Structure and morphology of polycarbonate synthesized by solid state polycondensation

S. Radhakrishnan*, V. S. Iyer† and S. Sivaram†
Polymer Science and Engineering, and †Polymer Chemistry Division, National Chemical Laboratory, Pune 411 008, India
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Polycarbonate obtained by solid state polycondensation (SSP) crystallizes in an orthorhombic configuration with $a=12.1$ Å, $b=10.1$ Å and $c=22.0$ Å. Its morphology is of non-spherulitic lamellar type, while that of melt or solution crystallized commercial polycarbonate is distinctly spherulitic. These changes in crystalline structure and morphology can be explained, in the present case, on the basis of restricted mobility of the chains and the crystal growth in an extended chain configuration during the SSP step.

(Keywords: polycarbonate; solid state polycondensation; morphology)

Polycarbonates based on bisphenol-A synthesized by conventional routes are known to be mainly amorphous materials having high glass transition temperatures (149°C) and very low crystallization rates[1,2]. However, supermolecular order can be induced in these polymers by prolonged annealing over several days[3] or by exposing them to certain solvent vapours[4]. The crystallization time may be reduced by the addition of nucleating agents[5]. In recent years there has been some interest in developing crystalline polycarbonates, because higher crystallinity is expected to improve the mechanical properties, heat distortion temperature and solvent/chemical resistance[6,7]. During our recent investigations on solid state polycondensation (SSP) of polycarbonates[8] we noticed a marked increase in the intrinsic viscosity (or molecular weight), which was accompanied by an enhancement of crystallinity as evidenced by a very sharp melting endotherm. This increase of molecular order and structure development has now been studied in detail and is reported in this communication.

The polycarbonate was synthesized by the SSP route in the same manner as described previously[8]. This consists mainly of preparing a prepolymer ($M_n=6450$) from bisphenol-A and diphenylcarbonate and blending it with disodium salt of bisphenol-A ($\leqslant 300$ ppm), followed by the SSP reaction carried out in vacuum (~ 133.3 Pa pressure) at temperatures ranging from 200 to 230°C for different lengths of time. Care was taken not to allow melting of the polymer during SSP. The prepolymer as well as the SSP product were characterized for structure and morphology by wide angle X-ray diffraction (WAXD), optical microscopy and differential scanning calorimetry (d.s.c.), in the manner described elsewhere[9,10].

The WAXD scan of polycarbonate synthesized by the SSP route, shown in *Figure 1*, contained mainly a very strong reflection at the diffraction angle of 17.1° accompanied by several other weak reflections on either side (curves B and C). The latter were confirmed by recording the WAXD scan at higher sensitivity (curves D and E), which also revealed that the major reflection around 17° in fact contained two overlapping components. The detailed analysis of these various reflections was carried out using standard iterative procedure and it was found that they conform to an orthorhombic structure with lattice parameters of $a=12.1$ Å, $b=10.1$ Å and $c=22.0$ Å. The analysis of the WAXD data, assignment of the various reflections and a comparison of the observed and calculated spacings are indicated in *Table 1*. This structure is different from those reported for polycarbonate in the literature. Two reports are available on the crystal structure of polycarbonate, namely an orthorhombic type[11] with $a=11.9$ Å, $b=10.1$ Å and $c=21.5$ Å, and a monoclinic type[12] with $a=12.3$ Å, $b=10.1$ Å, $c=20.8$ Å and $\gamma=84°$. Both these structures have been derived from WAXD patterns recorded on photographic plates which may not have fully resolved all the observed reflections because of large variations in their intensities or exposure. It may be noted that commercial polycarbonate, when crystallized from the melt for the duration of SSP (190°C, 8 h), exhibits only an amorphous halo (curve A, *Figure 1*). On the other hand, extended periods of crystallization for 24 h yields crystalline samples.

Figures 2a–c show the optical micrographs of, respectively, commercial polycarbonate (Lexan 121) crystallized from the melt at 190°C for 20 h, Lexan crystallized by slow evaporation from chloroform at 25°C, and polycarbonate synthesized by the SSP technique. It is clear that the morphology in the melt and solution crystallized samples is spherulitic but for the SSP synthesized sample the morphology is lamellar and non-spherulitic. These changes in morphological features may be understood on the basis of chain mobility during crystallization. For the melt and solution crystallization, the chain mobility is initially high owing either to the high temperature molten state or to the presence of solvent, as the case may be. On the other hand, for the SSP reaction the temperature used is 10 to 20°C below the melting point and the sample is always retained in solid form. Hence the chain mobility is restricted to amorphous regions

