Small-angle neutron scattering study of amorphous polycarbonate

D. G. H. Ballard, A. N. Burgess, P. Cheshire, E. W. Janke and A. Nevin
ICI Corporate Laboratory, PO Box 11, *The Heath, Runcorn, Cheshire WA*7 *4QE, UK*

and J. Schelten
Institut fur Festkorperforschung der Kernforschungsanlage Julich GmbH, 517 *Julich* 1, *Postfach* 1913, *W. Germany*

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Experiments have been performed on deuterated polycarbonate chains with five different molecular weights, randomly dispersed in a protonated polycarbonate matrix. There is evidence for some ester interchange in the melt. This requires that the values of M_w obtained from the SANS data be used. The measured radii of gyration were found to follow the relationship: $R_w = \beta M_w^{\alpha}$, with $\beta = 0.457(9)$ and $\alpha = 0.5$. The high value for β compared with that for polystyrene ($\beta = 0.27$) is a reflection of the stiffer backbone in polycarbonate.

INTRODUCTION

There are now many reviews on the use of small-angle neutron scattering (SANS) to investigate the structures of polymers in the solid state[1-3]. The technique is based on the difference in coherent scattering lengths for neutrons between ^1H and $^2H(D)$. The samples consist of deuterated polymer molecules (tags) randomly dispersed in a protonated matrix; small-angle scattering is observed from the contrast between the tags and the matrix.

Polycarbonate is noted for its toughness, a property which may be attributed in part to the amount of flow, either on a microscopic or macroscopic scale, which occurs during failure. Flow absorbs energy and its inhibition will embrittle the polymer[4]. Flow may involve the movement of chain segments and, possibly, ordered regions in the polymer. Flory[5] has suggested that the polymer chains in glassy polycarbonate assume a random coil configuration, but an alternative approach requires the existence of ordered regions in the solid phase. Yeh[6] described a folded-chain micelle model; Geil[7] suggested the existence of small, nematic liquid crystal-like domains, with the molecules passing between them and Aharoni[8] proposed small amorphous regions of uniform high density separated by less dense material.

SANS should allow experimental investigation into the physical properties of polycarbonate at the molecular level.

THEORY

The scattering cross-section for a deuterated polymer in a protonated matrix can be written, for small scattering vector, q ($q = 4\pi\sin\theta/\lambda$) as[1]:

$$\lim_{c\to 0}\frac{cK_N}{I(q)} = \frac{1}{M_w}\left[1 + \frac{1}{3}q^2R_z^2\right] \tag{1}$$

where $I(q)$ is the scattering intensity, c is the concentration of deuterated polymer, $R_z = \langle s^2\rangle_z^{1/2}$ and

$$K_N = \rho N_A\left[\frac{\nu\chi(b_D - b_H)}{M_m}\right]^2 \tag{2}$$

where ρ is density of the polymer, ν is number of replaceable hydrogens in the repeat unit, χ is degree of deuteration, M_m is the weight of the deuterated repeat unit, N_A is Avogadro's number and $(b_D - b_H)$ is the difference in scattering lengths between deuterium and hydrogen ($= 1.041 \times 10^{-12}$ cm). Thus, by careful calibration of the instrument, both the molecular weight M_w, and the radius of gyration, R_z, of the deuterated polymer molecule can be measured by SANS.

EXPERIMENTAL

Sample preparation

Deuteropolycarbonate (degree of deuteration 94%) was prepared and fractionated with chloroform as solvent and methanol as non-solvent. Five fractions with differing molecular weights were used for the neutron scattering experiments. Each fraction was solution-blended in chloroform at 5% w/w with protonated Makrolon 3000L matrix polymer ($M_w = 368\,000$, $M_w/M_n = 2.1$). The blends were precipitated into methanol and vacuum dried at 70°C.

Plaques (20 × 40 × 1 mm) were prepared for SANS by hot pressing at 190°C to remove bubbles followed by quenching in ice-water.

SANS

SANS measurements were made on the small-angle scattering apparatus at KFA, Julich, with sample-detector distances of between 4 and 6 m and a neutron wavelength of 7.5 Å. Background scattering from the matrix was removed by subtracting the signal from a protonated specimen with suitable allowance for differing sample thickness. The molecular weights of the deuterated polymer fractions were measured by gel permeation chromatography (g.p.c.), laser light scattering[10] and by SANS.

