Molecular Motion in Solid Amorphous Polymers

The Dielectric Relaxation of a Poly-Nonyl Methacrylate and Poly-n-Lauryl Methacrylate as a Function of Frequency, Temperature and Applied Pressure

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The dielectric relaxation of a polynonyl methacrylate (PNMA) and poly-n-lauryl methacrylate (PLMA) have been studied over a range of frequency, temperature and of applied hydrostatic pressure. Results for PNMA are consistent with α, β and ($\alpha\beta$) relaxations occurring in the polymer. For PLMA, the ($\alpha\beta$) relaxation decreases in magnitude with increasing pressure or decreasing temperature, with no apparent evidence for α and β relaxations. Activation energies are compared with those obtained for other amorphous polymers, and it is suggested that the ($\alpha\beta$) process in the higher methacrylate polymers has a slighly different mechanism from that observed in the lower alkyl methacrylate polymers.

The dielectric relaxation behaviour of polyalkyl methacrylates has been extensively studied.[1-12] It has been shown that α, β and ($\alpha\beta$) relaxation processes may occur in the polyalkyl methacrylates, where the ($\alpha\beta$) process results from the coalescence of α and β processes at high temperatures.[6, 8, 9] Both the α and ($\alpha\beta$) processes are thought to be due to the microbrownian motions of the ester dipoles,[6, 8, 9] which in the lower polyalkyl methacrylates correspond to the microbrownian motions of the polymer backbone. The β process involves the reorientation of the flexible ester group,[1-3, 11] but it has been suggested [9, 13] that intermolecular environments, viewed on a time scale short with respect to microbrownian motion, play an essential part in determining the magnitude of the process. The relative magnitudes of the α and β processes in a given polyalkyl methacrylate depend upon the stereoregularity of the polymer [1, 2, 10-12] and upon the pressure to which it is subjected at a given temperature.[5-8] The ($\alpha\beta$) process in certain polyalkyl methacrylates may be resolved into α and β processes by application of pressure.[5-8] Sasabe and Saito [8] demonstrated that the β process in conventional (free radical polymerized) poly-n-alkyl methacrylates decreased in magnitude with increase in the n-alkyl length so that the magnitude for this process beyond $n = 10$ (decyl) would be extremely small. In an earlier paper [6] it was suggested that the single process observed in a polynonyl methacrylate by Ishida and Yamafuji [3] was an ($\alpha\beta$) process and not an α process. The question of the nature of the dielectric relaxations in the higher polyalkyl methacrylates is best answered by a study using the hydrostatic pressure variable in addition to a wide frequency and temperature range. For this purpose such a study has been carried out on a polynonyl methacrylate and a polylauryl methacrylate.

EXPERIMENTAL

The polynonyl methacrylate $[R = (CH_2)_2CH(CH_3)CH_2C(CH_3)_2CH_3]$ and poly-n-lauryl methacrylate $[R = C_{12}H_{25}]$ were made by bulk polymerization of the monomer at

333 K using benzoyl peroxide as catalyst. The polymer was reprecipitated by the slow addition of a dilute solution in carbon tetrachloride to stirred methanol. This was repeated several times, and the polymer was vacuum dried at 333 K. The intrinsic viscosities were measured as 0.61 dlg^{-1} at 295 K for polynonyl methacrylate in carbon tetrachloride, and 0.11 dlg^{-1} at 303 K for polylauryl methacrylate in n-pentanol. Dielectric studies were made using a three terminal high pressure dielectric cell described previously [9] together with a General Radio 1620-A bridge assembly (10^2 to 10^4 Hz) and a Scheiber bridge [14] (10^{-2} to 10^2 Hz). The pressure transmitting medium was a light silicone oil.

