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Solid-State Polymerization of Poly(aryl carbonate)s: A Facile Route to High Molecular Weight Polycarbonates[1]

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Solid-state polymerization is a commonly practiced technique to obtain high molecular weight crystalline polymers such as poly(ethylene terephthalate).[2] This technique involves heating the prepolymer slightly below T_m under vacuum, resulting in chain extension by the reaction of suitably disposed end groups of the polymer in solid state. This technique has practical significance as polymers of such high molecular weights cannot be generally produced in a stirred reactor, under melt polycondensation conditions due to their prohibitively high melt viscosities.

Poly(aryl carbonate)s are a class of important engineering polymers also made by melt polycondensation methods.[3,4] However, they are amorphous, with a T_g of 149 °C. We now report that, under carefully controlled conditions, poly(aryl carbonate)s can undergo chain extension in the solid state to substantially high molecular weight polymers, until this time considered inaccessible through melt polycondensation reactions.[5] While our work was in progress, we also became aware of a patent describing a similar observation in which an amorphous poly(aryl carbonate) prepolymer having a $\bar{M}_n$ = 4000 was melted and extruded through die orifices in the form of a strand at 240 °C into a bath filled with acetone at 40–50 °C.[6] The strand was drawn and stretched into a fiber and then subjected to shearing action to convert it into particles. The prepolymer thus treated was dried and heated to 220 °C under a flow of nitrogen, whereby $\bar{M}_n$ increased to 13 000.

The prepolymer of poly(aryl carbonate) used in our study was prepared from Bisphenol A and diphenyl carbonate using a melt phase carbonate interchange reaction.[7,8] It had a η_{inh} of 0.33 dL g^{-1} (in chloroform at 30 °C), a $\bar{M}_n$(VPO) of 6450, and a hydroxyl number of 6.7.[9] This indicates the presence of approximately a 35 mol % hydroxyl group. Bisphenol A disodium salt (25–300 ppm by weight) was solution blended with the poly(aryl carbonate) prepolymer in chloroform. The solvent was evaporated, and the polymer dried under vacuum at 60 °C for 2 h.[10] The prepolymer was initially conditioned by gradually heating from room temperature to 210 °C over a period of 1 h and retaining the sample at 210 °C for 4 h under vacuum. Solid-state polymerization of this sample was conducted at 230 °C under vacuum (<1 Torr) for different lengths of time. Alternatively, the temperature of solid-state polymerization was gradually increased from 220 to 250 °C in intervals of 10 °C with a residence time of 2 h at each temperature. It was ensured that the reaction temperature was at least 3 °C below the onset of melting of the polymer. The results are shown in Tables I–III. It is evident that the polymerization proceeds in the solid state with a significant increase in the molecular weight. Polymers with a catalyst concentration greater than or equal to 125 ppm (Table III) were insoluble in chloroform even on boiling. However, heating the polymer to 300 °C under nitrogen and cooling caused it to dissolve in chloroform at room temperature. Alternatively, polymers could also be dissolved at room temperature using 1:1 (v/v) CF_3CO_2H/CH_2Cl_2. The reason for polymer insolubility in chloroform of a sample prepared using a catalyst concentration greater than 25 ppm is not readily apparent at the present time. An increase in the molecular weight was also accompanied by an increase in the polymer crystallinity as evidenced by the appearance of a melting endotherm in DSC and sharp crystalline peaks in XRD (Figures 1 and 2).[11]

Table I
Solid-State Polymerization of Polycarbonate: Effect of Time[a]

sample no.	time (h)	η_{inh}[b] (dL/g)	hydroxyl number[c] (mg of KOH/g)	T_m[d] (°C)	T_g[d] (°C)	crystallinity[e] (%)
1		0.33	6.70	225	130	26
2	2	0.67	2.70	254	157	37
3	4	0.71	2.50	262	158	nd[f]
4	6	0.78	2.40	264	151.5	38
5	8	0.79	2.33	266	159	nd[f]
6	10	0.81	2.30	268	157.5	43

[a] A total of 0.75 g of polymer passing through 22 mesh (<710 μm) was heated under vacuum at 230 °C and less than 1 Torr. A disodium salt of Bisphenol A (25 ppm) was used as a catalyst. [b] In $CHCl_3$ at 30 °C. [c] By UV. [d] By DSC. [e] By X-ray using Cu Kα radiation. [f] Not determined.

Table II
Solid-State Polymerization of Polycarbonate: Effect of Temperature[a]

sample no.	reaction conditions [temp (°C)/time (h)]	η_{inh}[b] (dL/g)	hydroxyl[c] number (mg of KOH/g)	T_m[d] (°C)	crystallinity[e] (%)
1	220/2	0.44	4.59	251	30
2	220/2, 230/2	0.52	3.38	254	29
3	220/2, 230/2 240/1	0.59	3.03	259	31
4	220/2, 230/2 240/2	0.66	2.71	262	36
5	220/2, 230/2 240/2, 250/2	0.78	2.68	263	36

[a] A total of 0.75 g of polymer passing through 22 mesh (<710 μm) was heated under vacuum using a disodium salt of Bisphenol A (25 ppm) as a catalyst. [b] In $CHCl_3$ at 30 °C. [c] By UV. [d] By DSC. [e] By X-ray using Cu Kα radiation.

