Pressure–volume–temperature properties of polymethacrylates: anomalous behaviour in the melt

D. J. Walsh*, T. Ougizawa, W. H. Tuminello and K. H. Gardner
Du Pont Company, Central Research and Development Experimental Station, PO Box 80356, Wilmington, DE 19880-0356, USA
(Received 5 November 1991; revised 21 February 1992; accepted 21 March 1992)

Pressure–volume–temperature measurements have been performed for a series of polymethacrylates. Samples of poly(ethyl methacrylate) that have been pressed and quenched show densification between 100 and 150°C which disappears up to 200°C. Samples which have been heated above 200°C appear not to show this effect on reheating. Densifications similar to the above are also observed for the propyl and butyl polymethacrylates. Densification is not seen for poly(methyl methacrylate) nor for polyacrylates. Several other initial observations were made using other techniques. D.s.c. peaks are seen in this region which depend on the thermal history. The rheology is very dependent on thermal history. Some small changes in X-ray patterns are produced by thermal treatments. These observations could be interpreted as suggesting that polymethacrylates can be partially crystalline.

(Keywords: properties; polymethacrylate; pressure effects; crystallinity)

INTRODUCTION

In this paper we will describe anomalous behaviour in the melt state of several polymethacrylates. The most striking phenomenon is a densification which takes place at temperatures well above the glass transition temperature, T_g. Very few effects can cause densification in what we believe to be equilibrium melt. One possible explanation is the development of small amounts of very imperfect crystallinity.

Poly(methyl methacrylate) (PMMA) and other methacrylates, as conventionally prepared by free radical polymerization, are usually thought of as amorphous polymers. There are, however, numerous reports of aggregation in solutions of atactic polymethacrylates, and these are discussed in a recent review of aggregation in all types of polymethacrylates[1]. The structure of atactic PMMA and other methacrylates has been extensively studied and they are known to be predominantly syndiotactic in nature. Typically, they are quoted to contain up to 60% of syndiotactic triads[2]. It is worth noting that this is not very different from poly(vinyl chloride) which is partially crystalline[3].

Changes in crystallinity show up as transitions above T_g in many polymers. Another sort of transition that has sometimes been postulated to occur in the melt is the liquid–liquid transition. There has been much heated argument concerning the existence or non-existence of such a transition. Changes in the thermal diffusivity, d.s.c. and thermally stimulated current in PMMA have been attributed to the liquid–liquid transition[4,5]. Some might consider the data presented here as further evidence for the existence of this transition. Another simpler explanation for the observations is the presence of small quantities of very imperfect crystals in methacrylates.

EXPERIMENTAL

Materials

The polymethacrylates were obtained from Polysciences. The powders were dried in a vacuum oven for 1 week and then pressed at 180°C, or a temperature suitable for the heat treatment required, to produce plaques which were broken into pieces for further testing. One sample of poly(ethyl methacrylate) (PEMA) was also synthesized. Ethyl methacrylate ($100\,\mathrm{cm}^3$, inhibitor removed) was dissolved in ethyl acetate ($400\,\mathrm{cm}^3$); benzoyl peroxide (0.2 g) was added and the mixture refluxed for 4 h. The product was precipitated into methanol, filtered, washed, dried and pressed into plaques as above. The yield was a rather low 20% due to the time, temperature and initiator used. This sample was used to check some of the results obtained with the commercial material.

Pressure–volume–temperature (PVT) measurements

The densities of the polymers were measured at room temperature and atmospheric pressure using an autopycnometer (Micromeritics), with samples of approximately 8 g. The changes in density as a function of temperature and pressure were measured using a PVT apparatus which has been fully described elsewhere[6]. It consists of a sample cell containing 1–2 g of sample with mercury as a containing fluid. A flexible bellows closes off one end of the sample cell. The expansion and contraction of this bellows under temperature and