* To whom correspondence should be addressed

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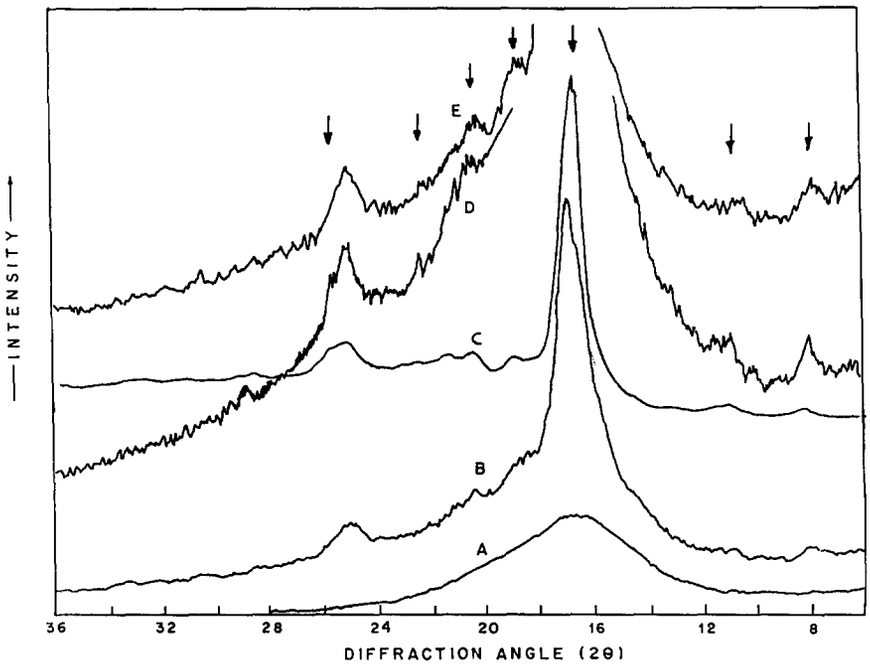

Figure 1 Wide angle X-ray diffraction scans for polycarbonate; (A) melt quenched or crystallized for less than 8 h; (B) commercial grade crystallized for extended periods (20 h) at 190°C; (C) solid state polymerized polycarbonate; (D) and (E) same as (B) and (C) but at higher sensitivity

Table 1 WAXD data and analysis for polycarbonate (PC) synthesized by solid state polycondensation

Ortho PC[a]			Monoclinic PC[12]			Lexan 121 (melt cryst.)[b]
d(Å) (observed)	d(Å) (calcd)	hkl	d(Å) (observed)	d(Å) (calcd)	hkl	d(Å) (observed)
11.06	11.00	002				11.06
			10.66	10.54	101	
8.12	8.13	102	8.05	7.623	111	
7.77	7.75	110				
			5.79	5.86	201	
	5.32	113	5.48	5.48	210	5.31
5.21	5.19	210	5.25			5.28
4.80	4.83	014		5.30	211	
			5.13	5.27	202	
4.62	4.69	212	4.75	4.70	121	4.7
4.27	4.29	122				4.31
4.19	4.16	023	4.10	4.09	220	
	4.13	105	4.06	3.99	302	
				4.01	221	
	3.87	220				3.87
	3.78	302				3.72
3.56	3.55	124				3.56
		302				
	3.54	312				
	3.36	030	3.28	3.34	030	3.3
3.14	3.16	224				3.19
2.94	2.94	230	3.02	3.05	400	
			2.8	2.79	230	
	2.73	233				2.76
2.68	2.65	404	2.45	2.412	240	

[a] Derived from orthorhombic structure $a = 12.1$ Å, $b = 10.1$ Å and $c = 22.0$ Å
[b] Sample melted at 230°C and isothermally crystallized at 190°C for 20 h

