Application of a Solid-State Postpolycondensation Method for Synthesis of High Molecular Weight Polycarbonates

W. KURAN,[1] C. DĘBEK,[1] Z WIELGOSZ,[2] L. KUCZYŃSKA,[2] M. SOBCZAK[1]

[1] Division of Polymer Synthesis & Processing, Warsaw University of Technology, 3 Noakowskiego Street, 00-664 Warsaw, Poland

[2] Division of Engineering Polymers, Industrial Chemistry Research Institute, 8 Rydygiera Street, 01-793 Warsaw, Poland
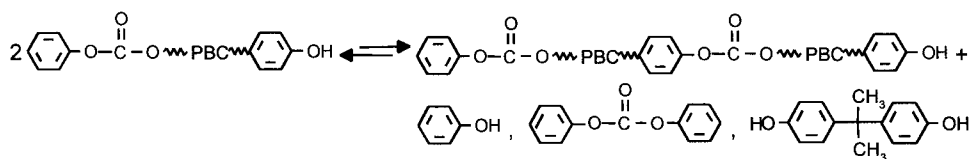
ABSTRACT: Studies on the possibility of the application of the solid-state postpolycondensation (SSP) process to increase the average molecular weight of bisphenol A-based polycarbonate (PBC) were carried out. The thermally stable PBC with a very high molecular weight reaching about 50,000 g/mol was obtained by the applied SSP technique. Some factors influencing the effectiveness of the SSP process were initially examined: the mode of preparation (crystallization) of the PBC prepolymer, condensation temperature and time, and the vacuum applied in the reaction vessel. It was found that the superior yield of the high molecular weight PBC was obtained by the employing as high as possible values of the parameters taken into consideration. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 2165–2171, 2000

Key words: high molecular weight polycarbonates; solid-state condensation

INTRODUCTION

The solid-state postpolycondensation (SSP) process is the industrial method applied to produce high molecular weight polyesters, for example, poly(ethylene terephthalate).[1–3] The SSP process regarding bisphenol A-based polycarbonates (PBCs) is of interest, too, although it has not yet been introduced into industry. The process consists of three steps: the synthesis of the prepolymer, its crystallization, and its condensation in the solid state. The condensation is realized by heating the crystallized prepolymer to a few degrees below the melting temperature, which enables end groups in the amorphous phase of the sample to undergo condensation,[1–6] which is an equilibrium reaction for PBC given by

Removing the by-products under very low pressure or by stream of the hot neutral gas permits one to obtain a high molecular weight product.

Several parameters crucial for the SSP process leading to high molecular weight polycarbonate were considered in the literature.[4–9] Among them, the mode of crystallization of the prepoly-

Table I Average Molecular Weight of the Prepolymer and Polycarbonate Obtained by SSP Process

Sample	$\bar{M}_n$[a] (g/mol)	$\bar{M}_w$[a] (g/mol)	$\bar{M}_v$[a] (g/mol)	$\bar{M}_v$[b] (g/mol)
Prepolymer	6800	9700	9100	8000
Polymer	24,500	41,500	40,500	38,500

The prepolymer was crystallized by acetone treatment for 96 h at a temperature of 222–248°C, 16 h of condensation, and pressure of 0.07 mmHg.

[a] Determined by gel permeation chromatography (GPC), tetrahydrofuran.

[b] Determined by viscometry (Ubbelohde viscometer, 25°C, chloroform).

mer, the catalyst applied for the condensation, temperature and time of the condensation, and the vacuum applied in the reaction vessel are the most important. The proper choice of these basic parameters allows one to obtain a thermally stable, colorless polycarbonate of an average molecular weight of about 50,000 g/mol and higher.[4–9]

For example, Iyer et al.[4–7] crystallized a low molecular weight PBC prepolymer ($\bar{M}_v$ about 6000 g/mol) by heating the sample at a temperature of 180–210°C for 4 h. The condensation was then carried out under reduced pressure (below 1 mmHg) for 7–15 h. It was observed that the melting temperature of the sample constantly increased during the course of the reaction, which allowed for enhancing the reaction temperature from 220 to 250°C, thus improving the condensation conditions. In this way, PBC of $\bar{M}_n$ from 24,000 to 83,000 g/mol was obtained.