---

*To whom correspondence should be addressed

0032-3861/92/224793-05

pressure changes is used to calculate the volume change of the sample, making allowance for the volume change of the mercury. In the isothermal mode, volume readings are taken at fixed pressure intervals, 10 MPa or 100 kg cm^{-2} apart at a constant temperature. Following measurements along an isotherm, the temperature is changed by, for example, 10 K and the process repeated. In the isobaric mode, the presence is held constant while the temperature is changed at, in this case, either 0.25 K min^{-1} or 2.5 K min^{-1} and the volume monitored constantly. The absolute accuracy of the device is about 2×10^{-3} cm^3 g^{-1}; however, much smaller volume changes can be resolved. The isobaric runs were performed using a newer version of the machine designed to give data in MPa instead of kg cm^{-2} (technical atmospheres). (A version of the apparatus is available as a complete instrument from Gnomix Research, Boulder, CO, USA.)

Thermal, structural and rheological measurements

Several other techniques were used to examine the polymethacrylates, but they were not pursued as extensively as the PVT experiments and the results are less conclusive. They may, however, provide pointers to others interested in this area.

D.s.c. measurements were made using a Mettler DSC30 instrument. Samples of approximately 13 mg were used with a heating rate of 20 K min^{-1}. Samples 1 mm thick were pressed at 140°C. They were then heated to a series of temperatures in a hot press and quenched by transferring to a cold press. Small samples were then removed from these for analysis.

PEMA films were investigated by symmetrical transmission diffractometry using an automated Philips powder diffractometer (curved crystal monochromator; pulse height analyser; receiving and divergent slits, 0.25° and 0.2°, respectively; rotating samples; Ni-filtered CuKα radiation). Data were collected in a fixed time mode with a step size of 0.05 2θ and from 3 to 50° 2θ.

Rheological measurements were performed in the dynamic mode using a Rheometrics System IV rheometer. Samples 25 mm in diameter and 1 mm thick were compression moulded at 130°C under vacuum. Some samples were later heat treated by heating to 190°C on a preheated press for 2 min and then quenching. In the rheometer, the samples were held between parallel plates and the upper plate oscillated in torsion at 5 rad s^{-1} at a strain of 1%. In one experiment, the dynamic complex viscosity was measured at 10 K intervals as the temperature increased from 100 to 200°C with intervals of approximately 4 min between measurements. In a second experiment, the temperature was held at 130°C while the viscosity was measured as a function of time.

RESULTS

PVT measurements

A typical PVT result in the isothermal mode is shown in *Figure 1* for a sample of PMMA pressed at 180°C for 5 min and then quenched in a cold press. The pressure dependent T_g may be observed. To the left of line AB are PVT data appropriate for the particular glass loaded into the machine; to the right of line AC are data for the equilibrium melt. Between these two lines, the production of various glasses under pressure is seen.

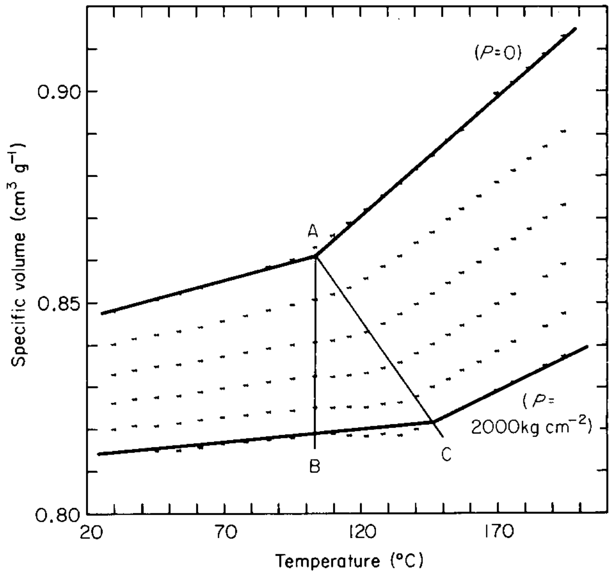

Figure 1 PVT data for PMMA for $P = 0$–2000 by 400 kg cm^{-2}, showing lines through isobars at $P = 0$ and 2000 kg cm^{-2} and the pressure dependent glass transition in the region ABC

