constructed in fig. 3 the master plot of $(\varepsilon''/\varepsilon''_{max})$ against log (f/f_{max}), at 1 atm, taken from the data of Ishida and Yamafuji [6] at 64, 75·5 and 87·0°C. This master curve (continuous line) is more symmetrical about log $(f/f_{max}) = 0$ than that obtained for the α relaxation in linear polymers.[7, 8, 11] In fig. 3 we show points corresponding to the $(\alpha\beta)$ relaxation at higher pressures. From fig. 1 and 2 we know that the $(\alpha\beta)$ relaxation is maintained only up to a certain pressure at a given temperature; as the temperature is increased, so the pressure range of the maintained $(\alpha\beta)$ relaxation is increased. Thus, in fig. 3, at 90·6°C, we show the 1000 and 1500 atm reduced plots. The 1000 atm plot (open circles) falls on the 1 atm master curve satisfactorily. The 1500 atm curve is broader, indicating the decomposition of the $(\alpha\beta)$ relaxation into its components. The plots at 80·5°C (500 and 1000 atm) and 70·5°C (500 atm), are a little broader than the 1 atm curve, showing again that the $(\alpha\beta)$ process is just beginning to decompose. Thus the $(\alpha\beta)$ relaxation in PBMA retains its character at high temperatures to very high pressures. The shift of log f_{max} with pressure (x_T) is lower than that observed previously for the α relaxation, but is less sensitive to variation of temperature.

The β process is only resolved in our range at 60·5°C and high pressures. In fig. 2 the location of the resolved β process is essentially independent of pressure, with $x_T = -0\cdot1\times10^{-3}$ atm^{-1}, compared with $x_T = -1\cdot1\times10^{-3}$ atm^{-1} for the $(\alpha\beta)$ process. For polymethyl methacrylate and polyethyl methacrylate, the β relaxation

is well resolved at 60·5°C and for both polymers $(\log f_{max})_\beta = 2\cdot25$ at this temperature.[6] The temperature dependence of the β processes are identical for polymethyl methacrylate and polyethyl methacrylate.[4, 6]   Also the β peak in polymethyl methacrylate [12] is independent in location and magnitude $(\varepsilon_0 - \varepsilon_\infty)$ of the degree of plasticization of the polymer.   We may regard the above as evidence that the β relaxation in n-alkyl methacrylates is intramolecular, and independent of the length of the n-alkyl group for reasonably short lengths of substituent.   We therefore would expect the β relaxation in PBMA to occur at the frequency-temperature locations observed for polymethyl and polyethyl methacrylates.   This is found to be the case at 60·5°C, since extrapolation of $(\log f_{max})_\beta$ in fig. 2 to 1 atm pressure gives a value of 2·0, compared with 2·25 observed in PMMA and PEMA.
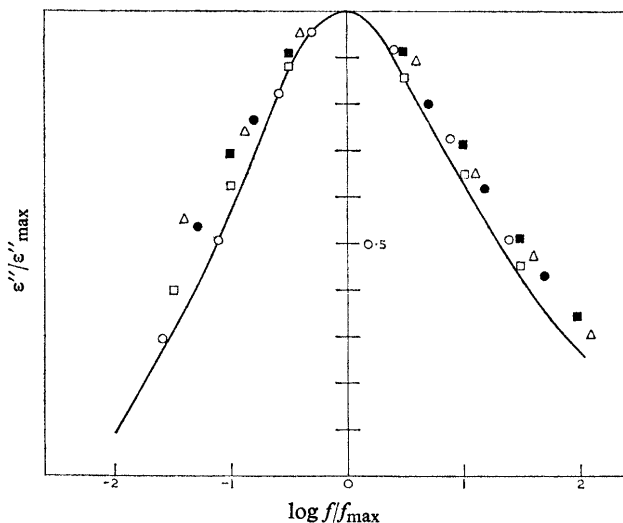

FIG. 3.—Normalized loss curves as a function of reduced frequency.   Continuous line represents the 1 atm master curve (from ref. (6)).   (○, ●) points obtained at 1000 and 1500 atm respectively at 90·6°C.   (□, ■) points obtained at 500 and 100 atm respectively at 80·5°C.   △ points obtained at 500 atm, 70·5°C.

The half-width of the resolved β peak at 60·5°C and high pressures is near four decades of frequency which is to be contrasted against the 2·4 decades obtained for the $(\alpha \beta)$ relaxation in fig. 3.   The half-width of the β relaxations in PMMA and PEMA are near four decades of frequency; thus, we confirm that the resolved peak in fig. 1 at 60·5°C is a β peak analogous to that observed in PEMA and PMMA.

There remains one major difficulty in understanding the experimental results for the β process.   The location is nearly independent of pressure, which would indicate a relaxation governed by intramolecular forces, and yet the intensity of the β process decreases rapidly with increasing pressure.   We could conclude (tentatively) that the intensity decrease reflects the coupling between α and β processes even when the two processes are resolved, and this is in agreement with the theory of Ishida and Yamafuji.[6]   Alternatively, the rate of relaxation is governed by the intramolecular barrier restricting the rotation of the ester group.   This will be unaffected by increased pressure on the system.   The equilibrium conformations of the ester side group determine the magnitude of the β relaxation, and pressure acts in a manner which upsets the relative levels of minimum energy conformations, resulting in a decrease in the intensity for the β process, without affecting the barrier to rotation.

CONCLUSIONS

Increased pressure at a given temperature has a remarkable effect on the single dipole relaxation region. At high temperatures, the ($\alpha\beta$) relaxation region initially moves uniformly to lower frequencies with increased pressure, but at high pressures the shape of the absorption changes rapidly with increased pressure. At lower temperatures, the pressure required to decompose the loss curve is continuously decreased with decreasing temperature. At 60·5°C, and high pressures, the resolved β relaxation is observed.

The ($\alpha\beta$) relaxation may be assumed to occur by the co-operation motions of the monomer units along the chain. As the monomer reorients, the internal rotation of the side group occurs at a comparable rate, and the backbone (α) and side group (β) motions are merged into a single process, which couples with the similar motions of monomers along the chain, leading to a broad distribution of relaxation times.[13] The ($\alpha\beta$) relaxation has a shape similar to that observed for normal α relaxations, and depends upon temperature and pressure in a manner similar to the normal α relaxations.

The β relaxation is not observed at an accessible frequency range in studies at 1 atm, for PBMA, although it is in PEMA and PMMA.[6, 12] This is due to the fact that in PBMA the chains are further apart than in PEMA and in PMMA. This "internal plasticization" makes easier the backbone (α) process, and this process moves to higher frequencies into the β relaxation region. The result is the ($\alpha\beta$) relaxation, and the β process cannot be observed at 1 atm. By increasing pressure, the backbone motions are rapidly slowed down, whereas the side group (β) process is hardly affected. At high pressures the ($\alpha\beta$) process is decomposed into its components, and we observe the resolved β process at 60·5°C, whose location is hardly affected by increased pressure. The relaxation frequency of the resolved β process extrapolated to 1 atm pressure at 60·5°C, occurs at the same frequency as that observed for the β process at 60·5°C for PMMA and PEMA. This shows that if it was possible to "freeze" the backbone motions in PBMA at 1 atm, we would observe the β relaxation, identical in position and shape with that observed in PMMA and PEMA.

Thus, dielectric relaxation studies at high pressure can be useful in the evaluation of the mechanism of molecular motions. The relaxation in PBMA at 1 atm has the properties of an ($\alpha\beta$) mechanism, and not α in which a small β process is submerged [6] or a β process [3, 5] as had been previously supposed.

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