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Characterization of densified polystyrene using SANS and thermal measurements

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Previous work by ourselves^{1,2} and others has shown that atactic polystyrene is a random coil in the glassy state and that no significant change in the radius of gyration occurs on heating above the glass transition. More recently this study has been extended and the radius of gyration measurements carried out on polymers with molecular weights as low as 2300. The latter samples were also heated above T_g and subjected to a pressure of 6 Kbars, then cooled to 23°C; measurements were carried out at atmospheric pressure. The volume changes associated with this treatment are shown in *Figure 1*. The curve CBA is the volume-temperature behaviour at atmospheric pressure³. The volume changes to which the samples are subjected is shown by the path CBAEFG and the percentage volume changes are listed in *Table 1*. The

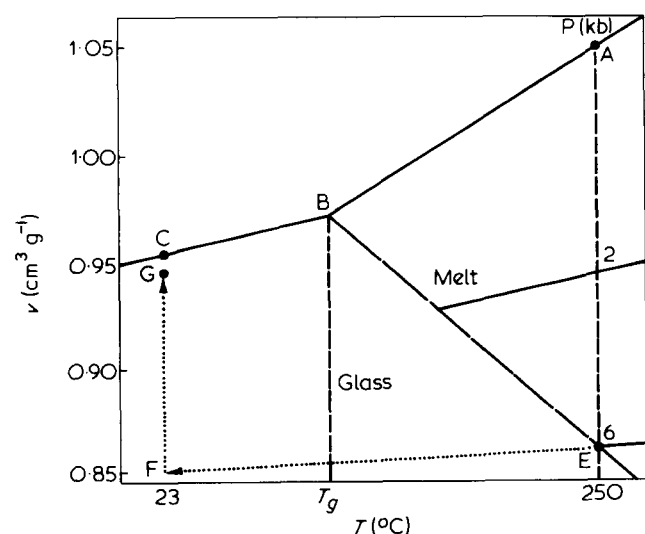


Figure 1 Volume-temperature diagram of atactic polystyrene and densification cycle

radius of gyration obeys the $M_w^{1/2}$ law precisely, and the following relationships were determined:

$$R_w = (0.27 \pm 0.017)M_w^{1/2} \text{ cooled below } T_g \text{ at 1 bar} \quad (1)$$

$$R_w = (0.22 \pm 0.015)M_w^{1/2} \text{ cooled below } T_g \text{ at 6 kbars} \quad (2)$$

The contraction of the coil is more than 30 times larger than the overall volume change in the bulk material as determined from the density measurements; the data is summarized in *Table 1*. However, it is only twice as large as the volume change produced in the melt on compression at 6 kbars. It would appear, therefore, that the polymer in the glassy state can expand (represented by the volume change from F to G in *Figure 1*) without the coil expanding. Expansion of the coil is achieved by heating the samples to a temperature below the glass temperature at which calorimetry measurements (d.s.c.) show that a small but significant heat absorption occurs. The results are summarized in *Table 2* and the effect is most noticeable at the highest molecular weight. The plaque, which is in the condition described by the point G in *Figure 1*, on heating to 80°C absorbs 0.49 cal g⁻¹ of heat and this is accompanied by an expansion of the coil to the equilibrium value at atmospheric pressure. Further heating above T_g produces no addition expansion. Similar changes are observed at the lower molecular weights.

Table 1

Volume contraction of coil on compression. Calculated from equations (1) and (2)	46%
Volume contraction on compression of melt at 250°C at 6 kbars (at point E, <i>Figure 1</i> , ref 3)	23%
Overall volume contraction on compression of melt at 250°C at 6 kbars, cooled to 23°C measurements at atmospheric pressure (point G, <i>Figure 1</i> , ref 3)	1.4%

Table 2 Thermal and radii of gyration measurements on samples of polystyrene pressured at 6 kbars and 250°C for 24 h measurements at 23°C

Deutero polystyrene matrix molecules		Protopolystyrene tagged molecules				Thermal measurements		
M_w	Dispersity	M_w	R_z (Å) at G	R_z (Å) after heating to endotherm temp.	R_z (Å) after heating above T_g	Temperature of endotherm	Endotherm (cal/g)	T_g
2800	1.09	2800	10.7	—	12.8	53	0.94	53
29 200	1.23	30 900	45.4	48.0	47.0	73	0.68	95.5
158 000	1.47	214 600	120	158	154	80	0.49	99.0

The reduction in radius of gyration of the polymer molecule on compression probably arises from the rotation of the phenyl side groups to achieve closer packing in the melt. This could result from the apparent shortening of the chain due to the coil becoming partly helical or due to the molecule occupying space closer to the centre of mass. On cooling below T_g this structure becomes frozen and persists even when the pressure is removed and the bulk material expands to give nearly the same density as the normal polystyrene. Since the macromolecules do not change their conformation this fall in density must be due to the formation of voids of molecular dimensions between chains.

The fact that the chain assumes normal conformation on heating to temperatures well below the glass transition temperature means that the molecule has freedom to move at these temperatures. Also no density change of any significance is involved implying that chains can slip by one another. The mobility at 20°C below the literature values of T_g however is of low order and not comparable in magnitude with the molecular motions occurring above this tran-

sition. Our measurements of the values of the heat absorbed agree reasonably well with those of Brown *et al.*⁴

Finally, it should be noted that since equations (1) and (2) apply at low molecular weights, this is reasonably good evidence that stems greater than 40 Å are absent from the structure. It has recently been shown⁵ that in crystalline polymers where stems greater than 120 Å are known to be present, at low molecular weights $R_w \propto L_n$, (L_n is the dominant stem length) and is independent of molecular weight in this region.

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Phenolic poly(acryloyl morpholine)-based bead matrix for solid (gel) phase peptide synthesis

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The classical Merrifield method of polymer-supported peptide synthesis has been developed mainly using supports based on crosslinked polystyrene. Such matrices undergo gelation (constrained dissolution) most readily in non-polar solvents whereas attached peptide chains are solvated best by solvents of very high polarity. Thus, the non-polar solvents which expand the matrix may cause collapse of the peptide chains and *vice versa*. It has been suggested that steric interactions, arising from this effect, are a major cause of incomplete reaction during solid (gel) phase synthesis¹.

Efforts have been made to devise alternatives to polystyrene-based supports²⁻⁴. Atherton *et al.*⁵ have described the synthesis of a poly(*N,N*-dimethylacrylamide)-based resin which enables all protected amino-acid coupling reactions and all polymer-supported peptide *N*-terminal

deprotection steps to be carried out in highly polar organic media. The chains of the copolymer matrix and of the attached peptide are solvated fully throughout. In solid (gel) phase synthesis, the resin gave results much superior to those obtained using polystyrene-based supports.

In our laboratory, we have synthesized a number of speciality copolymer networks incorporating acryloyl morpholine as the predominant monomer^{6,7}. Such copolymers incorporate many exposed ether linkages and undergo gelation readily in all the polar solvents used commonly in peptide synthesis. For some time, we and others⁸ have appreciated the potential of poly(acryloyl morpholine)-based matrices as supports for solid (gel) phase peptide synthesis. Our materials also bear a clear structural similarity to the poly(*N,N*-dimethylacrylamide)-based support. We describe