

Dynamic compressibility of poly(vinyl acetate) and poly(methyl methacrylate): effects of molecular weight

Tien-Sheng Lin* and A. W. Nolle†

Department of Physics, The University of Texas at Austin, Austin, TX 78712, USA

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The complex dynamic compressibility of poly(vinyl acetate) samples L, M, H, having number-average molecular weights $M_n = 52\,700$, $63\,600$, and $89\,900$ was measured from 0° to 56°C , at pressures of 12 and 81 atm. We used a computer controlled version of the apparatus of McKinney, Edelman, and Marvin, which involves two piezoelectric transducers in a thick-walled chamber. Test frequencies were 0.25 to 1.0 kHz. The 1 kHz loss maximum at 12 atm is near 52°C , within 1° of an earlier result of McKinney and Belcher. Using a numerical procedure for superposition of curves, we found that the loss peak for M is 0.4° lower than that for H, and the peak for L is 0.8° lower than that for H. These shifts agree with the known dependence of the glass temperature on $1/M_n$. Two samples of poly(methyl methacrylate) show no effect of molecular weight on dynamic compressibility. This is expected because in this case the test range is in the glassy region.

(Keywords: dynamic compressibility; poly(vinyl acetate); poly(methyl methacrylate); molecular weight; bulk loss peak)

INTRODUCTION

This paper is concerned mainly with the effects of molecular weight upon the complex dynamic compressibility $K^\dagger = K' - iK''$ of poly(vinyl acetate) in the temperature range 0° to 56°C , which includes the glass transition temperature T_g near 30°C and much of the range in which relaxation behaviour is observed. The superscript \dagger indicates a complex quantity. For example, for frequencies below 1 kHz and pressures below a few hundred bars the non-negative loss part K'' has a maximum in the neighbourhood of 50° to 60°C , according to the data of McKinney and Belcher¹ (MB). Further discussion of their work will explain our interest in the effect of molecular weight. Covering the range 0 to 981 bars gauge pressure and 50 to 1000 Hz, MB converted data for K' and K'' to single experimental curves by the reduced-variables method of Williams, Landel and Ferry². The curve shifting factors were related to a free volume having its own thermal expansion coefficient and compressibility, following a concept that had been used with success for shear data. In this reduced-variables treatment of dynamic compressibility data, MB were able to use values of the free volume at T_g and of the increase of the free volume with temperature, the basic fitting parameters, that were nearly the same as those given by Ferry³ for shear data for the same polymer. This indicates that motion of long portions of chains, which is involved in shear relaxation in the rubber-like temperature range, is also involved in compressional relaxation. This is contrary to a possible intuitive view that hydrostatic pressure causes only a local response.

Struik⁴ has given arguments consistent with this conclusion, based on a wider set of physical observations

which include physical ageing. He also used the free-volume concept. He concluded that it gives a unified understanding of processes having time scales from fractional milliseconds to years, and that all deformation processes, including volume changes, require segmental motion, in turn determined by the free volume. At the glass transition, all important retardation times have reached perhaps 100 s, and the free volume has reached a corresponding definite value, in practice always less than 5% of total volume. More recently, in a discussion of volume relaxation below the glass transition, Struik⁵ has remarked that the secondary peaks for amorphous polymers are usually found in both shear and bulk. These considerations show that a comprehensive view may be taken of relaxation over a wide range of temperature and time scale. However, because of the properties of the experimental method, the present work is concerned mainly with behaviour above the glass transition.

If relaxation processes in compression for a particular polymer involve segmental motions qualitatively similar to those involved in relaxation processes in shear, then it is expected that the retardation times for the compressional processes will decrease with decreasing molecular weight, in line with the well known effect of molecular weight on shear processes. In both cases, the following explanation in terms of the free volume concept can be applied. Retardation times are proportional to viscosity. Viscosity varies as $\exp(1/f)$, where f is the free volume fraction. Chain ends contribute more free volume than other chain units^{6,7} and as molecular weight is reduced, an increasing fraction of chain units are end pieces. Overall, when molecular weight decreases, retardation times decrease, or equivalently, the temperature for which K'' is maximum, as well as T_g , will decrease. Quantitatively, a linear connection is predicted between T_g and the reciprocal of molecular weight^{6,7}. Also, the shift in the maximum of K'' is expected⁸ to be nearly

* Present address: Department of Radiology, University of Texas Medical School at Houston, Houston, TX 77030, USA

† To whom correspondence should be addressed

equal to the shift in T_g . It will be shown in the later discussion that this approach gives agreement between our work on dynamic compressibility and other measurements.