RESULTS

(A) ATMOSPHERIC PRESSURE

Fig. 1 and 2 show the dielectric loss factor ε'' against log f(Hz) at given temperatures and atmospheric pressure for polynonyl methacrylate (PNMA) and polylauryl methacrylate (PLMA). For PNMA, the loss curves broaden as temperature is reduced, but the magnitude of the process (as judged by $\int \varepsilon'' \, d \log f$) does not appear to change significantly. The behaviour shown in fig. 1 is very similar to that obtained
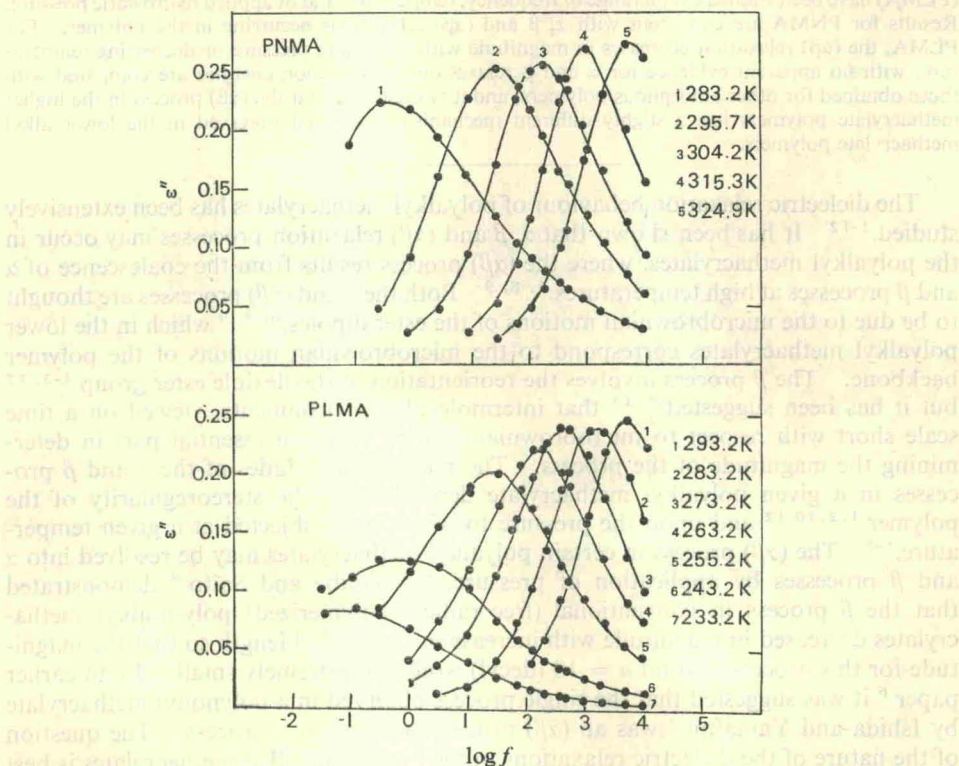

FIG. 1.—ε'' against log f(Hz) for PNMA at atmospheric pressure.
FIG. 2.—ε'' against log f(Hz) for PLMA at atmospheric pressure.

by Ishida and Yamafuji for a polynonyl methacrylate,[1, 3] both in the frequency-temperature location of the process, and the change of shape with temperature. There is no evidence in fig. 1 that the narrow process obtained at high temperatures actually resolves into α and β processes as temperature is reduced. Fig. 2 for PLMA shows