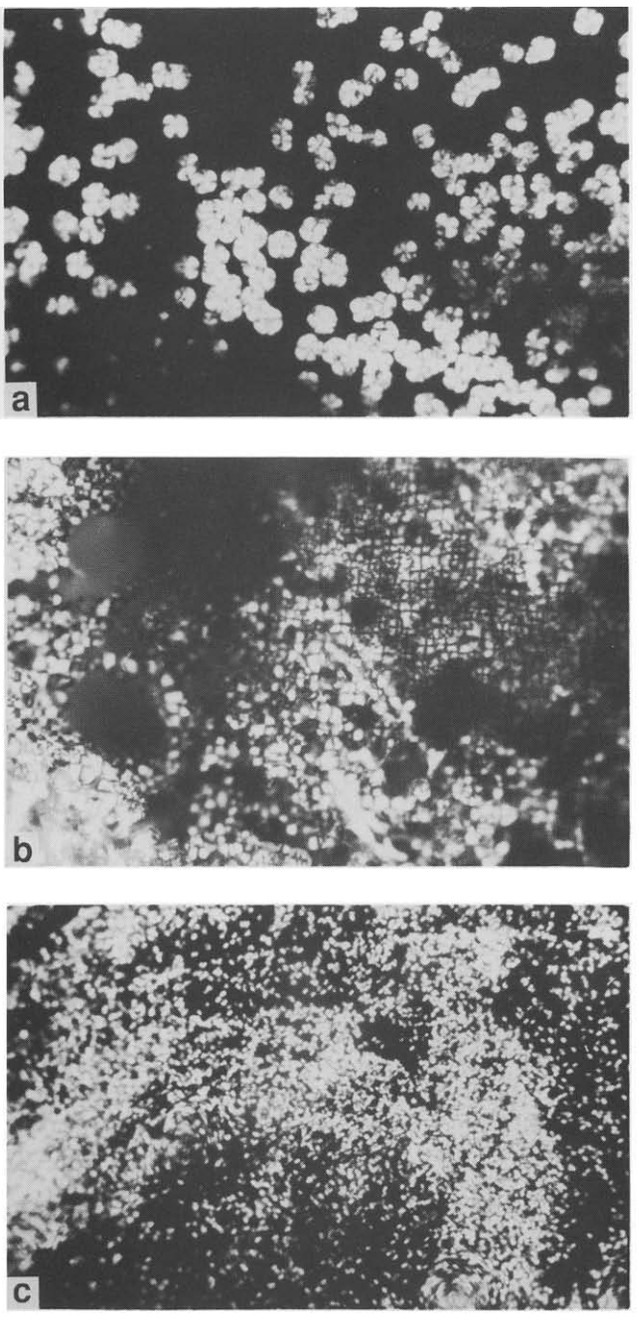

Figure 2 Optical polarizing photomicrographs of polycarbonate: (a) Lexan melt crystallized at 190°C for 20 h; (b) Lexan that has undergone solvent-induced crystallization; (c) solid state polymerized polycarbonate

and/or end groups where polycondensation occurs. Thus the growth of the crystallite in this case takes place in the confined regions and would occur in extended chain rather than folded chain configuration. This can lead not only to different morphological features but also to crystal lattice parameters, as we observed.

The d.s.c. studies of these samples reveal some interesting features in the melting curves, as shown in *Figure 3*. Initially the crystallinity is low and the melting curve is broad, occurring at 220°C. With the increase of SSP this peak shifts to higher temperature and becomes progressively sharper. Interestingly, the melting curve at intermediate stages apparently contains two components, the relative contribution of each decreasing

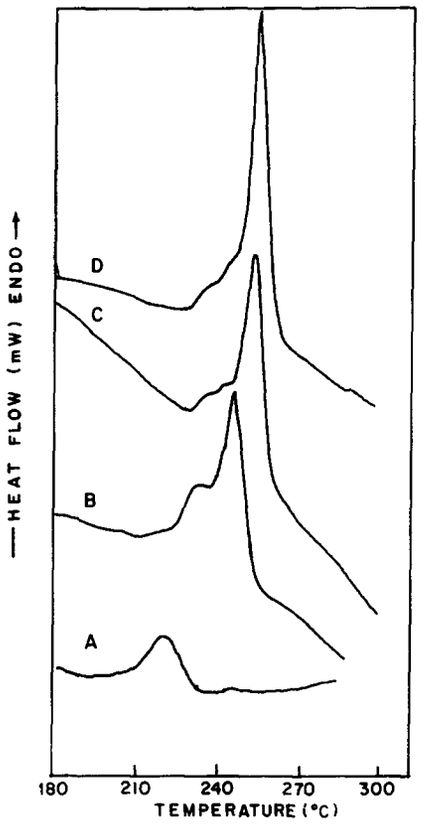

Figure 3 D.s.c. scans for polycarbonate at different SSP times: (A) 0 h; (B) 6 h; (C) 10 h; (D) 12 h. Starting polymer, 4% crystallinity; catalyst concentration, 250 ppm

and increasing, respectively, with the increase of SSP time. This suggests that extensive reordering is taking place in the solid phase leading to more perfect crystallites[13] having a higher melting point (260°C) during the SSP step. It is also reminiscent of 'intermolecular healing' as suggested by Fakirov[14,15] for polycondensation of poly(ethylene terephthalate), nylon and other materials.

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