Another feature of the work of MB which suggests that the compressional processes involve long chain motions is that the dispersion range covers eight decades, rather than about two decades as would be the case for a single retardation time.

Our primary experimental objective is to evaluate the small differences in the temperature of maximum K'' for samples of different molecular weights. In addition, we look at limited ranges of the variables temperature and frequency, in order to compare our results with those of MB. Finding agreement with their data on the shift of the loss peak with respect to temperature and frequency changes, as well as on the magnitude of the dynamic compressibility, shows that the results of MB were not seriously affected by some anomalous properties of their sample (unusually low T_g , and 2% weight loss in vacuum), and reveals consistency between our apparatus and theirs.

Condensed data for poly(methyl methacrylate) are shown in the Appendix. No effect of molecular weight is detected for this polymer in the temperature and frequency range of our study.

Following the nomenclature of the MB paper for the complex bulk compressibility (compliance), we will refer to K' as storage compliance and to K'' as loss compliance (positive K'' indicates loss). MB represented the bulk compliance by $B' - iB''$. However, B is strongly associated with bulk modulus in current textbooks and in many research papers.

EXPERIMENTAL

General principles

The central part of the apparatus is a thick-walled chamber containing two piezoelectric transducers, an electrically non-conducting liquid under controlled static pressure, and a test sample. This is similar to the system described by McKinney, Edelman, and Marvin⁹ (MEM). A sinusoidal electrical signal of real amplitude E_i is applied to one transducer, producing periodic pressure changes in the cavity. The second transducer generates an output voltage, proportional to the time-dependent part of the pressure, having complex amplitude E_0^\dagger . Test frequencies must be low enough to make the wavelength of sound in the liquid much greater than all dimensions of the chamber. In this case the deformation of the sample approximates an all-sided compression without shear and the dynamic compressibility of the sample is given by

$$K_s^\dagger = K_l + (r_s^\dagger - r_l^\dagger)/D^\dagger V_s \quad (1)$$

a form of the relation derived by MEM. Here K_l is the known compressibility of the liquid, D^\dagger is a constant of the apparatus, V_s is the volume of the sample, r_s^\dagger is the ratio E_i/E_0 observed when the chamber contains both the polymer sample and the liquid, and r_l^\dagger is that ratio measured when the chamber is filled with liquid only, in a second experimental run. In a third run, a sample having very small, known compressibility (iron) is used instead of the polymer, permitting the apparatus constant D^\dagger to be calculated. From the three runs there is then sufficient information to calculate K_s^\dagger for the polymer.

The quantities K_l and V_s are taken to be real, as is the compressibility of the iron sample.

We used disc transducers of Kezite K-85 (modified lead metaniobate), 7 mm in diameter by 0.07 mm thick. Typical voltages were 10 V rms applied to the source transducer and about 10^{-4} V rms developed by the receiving transducer. The complex voltage ratios r^\dagger were measured with a two-channel lockin detector (Brookdeal Ortholoc 9502) with 1000:1 voltage preamplifier. Typically the data from the two channels ('in-phase' and 'quadrature' or 90° components) corresponded to an accuracy of approximately 0.5% in the magnitude of r^\dagger and of 0.01 rad in the phase angle. The two outputs of the lockin detector were computer sampled to 12 bit precision and stored for data reduction. Use of the lockin detector was important not only for phase determination but for improvement of the signal-to-noise ratio.

Heydemann¹⁰ used equipment based on the apparatus of MEM to measure the real part of the dynamic compressibility of a number of polymers. Tanaka and Nishi¹¹ have described a version of the apparatus in which an increased time-dependent pressure is obtained by use of a long laminated transducer.