Komiya et al.[8,9] crystallized the low molecular weight PBC prepolymer $\bar{M}_n$ 3000 g/mol) in ace-

tone. Then, the prepolymer was subjected to condensation at a constant temperature of about 220°C under reduced pressure for 16 h. Thermally stable PBC of $\bar{M}_w$ from 15,000 to 60,000 g/mol was obtained. The application of the double cycle of the crystallization in acetone and the condensation allowed them to obtain PBC of $\bar{M}_w$ reaching 95,000 g/mol.[9]

Considering the aforesaid advantages of the SSP process, namely, employing the precrystallization of the sample, the high-temperature condensation, and reduced pressure in the reaction vessel, we decided to examine the PBC formation in terms of the influence of individual parameters on the course of the SSP process. The aim of the work was to establish the dependence of the PBC yield and the molecular weight on the prepolymer crystallization, condensation temperature, and vacuum applied in the reactor.

EXPERIMENTAL

Materials

A prepolymer, oligo(bisphenol A carbonate), was obtained by the transesterification method in a melt according to the procedure applied generally. The essential characteristics of the oligomer are presented in Tables I and II.

Samples for SSP processing were prepared by dissolving 35 g of the oligocarbonate in 450 mL of methylene chloride, adding 50 ppm disodium bisphenol A salt as a catalyst. The solution was poured between glass plates and evaporated slowly, then dried at 80°C for 96 h under a vacuum. The prepolymer was crumbled by a mortar

Table II Thermal Properties of the Prepolymer and Polycarbonate Obtained by SSP Process with Those of the Prepolymer

Sample	T_g[a] (°C)	T_m[b] (°C)	Extrapolation Temperature of Destruction[b] (°C)	ΔH_m[a] (J/g)	Crystallinity Degree[c] (%)
Prepolymer	123	223	462	5.7	4
Precrystallized prepolymer	122	227		17.4	12
Polymer	154	267	458	30.3	21

The prepolymer was crystallized by acetone treatment for 96 h at a temperature of 222–248°C, 16 h of condensation, and pressure of 0.07 mmHg.

[a] Calorimetry DSC 20°C/min.

[b] Calorimetry TG 10°C/min.

[c] Calculated from ΔH_m, using the proportion 147.7 J/g per 100% of crystallinity.[10]

to a powder. A part of the crumbled prepolymer was swelled in acetone for 96 and 192 h, then dried again under reduced pressure for 96 h at a temperature of 80°C. The prepolymer was kept in a desiccator over anhydrous calcium chloride.

SSP Process

SSP processing was carried out in a cylindrical, glass reaction vessel of 100-mL capacity, equipped with vacumeter with a range from 766 to 0.01 mmHg. The vessel was charged by 5.0 g of the PBC precursor, thermostated initially for 2 h at a temperature of 210 $\pm$ 1°C in a dry nitrogen atmosphere. Then, the pressure was reduced gradually for 1 h to 1.5, 0.15, and 0.07 mmHg and the temperature was increased to 210–231°C depending on the melting temperature of the prepolymer sample. The condensation reaction was carried out for 16–20 h, taking, after 4 h, a 0.5-g sample of the prepolymer in order to denote a molecular weight and melting temperature. The process was carried out at a constant temperature of 230°C, or gradually after 4 h, the temperature was increased and kept a few degrees below the actual, average melting temperature of the sample.

Measurements

Viscosity measurements were conducted at 25°C in an Ubbelohde-type viscometer in chloroform. The intrinsic viscosity was calculated using Blass–Langhammer's[11] equation of a single-point measurement:

$$[\eta] = 1/(2c)(\eta - 1/\eta) \qquad (1)$$

The viscometric-average molecular weight was calculated from $[\eta]$ values, using eq. (2)[12]:

$$[\eta] = 1.20 \times 10^{-2} \bar{M}_v^{0.82} \qquad (2)$$

Number- and weight-average molecular weights were determined by gel permeation chromatography (GPC; Shimadzu, Model C-R4a). Tetrahydrofuran was the solvent, and a polystyrene standard was used as a reference.

The melting temperatures of the SSP products were determined in a capillary. A sample was heated to a value of 15°C less than the expected melting temperature at 20°C/min, then reduced to 5°C/min, and the measurements were continued until complete melting of the prepolymer.

The glass transition temperature and the enthalpy of melting were measured by differential scanning calorimetry (DSC; Perkin–Elmer, Model DSC7). The sample was heated at a rate 20°C/min under a nitrogen atmosphere.

An extrapolated degradation temperature was determined by thermogravimetric analysis (Perkin–Elmer TG7). Samples were heated at 10°C/min in a normal atmosphere.

