

# Investigation of the thermal ageing of bisphenol-A polycarbonate by wide angle neutron scattering

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Physical ageing of bisphenol-A polycarbonate (BPAPC) was investigated by wide-angle neutron scattering (WANS). This technique, when used on perdeuterated samples, should be sensitive to local conformational changes allowing a close monitoring of subtle changes in the morphology. Two sets of experiments have been performed. The first set was on semicrystalline BPAPC aged at 110°C. Ageing times up to 5 days showed no WANS spectral changes. The second set was on amorphous BPAPC which also did not show definite spectral changes upon thermal ageing. It was concluded, within the experimental limitations, that the densification process (i.e. loss of 'free' volume) associated with thermal ageing probably results in no local relative conformational changes. The results are, rather, more consistent with a lattice contraction mechanism, whose rate is governed by the molecular structure of the glassy BPAPC.

(Keywords: bisphenol-A polycarbonate; wide-angle neutron scattering; thermal ageing)

## Introduction

The physical ageing of polymeric materials is of great concern because it is accompanied with important changes in physical properties. This process in glassy polymers, as extensively reviewed by Struik<sup>1</sup> and by Tant and Wilkes<sup>2</sup> among others, continues to be a point of experimental and theoretical interest. Robertson and co-workers<sup>3-5</sup> have proposed to associate the process of physical ageing with a free volume fluctuation in the glass that is accompanied by molecular conformational change. Neglecting the structural component within the Robertson model, Curro *et al.*<sup>6</sup> have modelled the lattice contraction of a glass during physical ageing as a diffusion model. From a different, but not incompatible viewpoint to that of Robertson, Bubeck and co-workers<sup>7-9</sup> have studied the physical ageing process in the context of increasing restriction of molecular moiety motional freedom. It was proposed that this restriction is associated with the shift in molecular conformation population towards that more favourable for ductile deformation. The reconformations were envisioned as relatively subtle changes less radical than, for example, *cis* to *trans* reconfigurations. Although recognizing that some kind of free volume decrease accompanies physical ageing, it was also proposed<sup>7</sup> that the decrease is a manifestation of the physical ageing process and not the cause of physical property changes, *per se*.

Neutron scattering is a valuable non-destructive tool to investigate condensed matter. Small-angle neutron scattering (SANS) has been extensively used to monitor conformational changes in partially deuterated polymers in solution or in the bulk state<sup>10</sup>. Wide-angle neutron scattering (WANS), on the other hand, has not been the subject of much attention from polymer scientists because of the high incoherent background from protonated (i.e. normal) samples and because of the high competition of wide-angle X-ray scattering (WAXS). However, when perdeuterated samples and a WANS spectrometer are readily available such experiments could be useful because they measure correlations involving deuterium (D-D, D-C, D-O) besides the usual correlations (C-C,

C-O, O-O) observed by WAXS and, therefore, yield slightly different spectra. (Relative peak heights are different for WANS and WAXS.) Also, neutron scattering from organic materials is characterized by low adsorption compared with X-ray scattering. This permits the use of (a few millimetres) thick samples and complicated sample environments. It should be emphasized that experiments similar to the ones described here can be attempted with WAXS since no specific sample environment is used. In fact, a number of investigations on bisphenol-A polycarbonate (BPAPC) have been performed using WAXS<sup>11-16</sup>.

It is the common belief that ageing is associated with a densification of the sample (i.e. a loss of free volume). The goal of the present study is to employ a 'microscopic' (i.e. molecular) probe to assess the amount of conformational changes that could manifest themselves as changes in local morphology. BPAPC has been chosen because it has shown signs of ageing after annealing times of the order of a couple of days<sup>7</sup> and because its glass transition temperature ( $T_g$ ) is convenient (about 150°C).

Very local modes (such as phenyl ring flips, etc.) in BPAPC have been observed by nuclear magnetic resonance<sup>17</sup>, and the ease of phenyl ring motion in a polycarbonate copolymer has been shown to change with physical ageing<sup>8,9</sup>. The goal of the present investigation is to attempt to observe larger scale motions such as displacement of chain portions which contribute to local conformational changes and therefore to changes in the WANS spectra. It should be mentioned that Saffell and Windle<sup>14</sup> investigated thermal ageing of BPAPC across  $T_g$ . They analysed the area underneath the first hump (located at  $0.8 \text{ \AA}^{-1}$ ) of WAXS spectra from amorphous samples. Carr *et al.*<sup>18</sup>, on the other hand have used electron microscopy to study the morphology of semicrystalline BPAPC.