Our chamber was cylindrical, turned from type 304 stainless steel, o.d. 76 mm. The final assembly included the two identical pieces shown in *Figure 1*, held together with six bolts. When the pieces were joined directly with a copper sealing ring, as in the figure, the chamber had its minimum volume (about 0.5 cm³) and behaved as assumed for equation (1) up to approximately 10 kHz. For the work to be reported, because we decided to use the frequency range 0.25 to 1.0 kHz, we increased the sample space by placing a centre stainless steel section of length 1.27 cm and inside diameter 0.95 cm between the two sections indicated in *Figure 1*, rather than only the copper sealing ring. The volume of the chamber, including 7.5 cm of tubing leading to the isolation valve, was then 1.4 cm³, about 10% less than that used by MEM. The pressure chamber was held in a bronze jacket that could be cooled or heated by circulating fluid from a temperature bath.

In each experimental run, at a fixed pressure, data were taken from 29 temperatures, nominally 0°, 2°, . . . , 56°C

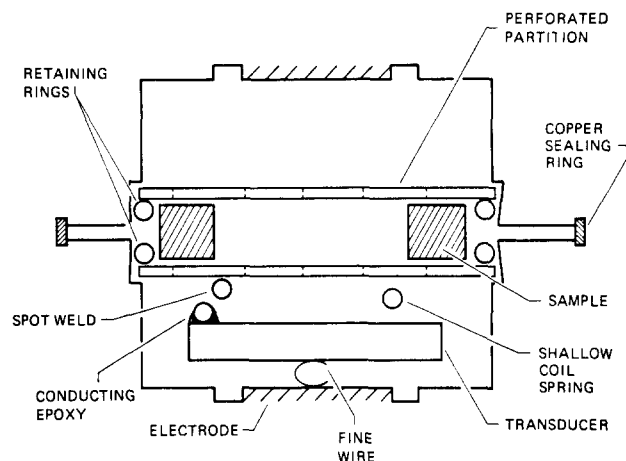


Figure 1 Section of working space in chamber, upper transducer omitted. Circular, 76 mm outer diameter stainless steel; axis of cylindrical symmetry is vertical. At partitions, inside diameter is 9.5 mm. Height between electrodes is 8 mm. These two identical end pieces form the basic chamber. To obtain increased volume for the present work, a matching stainless steel centre section of length 1.27 cm, with copper sealing rings at each end, replaced the single sealing ring shown

while the chamber temperature was increased steadily at about 0.4°C per min. Data collection started automatically whenever computer testing of a calibrated thermistor (solid-state resistance thermometer) showed a temperature within 0.2° of one of the standard values. Measurements at 0.25, 0.40, 0.63 and 1.00 kHz were then taken in about 30 s. Boxcar averaging for 0.5 s was done at each frequency by repeated sampling. The entire process was computer-controlled except that the experimenter had to operate the valve which isolated the chamber from the external fluid circuit where hydrostatic pressure was stabilized by a dead-weight gauge. The valve operations were timed so that during measurements the chamber was closed as assumed in the acoustical analysis, but otherwise the valve was open to prevent pressure changes due to thermal expansion.

The chamber was vacuum filled with liquid previously degassed by pumping. As a further help in avoiding air bubbles, we did all measurements above atmospheric pressure, at either 12 or 81 atm. Also, before beginning a run we kept the apparatus at 10 atm or more for 12 h, including an hour or more with the temperature below 0°C.

The small chamber assumption underlying equation (1) was well realized, because the chamber length was less than 2% of the shortest wavelength that occurs in the experiment. (This means that a standing-wave description of the pressure distribution in the unloaded cavity would entail spatial variations well under 1%.) Unfortunately, use of a chamber which is small compared to the wavelength does not alone guarantee that errors in measuring the loss part of the dynamic bulk compliance are small. The periodic volume changes of the fluid and sample involve fluid motion (except at the end of the chamber away from the source transducer), causing energy loss due to viscous flow around the transducer supports and the sample, and thus creating a spurious fluid viscosity contribution to the loss component of the polymer compressibility. This rises with increasing frequency. There is no simple correction. We reduced this error by choosing the relatively low frequency range 0.25–1.0 kHz. One indication that the error was kept small is that we were able to detect values of the loss tangent (K''/K') smaller than 0.04, without frequent occurrence of values of the wrong (negative) sign. Another motivation in our choice of frequency range was our desire to compare our results with the poly(vinyl acetate) data obtained by McKinney and Belcher with the MEM apparatus, which were best in the above range.