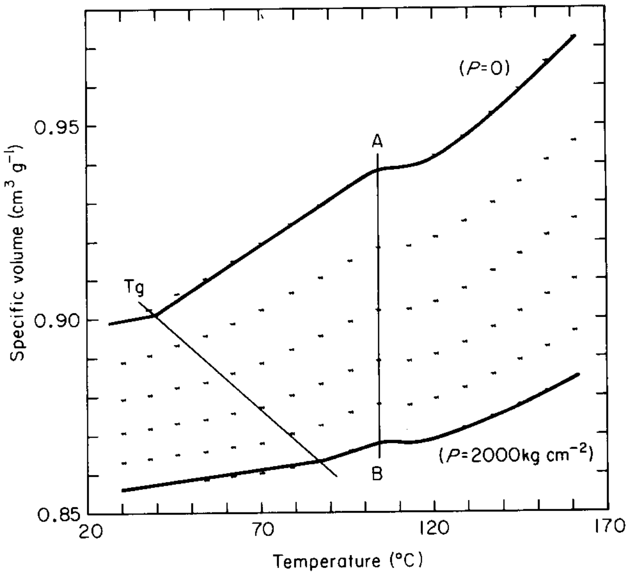

Figure 2 PVT data for PEMA for $P = 0$–2000 by 400 kg cm^{-2}, showing lines through isobars at $P = 0$ and 2000 kg cm^{-2}. The line AB is before the start of the transition believed to be due to crystallization

Figure 2 shows a similar plot for PEMA which was pressed at 170°C then quenched. The T_g is much lower and hard to discriminate but ends at about 90°C at higher pressures. There is also evidence of a densification between 110 and 130°C. There are very few effects that cause densification. The densification in *Figure 1* at high pressures between AB and AC results from the formation of new types of glass, but that in *Figure 2* is above T_g and occurs at all pressures. Similar results are obtained for samples of PEMA which we prepared as for commercial samples. One possible explanation of the densification is partial crystallization in the polymer which could occur at some temperature above T_g under the conditions of the experiment.

It should be pointed out that the pressure dependence of this transition might not be observed due to the mode of data collection; compression at constant temperature followed by heating at low pressure. If we are seeing crystallization then higher pressures would favour crystallization thermodynamically but be unfavourable kinetically. This could be compared to the effect of pressure on melting which is also not observed in this mode to a large extent. Once melted at low pressure, crystallization does not very readily occur on compression since the rate is very much reduced by pressure. This effect could be studied in the isobaric mode.

Figures 3 and *4* show that the same effect is seen for poly(propyl methacrylate) and poly(butyl methacrylate). It should also be noted that nothing of the sort is observed for poly(ethyl acrylate) or any other polyacrylate. One is therefore led to conclude that this is a common phenomenon for polymethacrylates. Since it is not observed for PMMA, it may be suggested that this is because of the higher T_g and the limited range between that and the degradation temperature.

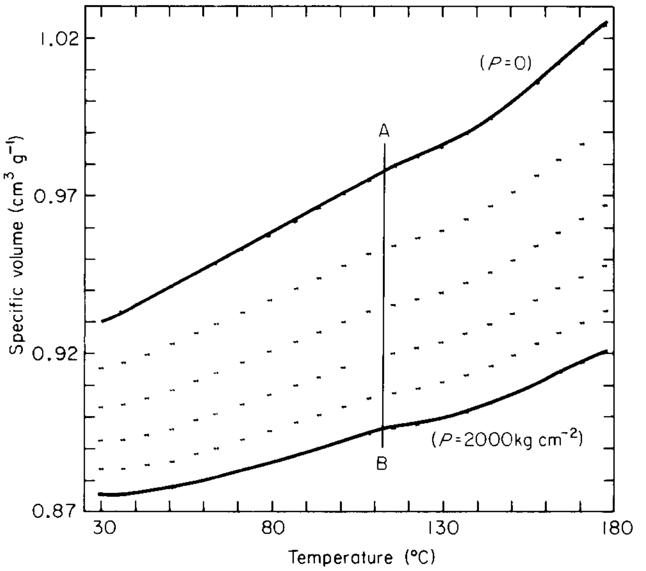

Figure 3 PVT data for poly(n-propyl methacrylate) for $P = 0$–2000 by 400 kg cm^{-2}, showing lines through isobars at $P = 0$ and 2000 kg cm^{-2}. The line AB is before the start of the transition believed to be due to crystallization