RESULTS AND DISCUSSION

Table 1 shows that there is disagreement between the molecular weights of the deuterated molecules measured

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Table 1 Values of R_w and M_w for polycarbonate measured by SANS

	G.p.c. data		SANS data		
Sample no.	$10^{-3} M_w$	M_w/M_n	$10^{-3} M_w$	R_z (Å)	R_w (Å)
PC1A	96.8	1.79	73.0	159	119
PC1B	75.2	1.38	38.0	113	96
PC1C	37.4	1.48	26.0	89	73
PC3	29.6	1.42	21.0	89	74
PC4	13.8	1.29	9.4	53	47

Errors in the values of R_w and M_w are typically of the order of 10%

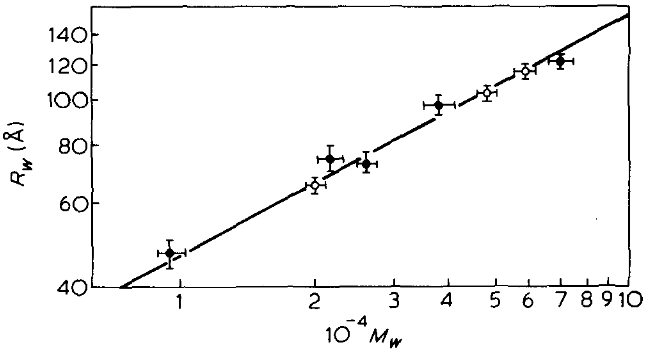

Figure 1 Radius of gyration vs. M_w for glassy polycarbonate plotted on logarithmic scales. ●, Present work: ⊕, from Ref 11; full line is the curve $R_w = 0.457\, M_w^{0.5}$

Table 2 Results of fitting $R_w = \beta M_w^{\alpha}$ to data on polycarbonate

β	α	χ^{2*}
0.457(9)†	0.5	0.464
0.69(26)	0.46(3)	0.446

$$^{*}\ \chi^2 = \frac{1}{(m-n)} \sum_{i=1}^{m} w_i (I_0^i - I_c^i)^2$$

where w_i is weighting = $1/\sigma^2 = 1/\text{error}^2$
m and n are the numbers of observations and parameters, respectively
I_0 and I_c are the observed and calculated values
† Numbers in parentheses are the errors in the numbers

by g.p.c. and SANS. G.p.c. molecular weights were corrected according to a procedure given by Dawkins *et al.*[9]. Condensation polymers are known to exchange molecular fragments at the ends of the molecule as shown by equation (3):

$$\mathrm{ROH + R'O{\cdot}COR'' \rightarrow R'OH + RO{\cdot}COR''} \qquad (3)$$

If ROH is a protonated residue and R'O·COR" the deuterated molecule, then a reduction in molecular weight of the tagged molecules will result. In order to estimate the extent to which this occurred, a variety of conditions were explored for mixing the deutero and protonated molecules. The procedure described in the experimental section gave the least decline in molecular weight due to ester interchange. Laser light scattering showed a reduction in M_w from 39 000 to 37 500 occurred with this procedure and g.p.c. data gave a similar decline in molecular weight with no change in polydispersity.

Previous experience has shown that values of molecular weight measured in the solid state using forward scattering are equally as accurate as solution techniques[2,3,13]. In *Table 1* values of M_w by the two techniques are compared. It is evident that the exchange reaction is more apparent at the high molecular weights.

From these considerations it appears reasonable to assume that the SANS values of M_w are the correct ones to use.

If the molecular weight distribution is log-normal, the weight-average radius of gyration, R_w, can be derived from the z-average, R_z:

$$R_w = R_z (M_w/M_n)^{-1/2} \qquad (4)$$

The polydispersities used were those measured by g.p.c. R_w is plotted against M_w on a log–log plot in *Figure 1*. Least-squares fits of the data to the relationship:

$$R_w = \beta M_w^{\alpha} \qquad (5)$$

are given in *Table 2*. The improvement of the fit when α was allowed to vary from its random coil value of 0.5 was statistically insignificant[12], but the two fits do emphasise the high correlation between the values of α and β.

Some recent results of Fischer *et al.*[11] are also included in *Figure 1* and they agree closely with the present values.

CONCLUSION

The chain conformation in polycarbonate has been measured by SANS for five different molecular weights. Several conclusions can be drawn from these results.

(a) Ester interchange occurs in the melt and neutron scattering is a sensitive method for observing such effects. SANS results appear self-consistent and agree very closely with other work.

(b) To within the experimental error, $R_w = 0.457\, M_w^{1/2}$. The value for α of 0.5 implies a random coil behaviour in glassy polycarbonate.

(c) β is related to the persistence length of the polymer. Its high value, compared with amorphous atactic polystyrene ($\beta = 0.27$)[13], is a reflection of the stiffer backbone in polycarbonate.

As it has proved possible to prepare deuterated polycarbonate, randomly dispersed in a protonated matrix, further SANS experiments are in progress including extensions to higher and lower molecular weights, densification and experiments on stressed polycarbonate.

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