RESULTS AND DISCUSSION

A prepolymer used for the SSP process was crystallized from a methylene chloride solution or by treating with acetone for 96 and 192 h. The condensation was carried out at constant temperature of 230°C or by continually increasing the temperature during the course of the process. To remove low molecular weight products, the process was run under reduced pressure (1.5, 0.15, and 0.07 mmHg). Typical reaction parameters and results of the postpolycondensation are presented in Table III.

The average viscometric molecular weight of the product of the SSP process for samples crys-

Table III   Parameters and Results of SSP Process

Reaction		Average Melting		
Time (h)	Temperature (°C)	Temperature (°C)	$[\eta]$ (dL/g)	$\bar{M}_v$ (g/mol)
0		227	0.21	9000
0–4	220	238	0.40	19,000
4–8	231	250	0.54	27,500
8–12	243	258	0.64	34,000
12–16	251	265	0.71	38,500

The prepolymer was crystallized in acetone for 96 h at a pressure of 0.07 mmHg.
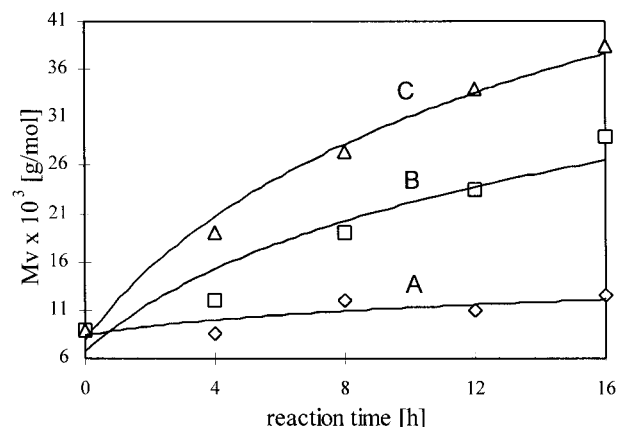
Figure 1 Average viscometric molecular weight of the products of the SSP process; the prepolymer was crystallized in acetone for 96 h at a pressure of (A) 1.5, (B) 0.15, and (C) 0.07 mmHg.

Figure 3 Average viscometric molecular weight of the products of the SSP process; the prepolymer was crystallized in acetone for 192 h at a pressure of (A) 1.5, (B) 0.15, and (C) 0.07 mmHg.

tallized from acetone for 96 h as a function of the reaction time for various pressures applied in the reactor is shown in Figure 1. The average melting temperature as a function of time is shown in Figure 2.

Similar results were obtained for the prepolymer crystallized in acetone for 192 h (Figs. 3 and 4). In both techniques, polymers of a very high average molecular weight were obtained and the increase of the molecular weight depended on the reaction time and pressure in the reactor.

The results shown in Figures 1 and 3 indicate that the pressure of 1.5 mmHg is not sufficient to reach a high $\overline{M}_v$ The best effects were observed at a much lower reaction pressure (0.07 mmHg).

This is understandable, considering that this is an equilibrium process. At a pressure of 1.5 mmHg, the increase of $\overline{M}_v$ reaches about 50%. Low molecular weight by-products are probably not removed from the reaction mixture in this case.

The increase of the melting temperature of the prepolymer is due to the cystallization (Figs. 2 and 4). Increasing the amount of the domain with ordered structures in the polycarbonate permits a constant increase of the reaction temperature.