that the narrow loss curve obtained at higher temperatures broadens with decreasing temperature and, in addition, that the magnitude of the process decreases with decreasing temperature. $(\varepsilon_0 - \varepsilon_\infty)$ was obtained directly from the dielectric permittivity results. It is found that $(\varepsilon_0 - \varepsilon_\infty)$ increases only slightly with decreasing temperature for the range 290 K to 250 K, but there is a marked decrease in this quantity below 250 K. It is possible that this behaviour is associated with side chain crystallization in the polymer, reported [15, 16] to occur in the temperature range 237-239 K. There is no indication of a resolution of the process into α and β processes as the temperature is decreased. If one inspects the plots of $\log f_{max}$ against T^{-1} for the lower polyalkyl methacrylates, [1,3,5,6,8] it is found that the resolved β processes in polymethyl methacrylate, polyethyl methacrylate and poly-n-butyl methacrylate all lie approximately on a common line. Decomposition of the $(\alpha\beta)$ process into α and β processes occurs when the $\log f_{max}$ for the $(\alpha\beta)$ process is equal to that for the β process. Since the location for the $(\alpha\beta)$ process in PLMA and PNMA is known from fig. 1 and 2, then if the resolved β process in these polymers lay on the common line indicated above, we would predict the (temperature, frequency of maximum loss) at which the $(\alpha\beta)$ resolves into α and β processes as (290 K, $\log f_{max} = 0.8$) for PNMA, and (228 K, $\log f_{max} = -2.5$) for PLMA. The results for PNMA show a broadening of the $(\varepsilon'', \log f)$ plot in the correct frequency-temperature location, but this is not so for PLMA.

(B) EFFECT OF PRESSURE ON PNMA

Fig. 3-6 show a portion of our data for ε' and ε'' against $\log f$(Hz) for given temperatures and different applied pressures. At the higher temperatures, the single $(\alpha\beta)$ process moves rapidly to lower frequencies with increasing pressure, and also broadens as the pressure is increased. The half widths of the ε'' plots at the highest temperatures and lowest pressures are near 2.3 decades of frequency, and the asymmetry, as judged [17, 18] by (Δ_h/Δ_l) is near 1.3. Thus the loss curves may be approximately fitted to the empirical representation of Williams and Watts,[17, 18] $\phi(t) = \exp\{-(t/\tau_0)^{\bar{\beta}}\}$, $0 < \bar{\beta} \leqslant 1$, with $\bar{\beta} \simeq 0.46$. The dielectric α process in a number of amorphous polymers may be represented [17, 18] by this empirical function, with $\bar{\beta}$ in the range 0.37 to 0.7. The significant feature of fig. 3-6 is that at the lower temperatures and higher pressures the single process develops a higher frequency shoulder, indicative of a resolution of a $(\alpha\beta)$ process into α and β processes. It is not possible to evaluate the exact frequency location of the maximum loss for the β process at a given temperature and pressure since one does not wish to assume a shape for the α process. The resolved β process in the lower polyalkyl methacrylates is only slightly shifted along the frequency axis by increased pressure.[6-8] It is thus interesting to observe in fig. 3 at 5.5×10^7 Nm^{-2} pressure, the β process would peak in the region (283 K, $\log f_{max} = 0$ to 1). This is very similar to that predicted in section A above. In the lower polyalkyl methacrylates, ε''_{max} for the resolved β process decreases rapidly with increase in pressure [5-8]; this is also observed for PNMA. Thus in fig. 4-6, as the β process is resolved from the α process in its frequency location, so the decrease in magnitude occurs, making the evaluation of $(\log f_{max})_\beta$ a difficult problem. Fig. 7 and 8 show $\log f_{max}$ as a function of temperature and pressure for the primary process in PNMA. Table 1 gives the values of $(\partial \log f_{max}/\partial P)_T$ as deduced * from fig. 7. They are quite similar to the range of values obtained for α relaxations in a range of polymers, [7-9, 19, 20] including the lower polyalkyl methacrylates,[5-8] which confirms

* Since $(\partial \log f_{max}/\partial P)_T$ increases with increasing pressure at a given temperature, the values given in table 1 for PNMA and PLMA correspond to atmospheric pressure.