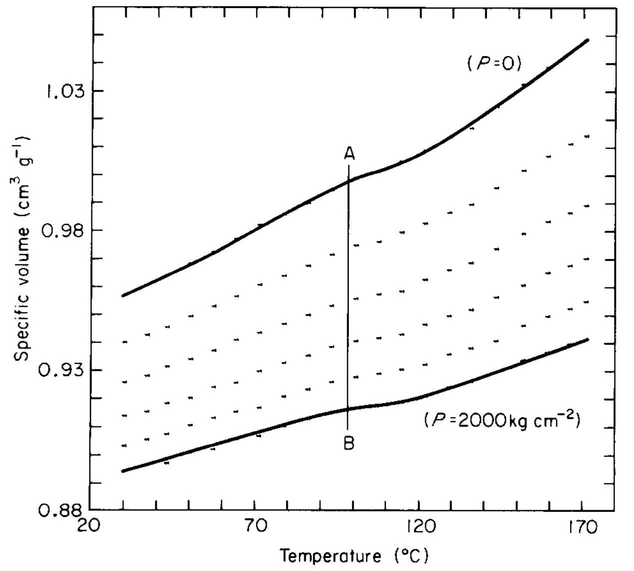

Figure 4 PVT data for poly(n-butyl methacrylate) for $P = 0$–2000 by 400 kg cm^{-2}, showing lines through isobars at $P = 0$ and 2000 kg cm^{-2}. The line AB is before the start of the transition believed to be due to crystallization

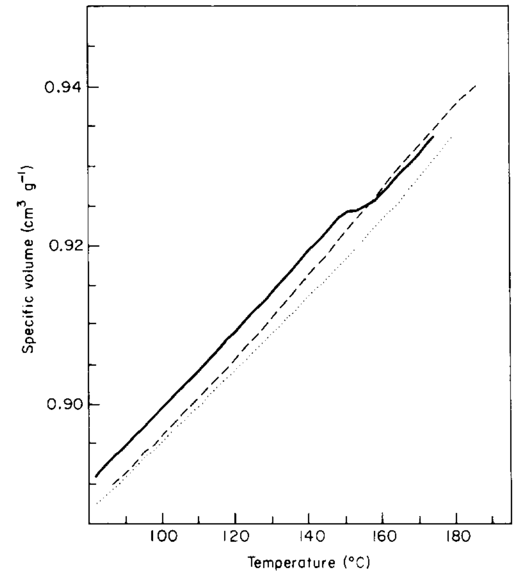

Figure 5 PVT plot for PEMA taken in isobaric mode at 2.5 K min^{-1} and 50 MPa. The first heating run (——) shows a densification at 150°C which is maintained on cooling (– – –) and enhanced on reheating (· · · ·)

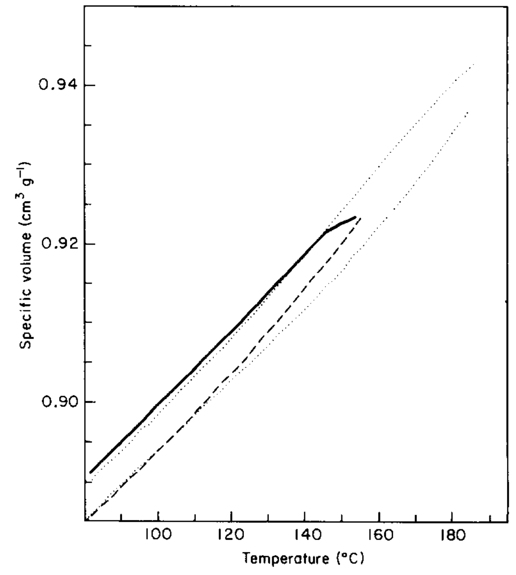

Figure 6 PVT plot for PEMA taken in isobaric mode at 2.5 K min^{-1} and 50 MPa. The first heating to 150°C (——) produces a densification which is maintained on cooling (– – –) but after being reheated (· · · ·) and heated for some time above 185°C the densification is removed and does not reappear on cooling (· · · ·)