The prepolymer crystallized from the solution of methylene chloride was subjected to the SSP process under a pressure of 0.07 mmHg (Fig. 5). The efficiency of the method expressed by the
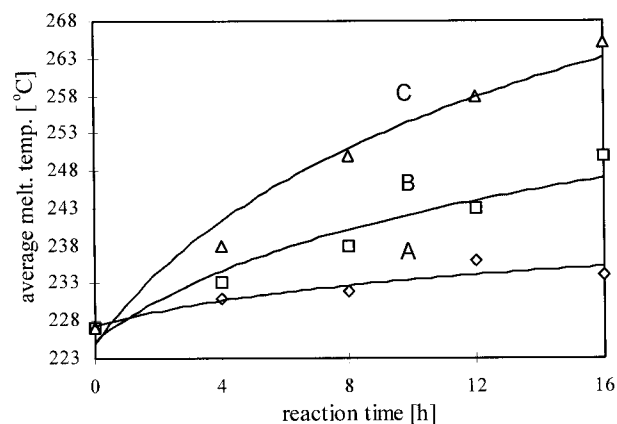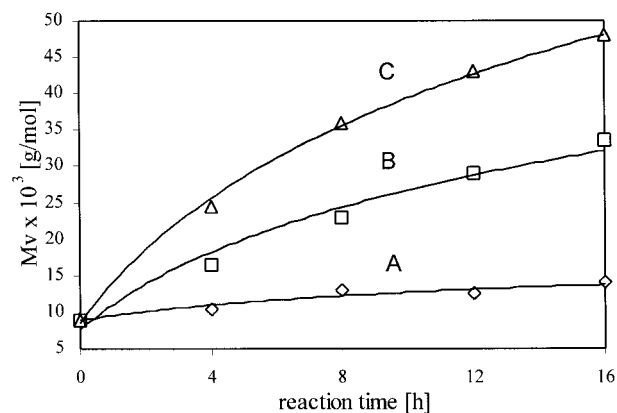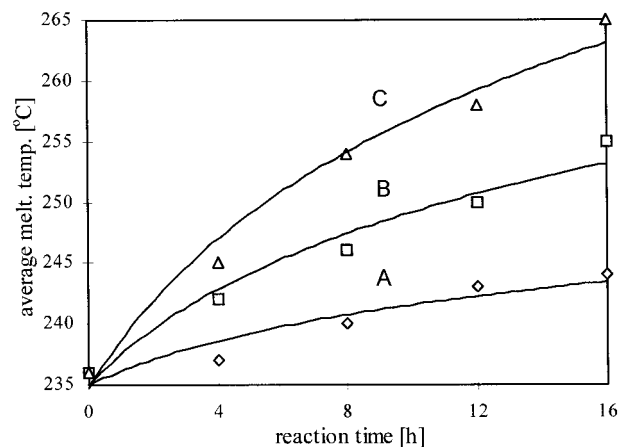

Figure 2 Average melting temperature of the products of the SSP process; the prepolymer was crystallized in acetone for 96 h at a pressure of (A) 1.5, (B) 0.15, and (C) 0.07 mmHg.

Figure 4 Average melting temperature of the products of the SSP process; the prepolymer was crystallized in acetone for 192 h at a pressure of (A) 1.5, (B) 0.15, and (C) 0.07 mmHg.
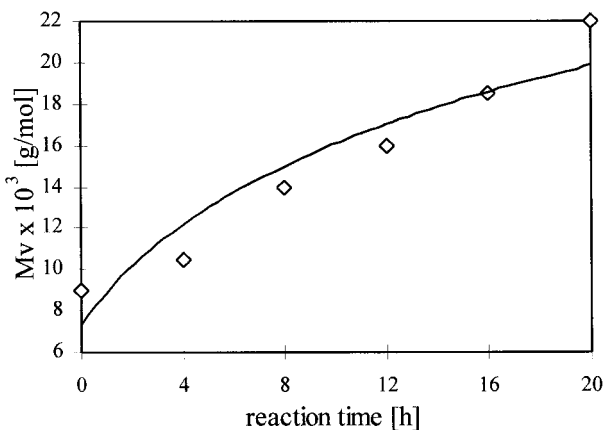
Figure 5 Average viscometric molecular weight of the products of the SSP process; the prepolymer was crystallized from a methylene chloride solution at a pressure of 0.07 mmHg.
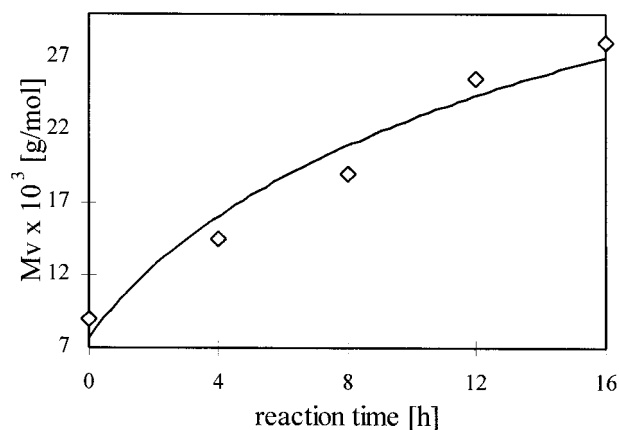

Figure 7 Average molecular weight of the products of the SSP process; the prepolymer was crystallized in acetone for 192 h at a pressure of 0.07 mmHg at a constant temperature of 230°C.

increase of $\overline{M}_v$ of the polymer formed appeared in this case considerably lower than that of the method involving additional crystallization of the prepolymer in acetone.