As a further precaution to reduce spurious energy losses due to fluid viscosity, we used samples which did not fill the entire cross-section of the chamber, both for calibration runs and polymer tests. A sample that almost fills the section causes increased flow velocity in the gap around the sample (unless there is a density match and the sample moves with the fluid), increasing the losses due to viscosity.

The experimental results give adiabatic rather than isothermal dynamic compressibility, as shown by MEM.

Samples

Data were taken for three samples of poly(vinyl acetate), which had different molecular weights, obtained from Scientific Polymer Products¹². The data in Table 1 was furnished by the supplier. The samples consisted of

Table 1 Data for poly(vinyl acetate) samples

Designation	M_n No. av. mol. wt.	M_w Wt. av. mol. wt.	Density 25°C, 1 atm g cm ⁻³
L	52 700	124 800	1.18
M	63 600	194 800	1.18
H	89 900	237 100	1.19

4 mm diameter pellets. About 0.7 g of polymer was used in a test.

The pressure fluid was di-2-ethylhexyl sebacate, obtained as the commercial product Monoplex DOS¹³. The 25°C density is 0.911 g cm⁻³. This was also the pressure fluid used with poly(vinyl acetate) by MEM. We confirmed their report that the fluid causes no observable swelling of the samples.

Data reduction

Applications of equation (1) give the compressibility of the sample from experimental voltage ratios that are obtained when the chamber contains (a) fluid only; (b) fluid plus iron sample; (c) fluid plus polymer sample. To reduce effects of random experimental error (noise), we generated a smoothed 29-point table of values as a function of temperature for each of the sets (a), (b), and (c). This was done by making a second-order polynomial fit to a set of five raw data points centred about each standard temperature (except that fewer points are used for each fit at the ends of the temperature range). Each raw data point was replaced by a value calculated from the fitted function centred at the temperature of the data point. Compressibility calculations were then made with the smoothed data.

To calculate the dynamic compressibility of the sample, the compressibility K_c of the test fluid must be known. This was obtained by interpolating in a table of adiabatic compressibility data for DOS, supplied by McKinney¹⁴. To 0.1% accuracy, the data taken from the tables can be summarized by the following polynomial fits: for 12 atm, $K_c = 4.150 + 0.0274T + 3.08 \times 10^{-5}T^2$, in units $10^{-11} \text{ cm}^2 \text{ day}^{-1}$ (T is in °C). Similarly for 81 atm, $K_c = 4.019 + 0.0261T + 2.92 \times 10^{-5}T^2$.

The volume of the sample for the compressibility calculations was determined from the sample mass and from the specific volume of poly(vinyl acetate) at each temperature and pressure, found by interpolating in tables of McKinney and Goldstein¹⁵. Within 0.1%, the specific volume in $\text{cm}^3 \text{ g}^{-1}$ can be expressed for 12 atm as $0.8319 + 1.9 \times 10^{-4}T + 4.37 \times 10^{-6}T^2$ and for 81 atm as $0.8300 + 1.79 \times 10^{-4}T + 4.05 \times 10^{-6}T^2$.

