Effect of vitrification pressure on radius of gyration, specific heat and density of amorphous polymers

J. M. O'Reilly
Research Laboratories, Eastman Kodak Company, Rochester, New York 14650, USA

and R. S. Stein and G. Hadziioannou*
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003, USA

and G. D. Wignall
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA
(Received 8 October 1982)

The effects of vitrification pressure (to 500 MPa) and temperature (to 180°C) on the radius of gyration (as determined by small-angle neutron scattering), specific heat, and density were measured for polystyrene and poly(methyl methacrylate). The radius of gyration increased slightly (5×10^{-3}/°C) in both polymers; this increase is near the experimental uncertainty in the measurements. The small observed values are due to either small intrinsic effects of temperature or pressure on the conformation or competing effects of temperature and pressure. Density and specific heat showed changes which have been observed before and are attributed to intermolecular factors.

Keywords Vitrification; pressure; radius of gyration; density; specific heat; polystyrene; poly(methyl methacrylate)

INTRODUCTION

The effect of pressure on the physical properties of polymers such as viscosity, T_g, T_m, and rate of crystallization is marked. However, little is known about the effect of pressure on the polymer conformation in the melt and in the glassy state. In solution, pressure decreases chain dimensions[1] through a change in polymer–solvent interaction as well as through a direct effect of pressure on the unperturbed dimensions. Pressure should affect the unperturbed dimensions of a polymer chain through the difference in volume of the different conformations of the polymer backbone. This effect is analogous to the effect of temperature on chain dimensions through the energy differences among polymer conformations.

Ballard and coworkers[2] measured the radius of gyration R_g of polystyrene (PS) in the glassy state of samples that were vitrified at 250°C and 600 MPa. The R_g of a 158 000 molecular weight sample decreased from 154 to 120 Å with vitrification under pressure. The purpose of the present investigation was to vitrify samples of PS and poly(methyl methacrylate) (PMMA) at different temperatures and pressures to produce glassy samples with different conformational populations and to measure the effect of pressure-induced changes in population upon R_g. Previous work has shown that spectroscopic[3] and calorimetric[4] measurements on poly(vinyl chloride) (PVC) can be used to follow changes in conformational populations with pressure. Specific-heat and density measurements are also used to characterize the effects of pressure and temperature on glassy-state properties.

EXPERIMENTAL

Sample preparation

The samples used were mixtures of 70% protonated and 30% deuterated polymer. The molecular characteristics of polystyrene and poly(methyl methacrylate) for the deuterated and protonated species are presented in *Table 1*.

The densified samples of protonated PS, PMMA, and their mixtures with the corresponding deuterated species were prepared[3] in a steel piston cell (1.27 cm diameter) with Teflon spacers (0.1 mm) heated with an insulated heating tape. The sample was held at temperature for 5–10 min, and then pressure was applied and held for 5–

Table 1 Molecular weights and polydispersities for the polymers used in our study

Polymer	M_w	M_w/M_n
Polystyrene (H)	100 000	1.06
Polystyrene (D)	92 000	1.09
Poly(methyl methacrylate) (H)	104 000	2.5
Poly(methyl methacrylate) (D)	102 000	2.8

---

* Present address: IBM Research Laboratory, San Jose, California 95110, USA.

0032-3861/83/101255-04$03.00

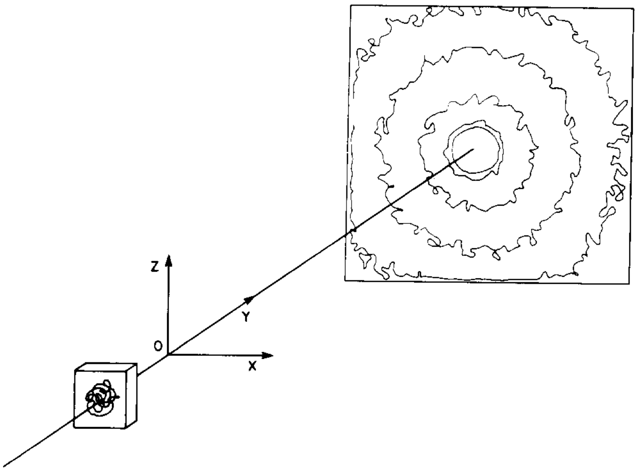

Figure 1 Geometry of experiment and intensity contour plot for scattering from amorphous poly(methyl methacrylate) (PMMA)

10 min. The sample was cooled as rapidly as possible ($\sim 10°C\ min^{-1}$) to room temperature. Temperature was increased in 20°C steps, and pressures were incremented in 100 MPa steps. This pressure leads to vitrification at each temperature before cooling. Temperature was measured with a Chromel–Alumel thermocouple. Duplicate samples were prepared with differential scanning calorimetry (d.s.c.) samples on top and bottom. No differences in the d.s.c. results were observed with position in the cell. In the melt above T_g, hydrostatic conditions should be obtained, whereas after vitrification deviations from hydrostatic conditions may occur. Small differences in hydrostatic conditions are not considered to be important at the high pressures used in these studies.