More information for PEMA was obtained from isobaric runs which can be obtained on heating or cooling at 2.5 K min^{-1} and 50 MPa as shown in *Figure 5*. On heating to 175°C, densification is observed at 150°C. On cooling, the increase in density is maintained. On reheating even more densification is gradually produced. A second experiment is shown in *Figure 6*. The first heating run is stopped at the point of initial densification and again on cooling the densification is maintained. However, after heating to 185°C and recooling, the density tracks along the original as-loaded line. If we consider that the densification is due to crystallization we would have to conclude that the crystals form and then melt on heating, and then cannot reform either due to chemical change in the polymer or destruction of nuclei when the sample is heated to high temperatures. The exact point at which this happens is difficult to detect since the apparatus overshoots by a few degrees and takes some time to stabilize before starting the cooling ramp. Once this has happened, even holding in the region where densification is expected produces little effect. Further heating runs on such samples also show no densification.

The densification is also found to be rate dependent. *Figure 7* shows data collected at 0.25 K $\min^{-1}$. The densification is found to take place at the lower temperature of 120°C and is also greater in magnitude. Again it is maintained on cooling, but is destroyed at high temperatures and cannot be reproduced even at these slow rates.

Figure 8 shows d.s.c. runs made on samples which have been heated and quenched from various temperatures as indicated. We could interpret these as showing crystallization followed by melting, each occurring over a broad temperature range. First run d.s.c. plots are, however, known to be unreliable.

Figure 9 shows the X-ray scattering results for two PEMA samples with different pressure/thermal histories. Curve A is a scan from a (cryoground) sample pressed at 160°C then annealed at 130°C. Curve B is a scan from a (cryoground) sample that was removed from the PVT apparatus after an isobaric heating to 200°C and cooling. These samples were chosen to give a minimum and maximum, respectively, of potential crystallinity. Both scans are similar in kind and can be deconvoluted into five overlapping Gaussian peaks (7.8°, 11.76°, 17.92°, 31.84° and 42.55° 2θ). There is some change in relative intensity of these scans at 17.9° 2θ ($d = 4.96$ Å) which suggests some change in the sample. The change is small and these results are inconclusive, but small quantities of small, imperfect crystals are very difficult to study by this method.

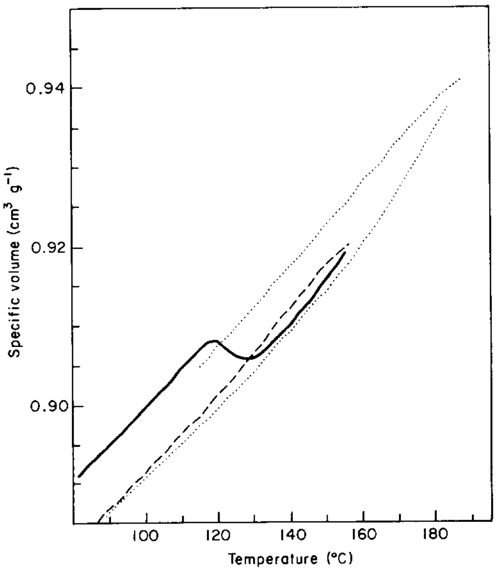

Figure 7 PVT plot for PEMA taken in isobaric mode at 0.25 K $\min^{-1}$ and 50 MPa. At the lower rate on first heating (——), the densification is greater and at a lower temperature than for the higher heating rate. It is maintained on cooling (– – –), but on further heating and cooling (····) and being held at high temperature, the densification is not reproduced even at this very slow rate