the similarity between the $(\alpha\beta)$ process in PNMA and α processes in general. The constant pressure apparent activation energy [19-21] $Q_p(T,P)$ obtained from fig. 8 increases with increasing T^{-1} at each pressure. At atmospheric pressure, $Q_p(T,P)$ increases from 110 kJ mol^{-1} at 324.8 K to 195 kJ mol^{-1} at 297.9 K, in contrast to the results of earlier studies on long side chain polyalkyl methacrylates.[22, 23] The constant volume apparent activation energy [19-21] $Q_v(T,V)$ was calculated to be
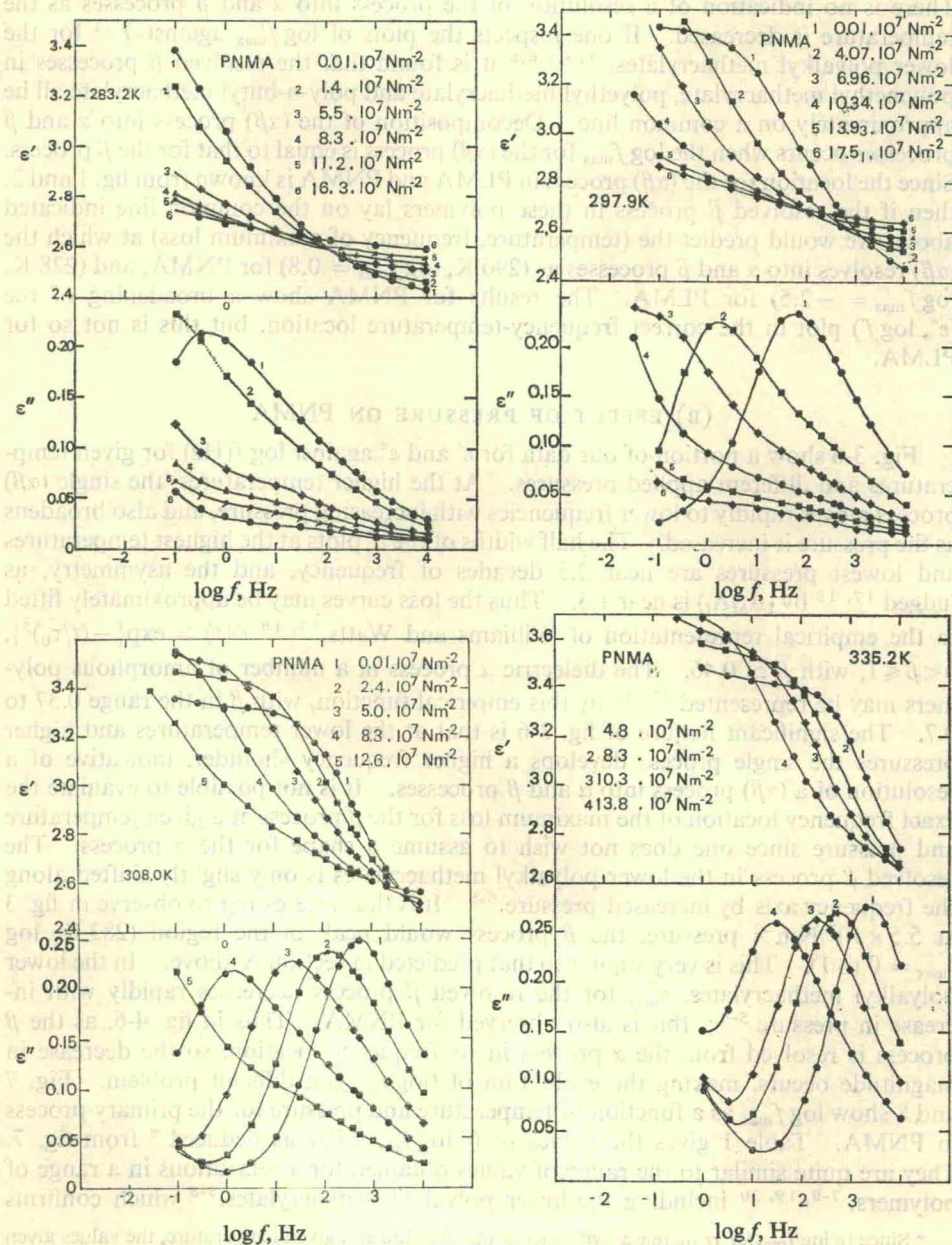

FIG. 3-6.—ε' and ε'' against log f(Hz) for PNMA at given temperatures and different applied pressures.