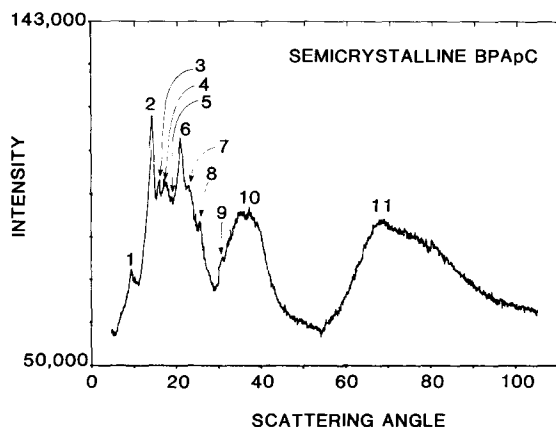
## Experimental

BPAPC was synthesized and characterized at the Dow Chemical Research Central Research Labs. Gel permeation chromatography measurements showed

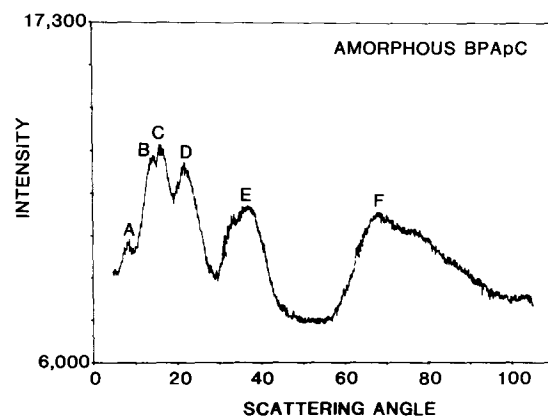
**Table 1** Relative heights of the main peaks in the WANS spectrum of semicrystalline deuterated BPAPC

Sample thermal treatment <sup>a</sup>	Peak 2	Peak 6	Peak 10	Peak 11	Peak 2	Peak 6	Peak 10
	14°	21°	39°	69°	Peak 11	Peak 11	Peak 11
As received powder	138719	121722	93499	91343	1.52	1.34	1.02
Heated to 210°C, then quenched	116874	111107	88790	89281	1.31	1.24	0.99
Aged at 110°C for:							
½ h	116702	114408	89882	90192	1.29	1.27	1.00
2 h	116622	113398	90181	90681	1.29	1.25	0.99
6 h	116568	111539	89823	90136	1.29	1.24	1.00
12 h	116685	110543	91929	89591	1.30	1.23	1.03
22 h	117017	111858	90755	90232	1.30	1.24	1.01
46 h	117426	109483	89207	88825	1.32	1.23	1.00
76 h	117165	112308	90489	90730	1.29	1.24	1.00
100 h	118050	111298	89818	90882	1.30	1.22	0.99
Aged at 130°C for 5 h	115645	108499	89005	88337	1.31	1.23	1.01
Aged at 150°C for 6 h	115760	109849	89157	88610	1.31	1.24	1.01
Aged at 180°C for 20 h	136311	118759	93792	89612	1.52	1.33	1.05
Heated to 210°C, then slowly cooled	137796	120118	92888	90745	1.52	1.32	1.02

<sup>a</sup> Peak shifts are less than 1° during annealing



**Figure 1** Wide-angle neutron scattering spectrum from semicrystalline deuterated bisphenol-A polycarbonate



**Figure 2** Wide-angle neutron scattering spectrum from amorphous deuterated bisphenol-A polycarbonate

rather low molecular weights around 20000 to which should correspond low thermal ageing time scales. The BPAPC powder was then dried in an evacuated oven at 190°C for 1 h then vacuum tight sealed in a vanadium cylindrical cell ( $\frac{1}{4}$ " diameter, 2" high) to avoid moisture intake.