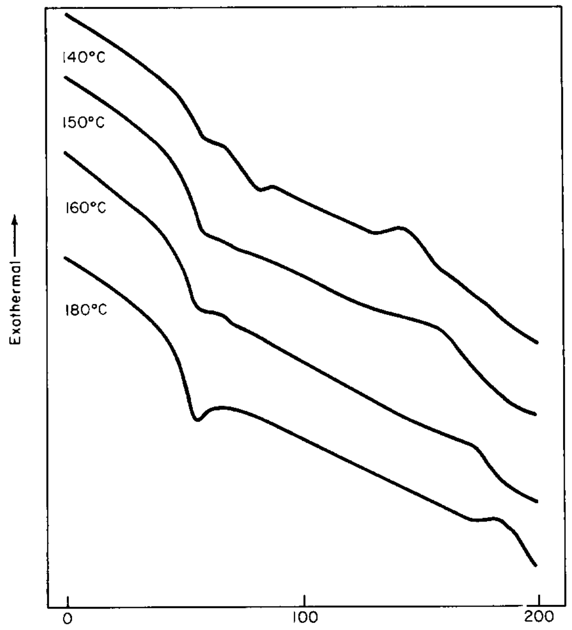

Figure 8 D.s.c. results for PEMA. The samples were annealed at the temperatures indicated and then the scans made at 20°C $\min^{-1}$. The glass transitions appear at the same temperature distorted by stress relaxations, etc. A second transition always appears around the temperature of annealing, which could be interpreted as crystallization

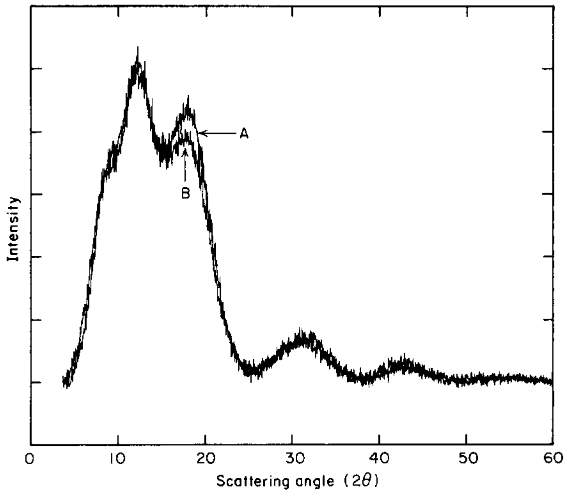

Figure 9 X-ray scattering results for PEMA after annealing at 130°C (curve A) and after heating to 200°C (curve B)

In the rheological measurements, one qualitative indication of the nature of the polymers can be obtained when the moulded samples are loaded into the rheometer. The sample is loaded at 100°C and pressed in place with a 200 g load. For liquid polymers, such as polystyrene, this cannot be maintained due to flow (which is the desired response so that perfect adhesion can be maintained). For all our samples, this was not the case, and it was necessary to maintain a 100 g load to minimize slippage. The sample which had been pressed at 130°C did not start to relax until 190°C. The sample which had been heated to 190°C and quenched, started to relax at 100°C but took several minutes to complete the process.

The results of the temperature scanning experiments are shown in *Figure 10*. The as-moulded sample starts out

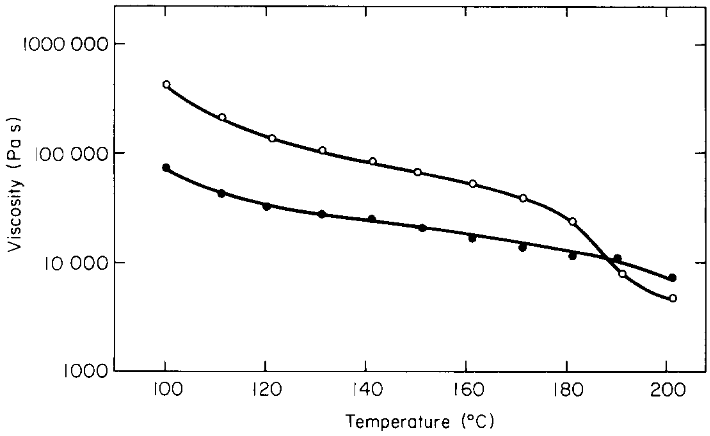

Figure 10 Plots of melt viscosity against temperature for PEMA. The sample that had been moulded at 130°C (○) shows a sharp reduction betweeen 170 and 200°C, which could be interpreted as melting. The sample that was quenched from 190°C (●) shows a lower initial viscosity but no sharp reduction