88 kJ mol⁻¹ at 297.9 K and atmospheric pressure, assuming a value [24, 25] of $(40 \pm 6) \times 10^7$ N m⁻² for the internal pressure of the polymer. Thus $Q_v(T,V)/Q_p(T,P) = 0.55$ at 297.9 K and atmospheric pressure. This is to be compared with a ratio in the range 0.65-0.75 for normal α relaxations.[6,7,9,19,20]
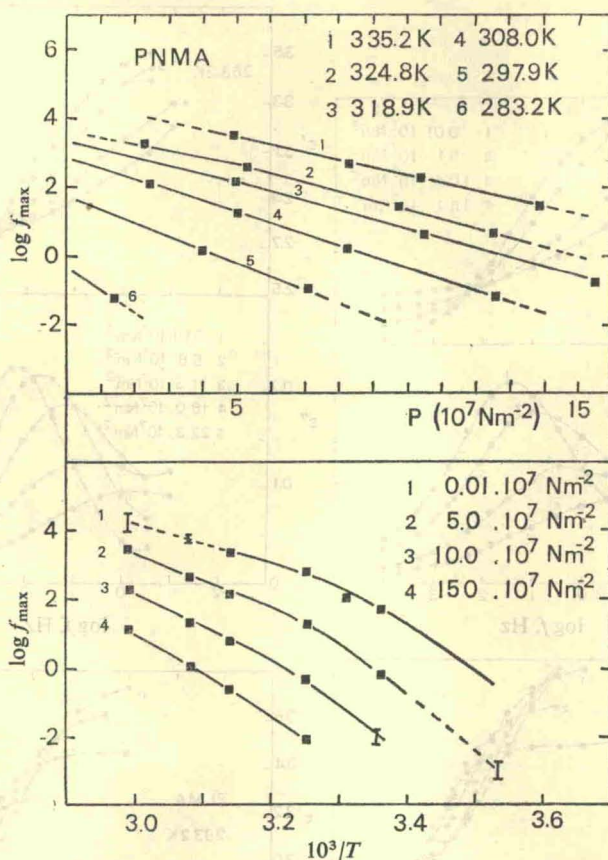

FIG. 7.—$\log f_{max}$ against applied pressure at given temperatures for the primary process in PNMA.

FIG. 8.—$\log f_{max}$ against T^{-1} at given pressures for the primary process in PNMA.

TABLE 1.

polymer	T(K)	$(\partial \log f_m/\partial P)_T$	polymer	T(K)	$(\partial \log f_m/\partial P)_T$
PNMA	283.2	$(5.3) \times 10^{-8}$ N⁻¹ m²	PLMA	255.2	0.95×10^{-8} N⁻¹ m²
	297.9	3.8×10^{-8} N⁻¹ m²		263.2	0.92×10^{-8} N⁻¹ m²
	308.0	3.1×10^{-8} N⁻¹ m²		273.2	0.78×10^{-8} N⁻¹ m²
	318.9	2.6×10^{-8} N⁻¹ m²		283.2	0.70×10^{-8} N⁻¹ m²
	324.8	2.4×10^{-8} N⁻¹ m²		293.2	0.65×10^{-8} N⁻¹ m²
	335.2	2.0×10^{-8} N⁻¹ m²			