We were particularly interested in evaluating small shifts in the temperature of the maximum of the imaginary (loss) part of the compressibility. The shifts are related to changes in molecular weight, frequency, or pressure. The problem is illustrated in Figure 2, where F_0 and F_1 are plots of two experimental functions, each of which is actually defined by a table of values at discrete temperatures. The maximum for one of the functions may occur outside the temperature range of the experiments (broken line). In practice the functions F_0 and F_1 have the property that the peak region of one of them (say, F_1) can be fitted closely over that of the other (say, F_0) by sliding the function along the temperature axis and multiplying the ordinate by some factor η . We take the temperature shift of the maximum between functions F_0 and F_1 to

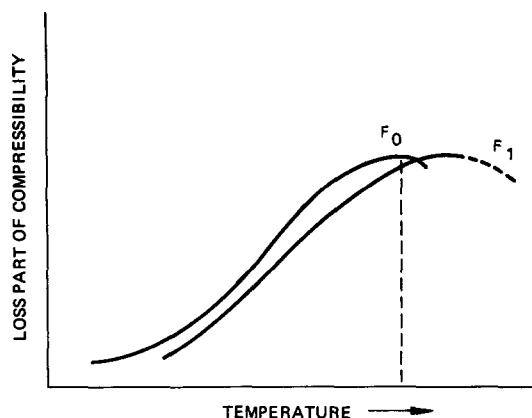


Figure 2 Schematic of a curve F_0 to be displaced horizontally and rescaled vertically to obtain a minimum error fit to F_1

be the shift ΔT that most nearly gives superposition. The calculation procedure is to evaluate the fitting error

$$E = \sum_i (\eta F_{1i}(T + \Delta T) - F_{0i}(T))^2 \quad (2)$$

where the sum is over the number of useful points in the data table, for a number of values of ΔT and η on an appropriate mesh. The shift in the temperature of the peak is then defined as the value of ΔT that gives the two-dimensional minimum of E . Because the functions are defined by tables, F_1 in Figure 2 is found by interpolation. Points that would require extrapolation were not considered. In practice, test values of η did not exceed 1.1. In principle, this procedure could be applied also to curves for the real (storage) part of the compressibility.

The foregoing procedure for evaluating the shifts of the loss peak, when applied to different curves for the same sample, is a simplified application of the principle

of superposition³. A complete application of the principle involves the dependence of the limiting low-frequency and high-frequency compliance on pressure and temperature. Because our main interest was in a comparison of samples differing in molecular weight, and not in a single sample, we did not make this refinement.

RESULTS

The samples designated L, M, H, in order of increasing molecular weight, are described in Table 1. Full data for the lower static pressure, 12 atm, are shown in Figure 3. In the condensed results for 81 atm, shown in Figure 4, results for only sample H are given.

As a reference for our determinations of the temperature of maximum loss under various conditions, we use the temperature of the maximum for sample M at 1 kHz, 12 atm. By visual examination of an enlarged plot similar to the lower part of Figure 3a, this temperature T_R is found to be 52°C.

Our special interest is in determining the shifts in the temperature of maximum loss as related to changes in molecular weight, frequency, and static pressure. (This discussion refers to the maxima of the imaginary or loss part of the compliance, not to the loss tangent.) These relatively small shifts were measured by the numerical superposition process described above and generally are too small to determine by visual inspection of the plots, although the shift with frequency is readily seen. (The small shifts related to pressure and molecular weight can be seen, however, in a comparison of Figure 3b and Figure 4b. Here the effects add to give a visible change.)

Shifts related to molecular weight

At 1 kHz, 12 atm, $T_{\max}(L) = T_R - (0.4 \pm 0.1^\circ\text{C})$, $T_{\max}(M) = T_R$ (by definition), and $T_{\max}(H) = T_R + (0.4 \pm 0.1^\circ\text{C})$.