Table III
Solid-State Polymerization of Polycarbonate: Effect of Catalyst Concentration[a]

sample no.	catalyst conc[b] (ppm)	η_{inh}[c] (dL/g)	hydroxyl number[d] (mg of KOH/g)	T_m[e] (°C)	T_g[e] (°C)	crystallinity[f] (%)
1	25	0.62	2.53	257	130	26
2	125	0.63	2.59	261	*g*	25
3	150	0.64	2.65	260.5	*g*	29
4	200	0.67	2.97	265	*g*	32
5	300	0.70	3.06	271	*g*	32

[a] A total of 0.75 g of polymer passing through 22 mesh (<710 μm) was heated under vacuum at 210 °C for 4 h and 230 °C for 4 h. [b] A disodium salt of Bisphenol A was used as catalyst. [c] In $CHCl_3$ at 30 °C. [d] By UV. [e] By DSC. [f] By X-ray using Cu Kα radiation. [g] Not detectable.

We can only speculate on the mechanism of solid-state polymerization and the origin of crystallinity in poly(aryl carbonate)s at the present time. Poly(aryl carbonate)s are reported to undergo crystallization upon annealing at elevated temperatures[12] (180 °C for 8 days), by solvent treatment[13] and by addition of nucleating agents such as sodium 2-chlorobenzoate or sodium phenolate.[14] However, in all these cases there was no chain extension accompanying crystallization. In our study, crystallization was accompanied by a chain extension reaction occurring in

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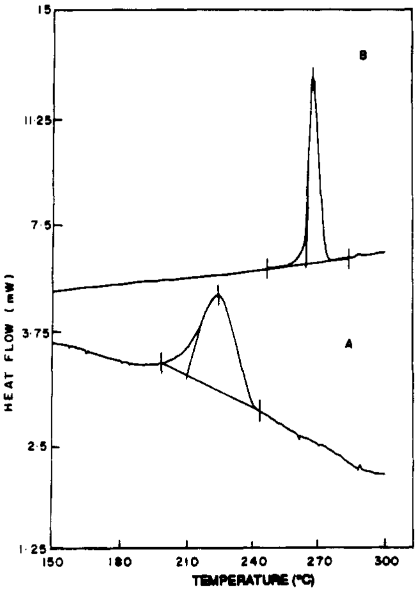

Figure 1. DSC thermograms of poly(aryl carbonate) prepolymer (A) after chloroform treatment (entry 1, Table I) and (B) after solid-state polymerization (entry 6, Table I).

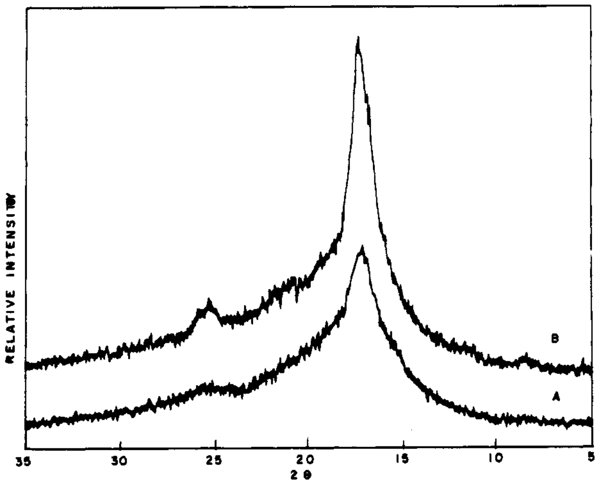

Figure 2. X-ray diffractograms of poly(aryl carbonate) prepolymer (A) after chloroform treatment (entry 1, Table I) and (B) after solid-state polymerization (entry 6, Table I).

the solid state. This implies that the molecular ordering of the prepolymer occurs under the conditions of reaction with reactive end groups oriented in the amorphous regions. Chain extension is thus accompanied by increasing crystallinity of the polymer. Further studies are in progress to elucidate the details of this reaction. Application of the solid-state polymerization technique thus provides a simple access to high molecular weight poly(aryl carbonate)s via a melt polycondensation process.

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References and Notes

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(8) Bisphenol A and diphenyl carbonate were polycondensed in the melt phase using 1.2×10^{-3} mol % tetra-*n*-butylammonium di-*o*-nitrobenzoate as catalyst at 230 °C with a programmed increase in temperature from 230 to 280 °C and a decrease in pressure from 760 to 1 Torr over a period of 3.5 h followed by heating to 280 °C for 2 h at 0.2 Torr.
(9) The hydroxyl number was determined using a Hitachi Model 220 UV/vis spectrophotometer and THF as solvent, using the reported ϵ for Bisphenol A and the polymer at 287 nm. (Shchori, E.; McGrath, J. E. *J. Polym. Sci., Appl. Polym. Symp.* **1978**, *34*, 103–117). The following expression was used:

OH number (mg of KOH/g of sample) =

$$\frac{\epsilon^{\text{Bisphenol A}} \times 2C_{\text{Bisphenol A}} \times A_{\text{sample}} \times 56.1 \times 10^3}{\epsilon^{\text{polymer}} \times A_{\text{Bisphenol A}} \times C_{\text{sample}}}$$

where $C_{\text{Bisphenol A}}$ is expressed as moles per liter and C_{sample} as grams per liter.
(10) When the poly(aryl carbonate) prepolymer was dissolved in chloroform and precipitated from methanol, the sample showed no T_m in the DSC. The crystallinity of the prepolymer was 22% as determined by XRD. However, when the prepolymer solution in chloroform was evaporated to dryness, the sample showed a T_m of 225 °C and an increase in crystallinity to 26% (Table I).
(11) T_g and T_m were measured by DSC using a Perkin-Elmer thermal analyzer (DSC-7) in a N_2 atmosphere at a heating rate of 10 °C/min. Powder XRD was recorded using Rigaku (Model D/Max III VC, Japan), Ni-filtered Cu Kα radiation = 1.5404 Å.
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