Small-angle neutron scattering (SANS)

The small-angle neutron-scattering experiments were done on the 30 m SANS facility with a pinhole collimation, a wavelength of 4.75 Å, and a two-dimensional multicounter (64 × 64 cells) placed 9 m from the sample.

Each experiment consisted of two successive scattering measurements, one for the background with the fully protonated polymer with no applied pressure and a second one with the densified sample, the solid solution of the protonated and deuterated polymer. Our solid polymer solutions were highly concentrated in polymer species. It has been shown that we can extract from this type of sample the single-chain form factor[4]. The coherent signal, which in fact is related to the single-chain form factor for the labelled chains, was obtained by subtracting the background signal from the sample signal. The detector efficiency was calibrated with pure water, whose scattering is totally incoherent and thus flat. Absolute calibration of the scattering cross section was made by using a mixture of protonated and deuterated polystyrene with matched and known molecular weight measured previously by the conventional light-scattering technique.

History of the samples

The densified samples were prepared on February 13–15, 1981, and stored under ambient conditions. SANS measurements were made on April 18–19, 1981. Specific-heat (C_p) measurements were made August 1–2, and density (ρ) measurements on August 7–8, 1981. The effects of annealing on R_g and density are not known but are expected to be small. The effect of annealing time on C_p is discussed by Prest *et al.*[5] and Weitz and Wunderlich[6]. After the samples were annealed for 30 days at room temperature, the changes in C_p were small.

RESULTS

The small-angle neutron-scattering experiments were conducted in such a way that the scattering intensity was measured for all orientations of the scattering vector $\vec{q}$* in the plane of the sample (*Figure 1*). We reduced those three-dimensional scattering patterns to two-dimensional ones by radial averaging; in *Figure 2* we represent intensity vs. scattering vector q. The radius of gyration and the molecular weight were obtained by using Zimm-plot analysis (*Figure 3*) on the reduced two-dimensional data restricted to the Guinier region ($qR_g < 1$). The R_g values are reported in *Table 2*. A small but systematic increase in R_g with increasing vitrification temperature and pressure was noted. The molecular weight decreased with increas-

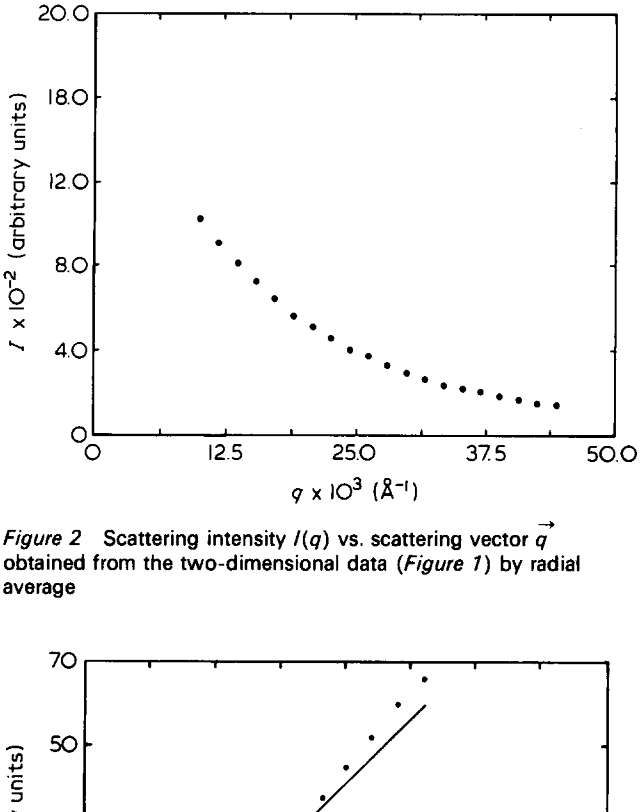

Figure 2 Scattering intensity $I(q)$ vs. scattering vector $\vec{q}$ obtained from the two-dimensional data (*Figure 1*) by radial average