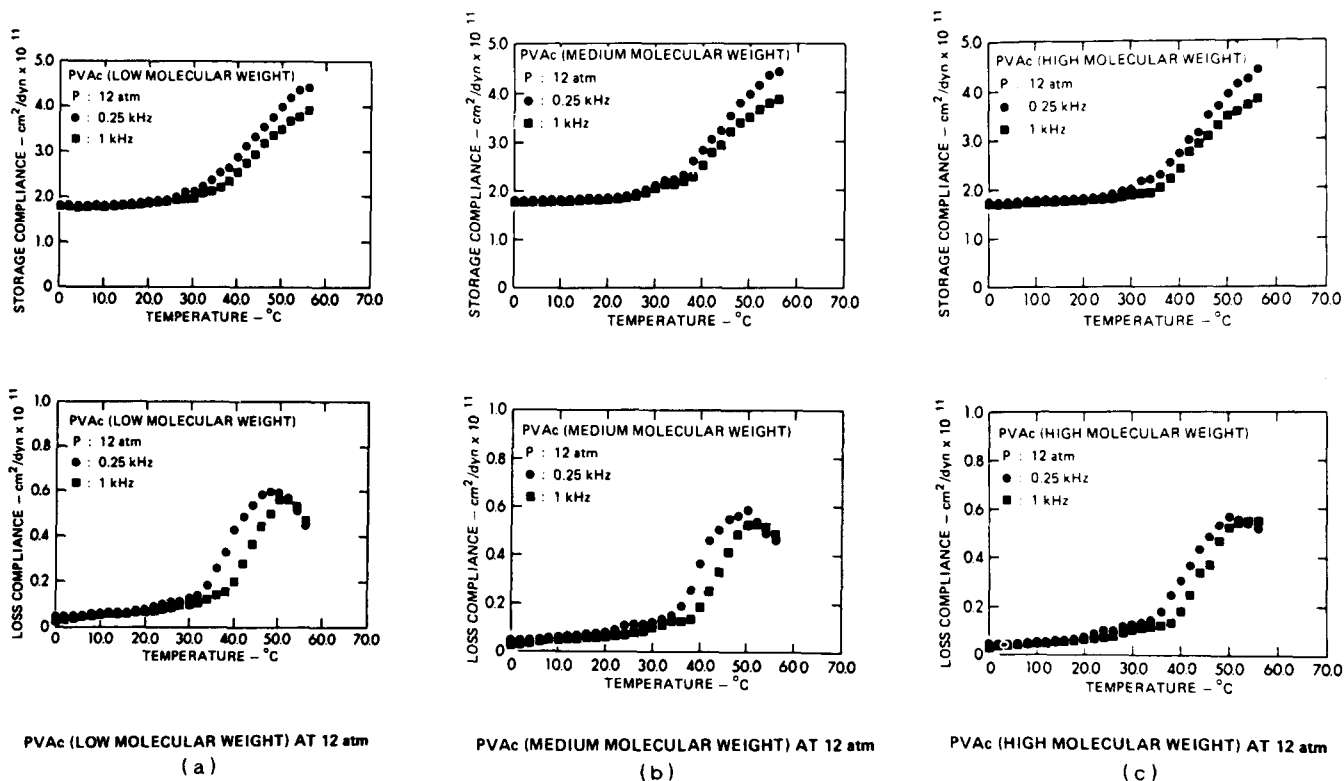


Figure 3 Loss and storage compliances for poly(vinyl acetate) at 12 atm gauge. (a), (b) and (c) are for samples L, M, H, respectively