The influence of the crystallinity degree (which results from crystallization of the prepolymer) on the increase of the average molecular weight with the reaction time can be seen in Figure 6, which presents the results of the SSP process for the prepolymer crystallized from the methylene chloride solution and by swelling in acetone for 96 and 192 h. A polymer of about 2.6 times greater the
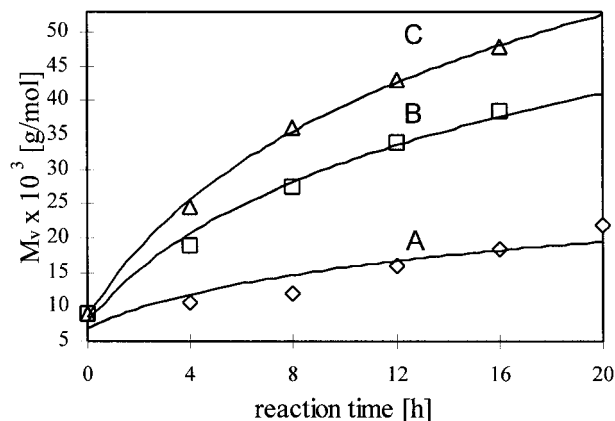

Figure 6 Average viscometric molecular weight of the products of the SSP process obtained from prepolymers of various crystallinity under a pressure of 0.07 mmHg: (A) prepolymer crystallized from methylene chloride solution; (B) prepolymer crystallized from acetone for 96 h; (C) prepolymer crystallized from acetone for 192 h.

$\overline{M}_v$ was obtained in the latter case as compared to the polymer obtained from the prepolymer crystallized only from the methylene chloride solution (curve A).

PBC oligomers crystallized in acetone for 192 h were condensed as well at the constant temperature of 230°C under the pressure of 0.07 mmHg. The dependence of $\overline{M}_v$ on the condensation time is presented in Figure 7. The increase of the average molecular weight, although considerable, is much lower than that observed in the process with the increasing condensation temperature.

The efficiency of the SSP process expressed by the $\overline{M}_v$ of polymers obtained under different experimental conditions is shown in Figure 8. The least increase of the average molecular weight appears in the case of the application of the prepolymer crystallized only from the methylene chloride solution (curve A). Curve B presents the process effectiveness for the PBC oligomer crystallized in acetone for 192 h, but which was condensed at a constant temperature. The best results are obtained by crystallizing the prepolymer in acetone (crystallinity grade) at a maximum condensation temperature and under as low as possible pressure (curves C and D).

These results are in agreement with expectations based on the equilibrium character of the condensation process. Application of a very low pressure and as high as possible temperature makes it easier to remove low molecular weight by-products from the reaction mixture and thus shift the reaction equilibrium to formation of high molecular weight products. Moreover, a higher
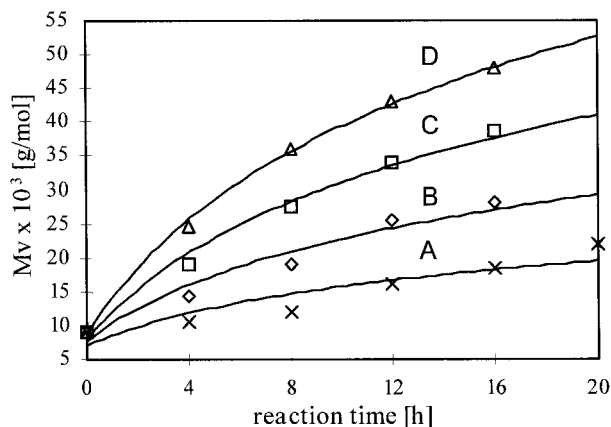
Figure 8 Average viscometric molecular weight of the products obtained in various conditions of the SSP process under a pressure of 0.07 mmHg: (A) a prepolymer crystallized from a methylene chloride solution; (B) a prepolymer crystallized in acetone for 192 h which was condensed at a constant temperature of 230C; (C) a prepolymer crystallized in acetone for 96 h which was condensed at an increasing temperature; (D) a prepolymer crystallized in acetone for 192 h which was condensed at an increasing temperature.

temperature makes chain ends more mobile, which results in increasing the effective interactions of end groups. Influence of a crystallization method (crystallinity degree) of the prepolymer also exerts an effect on the rate of increase of $\overline{M}_v$. Due to the freezing of considerable amounts of macrochains in the crystalline phase of a prepolymer, the central parts of these macrochains are protected against attack of low molecular weight by-products formed during condensation (involving degradation) and interaction only between end groups is forced. As a result of the SSP process, high molecular polycarbonates of various molecular weights are obtained. Some properties of typical polycarbonates obtained by this technique, in comparison with a prepolymer, are presented in Tables I and II. The examined product exhibits considerable crystallinity, high molecular weight, a high glass transition temperature, and very good heat resistance. Films made from these polycarbonates were colorless and perfectly transparent.