(c) EFFECT OF PRESSURE ON PLMA

Fig. 9-12 show ε' and ε'' against $\log f$(Hz) for given temperatures and different applied pressures. At the two higher temperatures the single absorption broadens and moves uniformly to lower frequencies as the pressure is increased. The half

widths of the loss curves at the highest temperatures and low pressures are near 2.1-2.3 decades of frequency; in this respect the curves are similar to those of PNMA at the highest temperatures.   For 254.7 K and 263.2 K there is a marked decrease in the magnitude of the loss process with increasing pressure which closely parallels the
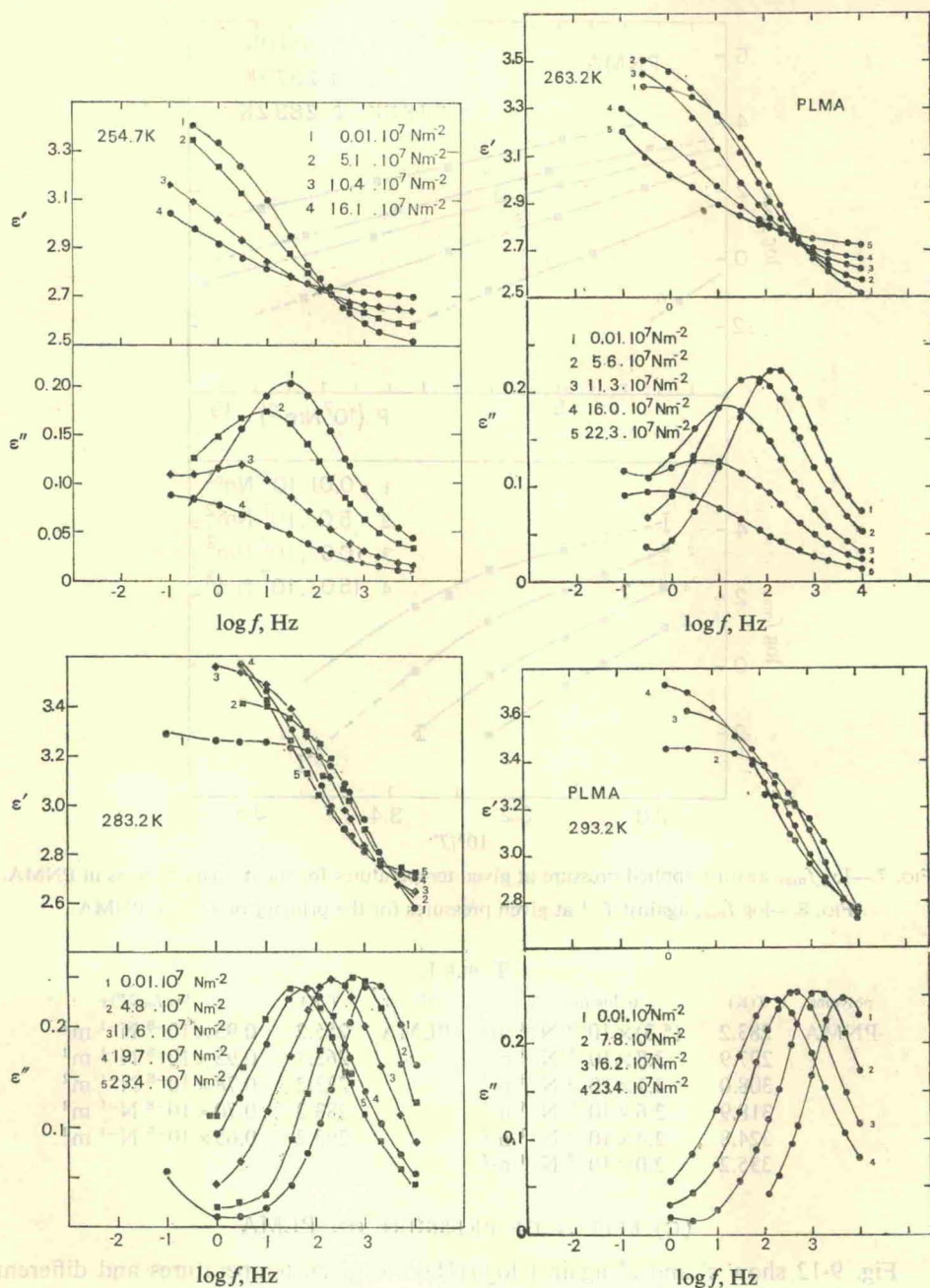