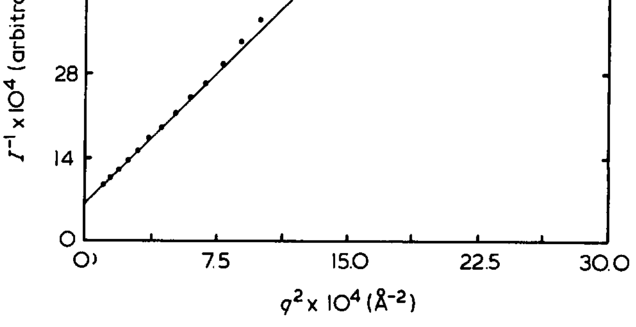

Figure 3 Typical Zimm-plot representation for PMMA pressurized at 400 MPa; R_g=111 Å; M_w=81.3×10³

---

* $|q| = (4\pi/\lambda)\sin(\theta/2)$ where λ is the wavelength of the neutron and θ is the angle between the incident and the scattered beams.

Table 2 Densities (ρ) and radii of gyration (R_g) for PS and PMMA as functions of pressure

PS				PMMA			
P (MPa)	T (°C)	ρ (g/cc)	R_g (Å)	P (MPa)	T (°C)	ρ (g/cc)	R_g (Å)
0	100	1.052	82	0	105	1.182	107
100	120	1.057	84	300	160	1.191	110
300	160	1.056	84	400	180	1.190	111
400	180	1.051	85	500	200	1.187	–

ing pressure. This effect is attributed to the decrease in scattering intensity due to density fluctuations with the decrease in density.

The d.s.c. results for PS and PMMA followed the general behaviour described for PVC[3,5], where the conformational changes were also observed by *FT*i.r. spectroscopy. In the samples vitrified under pressure, an endothermal peak occurred ~20°C below the T_g observed with rapid cooling and heating (20°C min^{-1} in this case). The endothermal peak sharpened, increased in intensity, and occurred at lower temperature as the pressure and the temperature of vitrification increased. Further effects of the higher pressure were the appearance of an exotherm following the endothermal peak (C_p pressure$<C_p$ normal) and a slightly higher glass transition (few degrees) for the densified sample. These results are illustrated in *Figure 4*.

The interpretation of these results is as follows: At the temperature T_{endo}, some volume recovery occurs, which leads to the absorption of energy, and strain energy ($P\Delta V$) is released, leading to the exotherm (C_p pressure$<C_p$ normal). Significant conformational changes are not implicated at the temperature in the endothermal peak by *FT*i.r. spectroscopy. The major conformation change occurs at the normal T_g, by *FT*i.r., and contributes about half of the change in specific heat. Since pressure should freeze polymer segments in high-energy states, the equilibration of these high-energy states should lead to an exotherm. The shift of a few degrees in apparent T_g with pressure is attributed to this effect, although a larger change was expected. There is the possibility for some exchange among the localized states in the glass, i.e., high-energy conformations could relax to lower-energy conformations with an increase in the segment strain energy.

The results for PMMA show the endothermal peak at slightly lower temperature. The amount of energy absorbed in the endotherm is 1.3 J g^{-1} and is comparable to the results of Ballard[2] and others[6].

Density measurements for the pressure-vitrified samples are listed in *Table 2*. The previously observed increase in density with pressure was observed, but a decrease with increasing pressure was found instead of a levelling off of the density at high pressure. Recent measurements of Oels and Rehage[7] show a distinct decrease in the observed densification at high pressure and long times.

DISCUSSION

The fact that R_g changes only slightly with vitrification pressure and yet significant changes are observed in the specific heat requires some explanation. There are several reasons why R_g may not change with pressure. We have implicitly assumed in this problem that high temperature will populate the high-energy conformation, which will lead to an increase or a decrease in R_g, depending on whether the *trans* or *gauche* state is the high-energy state. The change in unperturbed dimensions of the chain, $\langle r_0^2\rangle$, with temperature is given by:

$$\frac{\partial \ln\langle r_0^2\rangle}{\partial T}=-\frac{\Delta H}{kT^2} \qquad \Delta H=H_{gauche}-H_{trans}$$

for a simple two-independent-state chain. For polystyrene[8] and poly(methyl methacrylate)[9] the changes in $\langle r_0^2\rangle$ with 100°C temperature change would be about +5% and +20%, respectively. The experimental value is less than this, approximately $+0.5\times10^{-3}$/°C or 5% /100°C.