Two sets of experiments were performed. The first set was on this semicrystalline BPAPC sample. Crystallinity was induced on the sample at the last stage of the synthesis (precipitation in solution). A series of eight annealing steps (at 110°C) were performed for a total of 100 h. A WANS spectrum was taken at each step. Then a sequence of three other annealing steps was performed under vacuum at temperatures of 130 (for 5 h), 150 (for 6 h) and 180°C (for 20 h), respectively, on the three sample portions in order to test the effect of annealing close to and above  $T_g$ . The last WANS spectrum taken corresponds to a sample that has been heated up to 210°C and then slowly cooled with a 1 h cooling time. The second set of experiments consisted of monitoring WANS spectral changes in amorphous BPAPC due to thermal ageing. Another sample was then heated up to 400°C (i.e. above melting) and quickly quenched in ice water. The quenching time corresponds to the minimum lapse it takes to manually handle the sample (<1 s).

The WANS measurements were performed on the 2XD powder spectrometer<sup>19</sup> at the University of Missouri Research Reactor (MURR). This spectrometer operates at 1.29 Å incident wavelength and has a bank of three

linear position-sensitive detectors that covers a 25° angle span so that a wide spectrum (5–105°) can be scanned through four consecutive detector arm steps. This corresponds to characteristic lengths probed from 15 to 1 Å. An oscillating radial collimator is used between the sample and the detector bank to decrease background noise. Since high spectral resolution is not needed with the semicrystalline or amorphous cases, an 'open' incident collimation has been used yielding high count rates (1200 c.p.s.) and, therefore, good statistics for 12–15 h counting times. Powder samples (as the ones used here) are included in vanadium cylindrical cells of  $\frac{1}{4}$ " diameter and 2" high.

### Results and Discussion

WANS spectra are shown in Figures 1 and 2 for the semicrystalline and amorphous states, respectively, of the deuterated BPAPC sample. In these figures, crystalline peaks and broad amorphous humps are indexed for convenience and reported in Tables 1 and 2. In the tables, ratios of such maxima taken at low and high scattering angles are included. Such ratios represent the relative strength of density-density correlations, and therefore a good monitor of local conformational changes. It should be noted that no incoherent background correction has been included. Such a correction would involve an estimation of the Debye-Waller factor as well as of the relative contributions of the coherent/incoherent

**Table 2** Relative heights of the main broad peaks in the WANS spectrum of amorphous deuterated BPAPC

Peak 10 Peak 11	Thermal ageing time	Peak B 14°	Peak D 22°	Peak E 37°	Peak F 68°	Peak B Peak F	Peak D Peak F	Peak E Peak F
1.02	Not aged	11334	11073	11296	9728	1.17	1.14	1.16
0.99	1 h	11447	11307	9948	9670	1.18	1.17	1.03
	3 h	11588	11105	11447	9584	1.21	1.16	1.19
1.00	5 h	11292	11290	9964	9671	1.17	1.17	1.03
0.99	12 h	11370	11175	9696	9574	1.19	1.17	1.01
1.00	24 h	11260	10950	9799	9198	1.22	1.19	1.06
1.03	48 h	11282	11091	9578	9570	1.18	1.16	1.00
1.01	73 h	11337	10987	9553	9620	1.18	1.14	0.99
1.00	96 h	11245	11142	9568	9595	1.17	1.16	1.00

scatterings. Our goal was to observe qualitative trends. A pure densification process (i.e. loss of free volume) should appear as a uniform vertical scaling of the data and leave the reported ratios unchanged, whereas local conformational changes should rescale maxima with respect to each other. Both *Tables 1* and *2* correspond to the former case to within statistical fluctuations except for cases where the annealing temperature was above  $T_g$ .

The observations indicate that both the semicrystalline and amorphous systems do not show forms of molecular motions of chain portions of sizes bigger than a monomeric unit. The result for the first (semicrystalline) case was expected because crystallization is the ultimate form of thermal ageing (i.e. annealing above the crystallization temperature).

The assignment of the molecular origins of the observed WANS maxima for both semicrystalline and amorphous BPAPC has yet to be made. Given this limitation, and the fact that attempting to observe by WANS potential molecular conformational changes associated with a densification of less than 1%<sup>7</sup> is difficult, the result for the second case (amorphous) is consistent with the lattice contraction hypothesis by Curro *et al.*<sup>6</sup> It is believed that the densification process (i.e. loss of 'free' volume) associated with physical ageing results in no relative local major conformational reconfiguration. The lattice contraction is most likely coupled to the restriction of motion of molecular moieties as observed during physical ageing by n.m.r.<sup>8,9</sup> By implication, variations in the molecular structure of the polymer, such as with polycarbonate copolymers<sup>7-9</sup>, will change the rate at which the lattice contraction occurs. Thereby, molecular structure is coupled to changes in physical properties with physical ageing.

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