FIG. 9-12.—ε' and ε'' against log f(Hz) for PLMA at given temperatures and different applied pressures.

atmospheric pressure results of fig. 2. There is no evidence for a resolution of the $(\alpha\beta)$ process into α and β processes, which is not unexpected in view of (A) above. Fig. 13 and 14 show $\log f_{max}$ as a function of temperature and pressure. Values of $(\partial \log f_{max}/\partial P)_T$ deduced from fig. 13 are given in table 1. They are smaller than the values obtained for PNMA and for the α process in a number of polymers.[5-9, 19, 20] Values of $Q_p(T,P)$ at atmospheric pressure calculated from fig. 14 varied from 67 kJ mol^{-1} at 293.2 K to 115 kJ mol^{-1} at 254.7 K. These are much smaller than the values obtained for PNMA and for the $(\alpha\beta)$ or α processes that have been studied in the lower polylalkyl methacrylates and other polymers.[1, 2, 9] $Q_v(T,V)$ at atmospheric pressure ranged from 52 kJ mol^{-1} at 293.2 K to 95 kJ mol^{-1} at 254.7 K, and was obtained by assuming an internal pressure for the polymer to be $(40\pm6) \times 10^7$ N m^{-2}. Thus the atmospheric pressure values for $Q_v(T,V)/Q_p(T,P)$ ranged from 0.78-0.83 for the temperature range 293.2 K to 254.7 K.
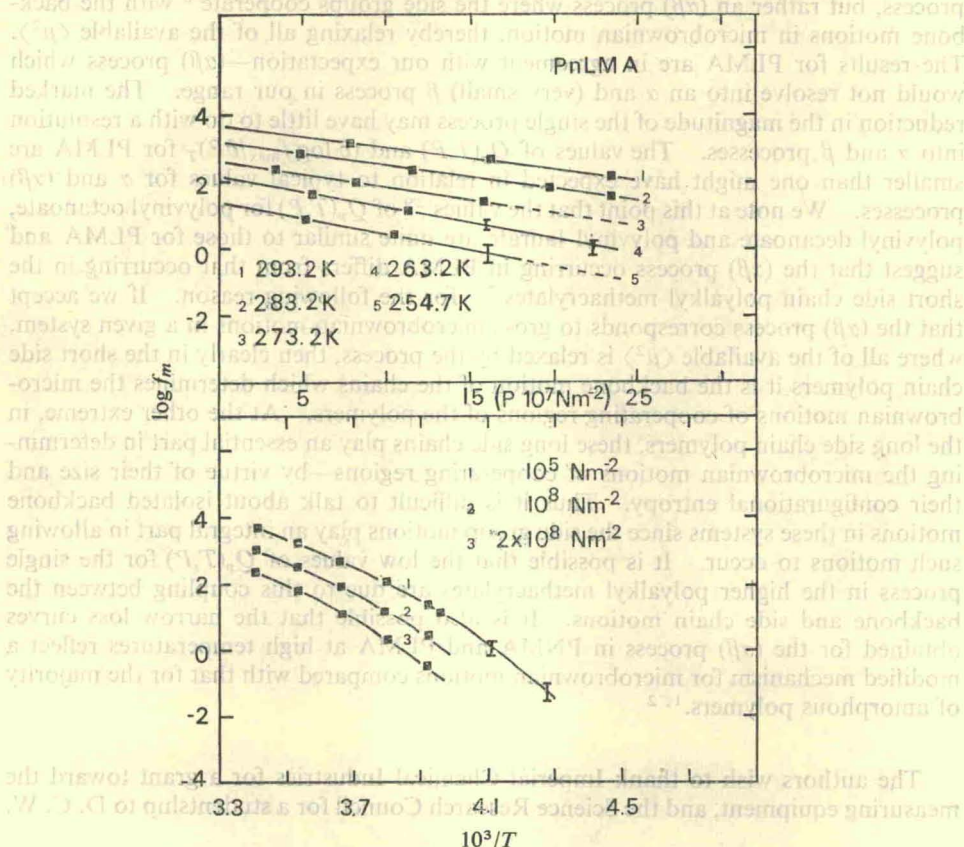