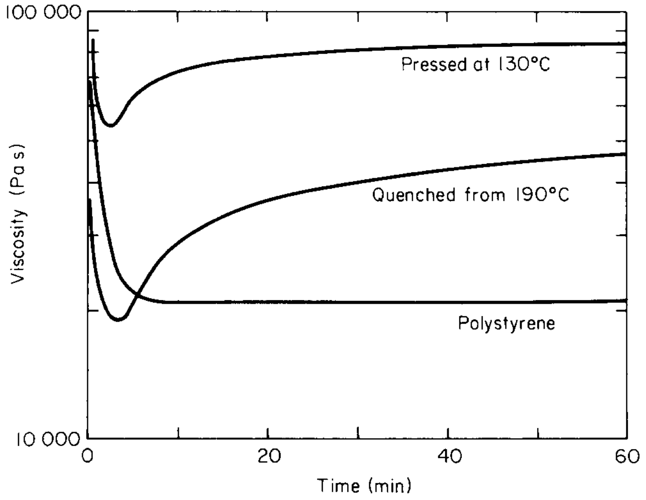

Figure 11 Plots of melt viscosity as a function of time at 130°C. All samples show an initial fall due to temperature equilibration. Polystyrene then shows a constant viscosity (the absolute values are one-half those shown). PEMA shows a rising viscosity: the sample moulded at 130°C shows a higher initial viscosity and a small rise whereas that quenched from 190°C shows a lower initial viscosity and a faster rise

with seven times the viscosity of the sample which had been quenched from 190°C. The viscosities converge at higher temperatures suggesting melting. We realize that absolute values may be affected by degradation and some of the initial lower viscosity may be due to degradation during the heating and quenching, but the relative movement between 170 and 200°C should not be influenced by this.

The results of the constant temperature experiments are shown in *Figure 11*. The viscosity of all samples initially decreases as a result of reaching thermal equilibrium. At 130°C, the heated and quenched sample has a lower viscosity and this increases over the time of the experiment. The as-moulded sample also increases slightly over the experiment. A comparison plot for polystyrene, an amorphous material, is also shown and shows no increase. The absolute values of the polystyrene data are one-half of those presented in *Figure 11*. The increase in viscosity of the PEMA samples could be taken as evidence for crystallization in this region.

CONCLUSION

We believe that we have presented fairly strong evidence for the presence of crystallinity in poly(ethyl methacrylate). It appears that crystallization followed by melting may occur in the region between 100 and 200°C. We also have some evidence of a similar effect in poly(propyl methacrylate) and poly(butyl methacrylate). We have no evidence in the case of poly(methyl methacrylate) but this could be a function of the high T_g which does not allow changes in crystallinity to occur so easily and makes study more difficult.

REFERENCES

1 Spevacek, J. and Schneider, B. *Adv. Colloid Interface Sci.* 1987, **27**, 81
2 Ferguson, R. C. and Ovenall, D. W. *Macromolecules* 1987, **20**, 1245
3 Maddams, W. F. 'Particulate Nature of PVC' (Ed. G. Butters), Applied Science, London, 1982
4 Ueberreiter, K. and Naghizadeh, J. *Koll. Z. Z. Polym.* 1972, **250**, 927
5 Gourari, A., Bendaoud, M., Lacabanne, C. and Boyer, R. F. *J. Polym. Sci. Phys.* 1985, **23**, 889
6 Zoller, P., Bolli, P., Pahud, V. and Ackermann, H. *Res. Sci. Instr.* 1976, **47**, 948