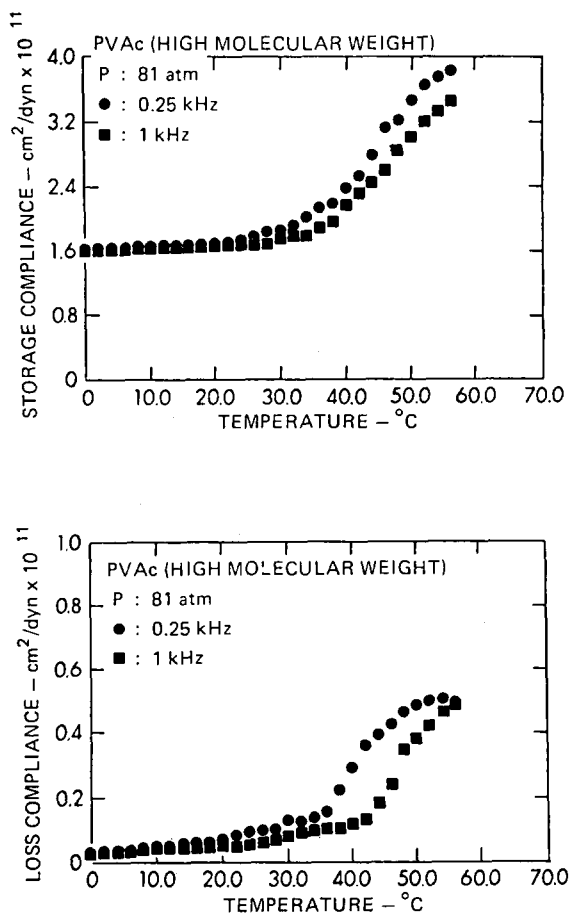


Figure 4 Loss and storage compliances for poly(vinyl acetate) at 81 atm gauge pressure. Sample H

Shifts related to frequency

For sample M, 12 atm, $T_{\max}(0.25 \text{ kHz}) = T_R - (3 \pm 0.2^\circ\text{C})$, and $T_{\max}(1 \text{ kHz}) = T_R$ (by definition).

Shifts related to pressure

Data for the samples were averaged because any dependence of the shift on molecular weight is smaller than the experimental uncertainty. For 1 kHz, $T_{\max}(12 \text{ atm}) = T_R$ and $T_{\max}(81 \text{ atm}) = T_R + 2^\circ\text{C}$, or the pressure shift is $0.029 \pm 0.004^\circ\text{C atm}^{-1}$.

The uncertainty of 1°C in the actual value of T_R is not involved in the results given for the shifts of the loss maximum.

DISCUSSION

We first compare key features of our results with those of MB as shown in Table 2. The comparison, which is for 1 kHz and 12 atm \approx 12 bars, is of special interest because MB found that their sample contained material of low temperature weight, as indicated by a weight loss of about 2% upon prolonged heating in vacuum. The comparison in Table 2 is made with data from our sample H, except that $\Delta T/\Delta p$ is an average for the three samples. The molecular weight of the MB sample is not stated specifically, but the intrinsic viscosity in cyclohexane at 20°C is given as 0.69 dl g^{-1} . The general agreement found in Table 2 shows that the results of MB were not seriously affected by the presence of low molecular weight material. The main discrepancy shown in Table 2 is in the

maximum value of K'' . This is not of serious concern in view of the difference in the samples and in view of our interest in the shifts of the K'' curves rather than in their absolute values.

Since the time of the McKinney and Belcher experiment, Plazek¹⁶ has published an extensive study of PVAc ($M_n = 5.9 \times 10^5$) that used a torsional creep apparatus, in vacuum, with magnetic bearings. A superposition treatment of the recoverable elastic compliance from the softening dispersion gave one version of a shift-factor function³ a_T , such that $-\Delta \log a_T/\Delta T$ is a logarithmic shift rate for retardation times, which may be compared with $\Delta \log \omega/\Delta T$ in Table 2. Treatment of the long-time (terminal) creep data gave a different a_T function. At 54°C , a temperature suitable for comparison to Table 2, Plazek's two determinations of a_T are in fair agreement regarding $-\Delta \log a_T/\Delta T$ and give the values 0.162 and 0.171, respectively. These numbers fall between values from the dynamic compressibility experiments of MB and ours (Table 2). The agreement confirms the conclusion of McKinney and Belcher that the shifts of retardation times that are revealed in dynamic compression and in shear processes are related to similar chain motions.

The value of $\Delta \log \omega/\Delta T$ shown in Table 2 for the results of MB is taken from direct examination of shifts of plots of K' in the dispersion range. This is comparable to the shifts which we report. The value used by MB in their reduced-variables calculations to get a master curve is smaller, approximately 0.12. The distinction is that the reduced-variables procedure attempts a basic separation of the curve-shifting processes into change of retardation times and the change with temperature of the zero- and infinite-frequency values of the compressibility. Similarly the values quoted from Plazek's work¹⁶ on shear refer to actual shifts of retardation times. However they lie close to our value of $\Delta \log \omega/\Delta T$.