FIG. 13.—$\log f_{max}$ against applied pressure at given temperatures for PLMA.
FIG. 14.—$\log f_{max}$ against T^{-1} at given pressures for PLMA.

DISCUSSION

The single process observed at higher temperatures for both the PNMA and PLMA is the $(\alpha\beta)$ process. This process breaks down into α and β procesess in PNMA as the temperature is reduced or the pressure increased, but for PLMA a marked decrease in the magnitude of the single process at lower temperatures or

higher pressures is indicative of an ordering of the side chains. The process in PLMA is associated with the apparent glass transition of the polymers. Thus at 10^{-2} Hz, the maximum loss occurs near 230 K which is to be compared with $T_g = 215$ K obtained by interpolation of literature data.[26, 27] However at 10^{-2} Hz the maximum loss for PNMA occurs near 274 K which is not in agreement with the literature value [1, 26-28] $T_g = 237$ K for PnNMA. This is probably due to the fact that the PNMA studied here has an isoalkyl side group, and it is well known that these give T_g values higher than the corresponding n-alkyl polymer.[1]

We consider that our results for PNMA are in agreement with our prediction [6] of α, β and $(\alpha\beta)$ processes in such a polymer, and with the prediction in ref. (8) that the β process would be very small. The values of $Q_p(T,P)$ are small for an $(\alpha\beta)$ process, and are similar to values obtained by Ferry and Strella for the n-hexyl and n-octyl methacrylate polymers. This should not be taken to imply that the process is a β process, but rather an $(\alpha\beta)$ process where the side groups cooperate [6] with the backbone motions in microbrownian motion, thereby relaxing all of the available $\langle\mu^2\rangle$. The results for PLMA are in agreement with our expectation—$(\alpha\beta)$ process which would not resolve into an α and (very small) β process in our range. The marked reduction in the magnitude of the single process may have little to do with a resolution into α and β processes. The values of $Q_p(T,P)$ and $(\partial \log f_{max}/\partial P)_T$ for PLMA are smaller than one might have expected in relation to typical values for α and $(\alpha\beta)$ processes. We note at this point that the values [29] of $Q_p(T,P)$ for polyvinyl octanoate, polyvinyl decanoate and polyvinyl laurate are quite similar to those for PLMA and suggest that the $(\alpha\beta)$ process occurring in PLMA differs from that occurring in the short side chain polyalkyl methacrylates [5-8] for the following reason. If we accept that the $(\alpha\beta)$ process corresponds to gross microbrownian motions in a given system, where all of the available $\langle\mu^2\rangle$ is relaxed by the process, then clearly in the short side chain polymers it is the backbone motion of the chains which determines the microbrownian motions of cooperating regions of the polymers. At the other extreme, in the long side chain polymers, these long side chains play an essential part in determining the microbrownian motions of cooperating regions—by virtue of their size and their configurational entropy. Thus it is difficult to talk about isolated backbone motions in these systems since the side group motions play an integral part in allowing such motions to occur. It is possible that the low values of $Q_p(T,P)$ for the single process in the higher polyalkyl methacrylates are due to this coupling between the backbone and side chain motions. It is also possible that the narrow loss curves obtained for the $(\alpha\beta)$ process in PNMA and PLMA at high temperatures reflect a modified mechanism for microbrownian motions compared with that for the majority of amorphous polymers.[1, 2]

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