Previous measurements of R_g vs. temperature for *PS*[10] and PMMA[11] had shown no change in dimensions with temperature. It does appear that the change in R_g with temperature and pressure is less than or equal to the experimental uncertainty, $\pm0.5\times10^{-3}$/°C. Underlying reasons for such a small effect are unclear. In the present experiments the additional effect of pressure on the conformational populations must be considered. Initially, we assumed that the pressure would only freeze in the conformational population at high temperatures without directly influencing the populations. In the previous *FT*i.r. spectroscopy studies, a direct effect of pressure favouring the low-energy conformer (assumed *trans*) of PVC was necessary to account for the changes in absorbance with temperature and pressure. The small changes of R_g with pressure could be produced in the same manner; if pressure favours the low-energy conformer because of a smaller conformer volume, then the change in dimensions with temperature and pressure would tend to cancel and produce an overall small effect. A difference in

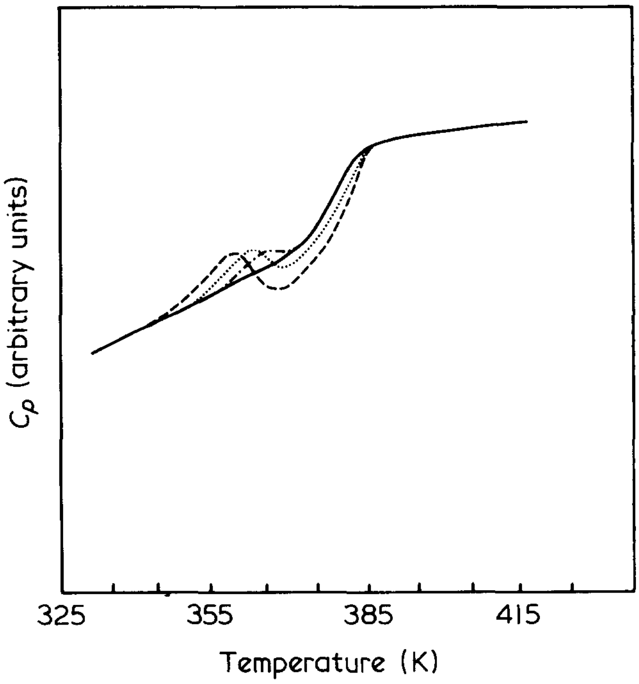

Figure 4 Specific-heat scans as a function of temperature for PS pressurized at 0 (——), 100 (–·–·–), 300 (···), and 400 (–––) MPa

volume between conformers of 1 cc/mole would lead to a change in dimensions of 4×10^{-4}/MPa. These results show only that effects of temperature and pressure on the dimensions and conformations of polymers deserve more detailed and careful study to elucidate the magnitude and causes.

The explanation by Ballard *et al.*[2] of the observed changes in R_g was in terms of intermolecular factors and phenyl-group interactions. Intermolecular factors and specific group interactions will need to be considered, but the rotational isomeric state calculations suggest that intramolecular factors are probably more important. Recent analysis by Bleha[12] supports this conjecture and is consistent with this discussion.

Changes in C_p are observed in d.s.c. experiments because pressure affects the vitrification process at $T_g(P)$. The endothermal peaks below T_g are associated with changes in frozen-in stresses occurring in the glassy state. Changes in C_p at T_g with pressure are smaller and suggest conformational changes. The changes in R_g expected with pressure and temperature would occur in the supercooled liquid state and not in the glass. Therefore, the difference between the d.s.c. and SANS measurements can be rationalized.

ACKNOWLEDGEMENTS

The small-angle neutron-scattering studies were performed at the National Center for Small-Angle Scattering Research, Oak Ridge National Laboratory. The NCSASR is funded by National Science Foundation Grant No. DMR-77-244-58 through Interagency Agreement No. 40-637-77 with the Department of Energy (DOE) and is operated by the Union Carbide Corporation under Contract No. W-7405-eng-26 with the DOE. We thank Dr J. Greener (Eastman Kodak Company) for the density measurements.

REFERENCES

1 Hammel, G. L., Schulz, G. V. and Lechner, M. D. *Eur. Polym. J.* 1979, **15**, 209
2 Ballard, D. G. H., Cunningham, A., Langman, G. W. and Nevin, A. *Polymer* 1979, **20**, 1443
3 O'Reilly, J. M. and Mosher, R. A. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1187
4 Prest, W. M. *et al. Polym. Sci. Eng.* 1981, **21**, 1181
5 Wignall, G. D. *et al. Polymer* 1981, **22**, 886
6 Weitz, A. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 2473
7 Oels, H. J. and Rehage, G. *Macromolecules* 1977, **10**, 1036
8 Orofino, T. A. and Ciferri, A. *J. Phys. Chem.* 1964, **68**, 3136
9 Schultz, G. V., Wunderlich, W. and Kriste, R. *Makromol. Chem.* 1964, **75**, 22
10 Ballard, D. G. H., Wignall, G. D. and Schelten, J. *Eur. Polym. J.* 1973, **9**, 965
11 Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 120
12 Bleha, T. *Makromol. Chem., Rapid Commun.* 1981, **2**, 35