We wondered whether our observed shift in the temperature of the loss peak for dynamic compressibility with molecular weight is consistent with the effect of molecular weight in other kinds of dynamic measurements. Marvin and McKinney⁸ proposed that the temperature of the loss maximum in dynamic data shifts by the same amount as T_g in response to changes in the number average molecular weight M_n (or other structural features). They used the relation

$$T_g = T_{g\infty} - (A/M_n), \quad (3)$$

which had been proposed by Fox and Loshaek⁷ for polymers including polystyrene, poly(methyl methacrylate), polyisobutylene, and polysilicone and was believed to have more general application. Here $T_{g\infty}$ pertains to

Table 2

Characteristic	Present work (sample H)	Data of MB ¹
Temperature for maximum of K'' , $^\circ\text{C}$	52.4 ± 1	51 ± 1
Maximum value of K'' , bar^{-1}	0.55×10^{-5}	0.39×10^{-5}
K' at temperature of maximum K'' , bar^{-1}	3.6×10^{-5}	3.4×10^{-5}
$(\Delta \log \omega/\Delta T)$, $^\circ\text{C}^{-1}$	0.20	0.16 (using shift of K')
$(\Delta T/\Delta p)$, $^\circ\text{C bar}^{-1}$	0.29	0.24 (slope, 1 to 500 bars)

infinite molecular weight. The value of the constant A is nearly the same for this wide variety of polymers. Considering in addition their own PVT work for PVAc having M_n of 190 000 or more, McKinney and Goldstein found $A = 1.0 \times 10^5$ for PVAc. With this value, equation (3) predicts a loss-peak shift of 0.33°C between our samples L and M, compared to the observed shift of 0.4°C . The predicted shift between samples L and H is 0.78°C , compared to the observed shift of 0.8°C . Thus the shift of the dynamic compressibility loss peak due to changes in M_n agrees with a relation that summarizes results obtained for T_g in quasi-static tests.

Equation (3) can be justified by the concept that chain ends make a characteristic contribution to free volume, as mentioned in the introduction.

We also tested samples of poly(methyl methacrylate) of two different molecular weights. Further details are given in the Appendix. No systematic shift was detected between curves for the two molecular weights. This gives a further test of consistency of the experimental findings. Because the T_g of 114°C for this polymer is well above the 56°C upper limit of the experiment, dependence of the results on molecular weight is not expected.

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APPENDIX

Results for poly(methyl methacrylate)

Two batches of powdered material, having (a) $M_n = 46\,400$ and $M_w = 93\,300$ and (b) $M_n = 119\,200$ and $M_w = 490\,200$, were obtained from Scientific Polymer Products¹² and were used to form clear transparent material under vacuum moulding. Representative results are shown in Figure 5. As expected, the loss tangent is very small, ≈ 0.04 , and the curves for K' and K'' have no significant shift with changes in molecular weight, with change of frequency from 0.25 to 1.0 kHz, or with change of pressure from 12 to 81 atm. Aside from the inclusion of samples having different molecular weights, the work on this polymer is not new. The storage part of the dynamic bulk compliance was studied by Heydemann¹⁰ in 1959. He reported that a β -dispersion around 1 Hz in shear and extension measurements, reported by Heijboer¹⁷ and by Koppelman¹⁸, is absent in the bulk measurements. Kono¹⁹ measured the bulk modulus from 20° to 190°C in the MHz frequency range.

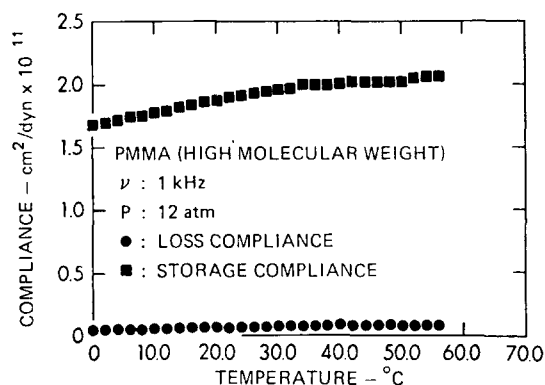


Figure 5 Bulk compliance data for poly(methyl methacrylate), 12 atm gauge, 1.0 kHz for the sample of higher molecular weight