The observed increase of crystallinity of the prepolymer by measuring the melting temperature (in the capillary) was confirmed by DSC thermograms of a prepolymer crystallized from a methylene chloride solution in acetone for 96 h and of a polymer obtained in the SSP process.

Figure 9 presents curves of the melting enthalpy of a prepolymer and a postpolycondensation product.

The lowest crystallinity is in the prepolymer crystallized only from a methylene chloride solution (curve A). After crystallization in acetone, the melting endotherm is shifted toward higher temperature and the enthalpy has a higher value (Table II). As a result of the SSP process, the melting peak (curve C) shifts toward very high temperatures (250–280°C). The melting enthalpy of the SSP product reaches a value of 30.3 J/g, which approximately gives 21% crystallinity of the polymer.

The temperature width of the melting endotherm is considerable. More perfect forms of ordering are at higher temperatures and they probably are a reorganized form of the starting crystalline structures of the prepolymer. Crystalline forms disappearing at lower temperature of a less perfect structure are thought to have been created in the course of the SSP process.[1,5]

CONCLUSIONS

Studies on an SSP method to produce high molecular weight polycarbonates revealed that very
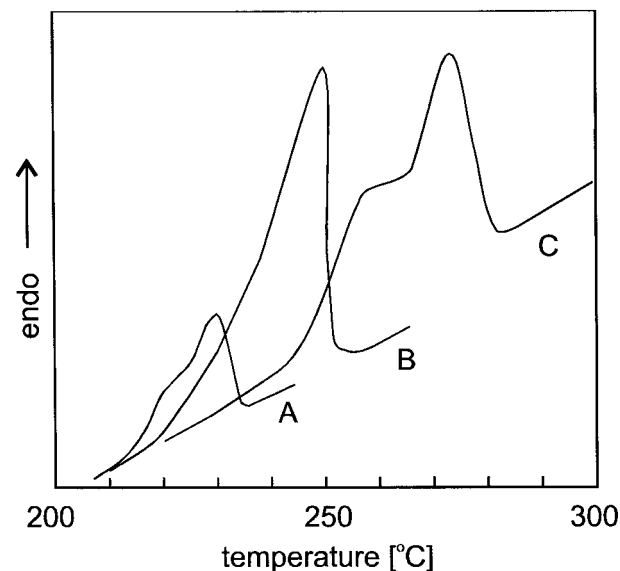

Figure 9 Fragments of DSC curves presenting melting enthalpy: (A) a prepolymer crystallized from a methylene chloride solution; (B) a prepolymer crystallized in acetone for 96 h; (C) a polymer obtained via SSP at a pressure of 0.07 mmHg, time 16 h, and reaction temperature of 222–248°C.

high molecular weight products can be obtained by using prepolymers of a high degree of crystallinity under a high condensation temperature and with a long reaction time under lowered pressure. In this way, poly(bisphenol A carbonate) of an $\overline{M}_v$ reaching about 50,000 g/mol was obtained.

REFERENCES

1. Karayanadis, G.; Sideridou, I.; Zamboulis, D.; Stalidis, G.; Bikiaris, D.; Lazaridis, N.; Wilmes, A. Angew Makromol Chem 1991, 192, 155.
2. Zhi-Lian, T.; Gao, Q.; Nan-Xun, H.; Sironi, C. J. Appl Polym Sci 1995, 57, 473.
3. Tybora, Z.; Wilczek, A.; Olejniczak, M.; Lapienis, D. Wlokna Chem 1985, 11, 135; Chem Abstr 1985, 104:34, 345.
4. Iyer, V. S.; Sehra, J. C.; Ravindranath, K.; Sivaram, S. Macromolecules 1993, 26, 1186.
5. Radhakrishnan, S.; Iyer, V. S.; Sivaram, S. Polymer 1994, 35, 3789.
6. Ravindranath, K.; Sivaram, S.; Sehra, J. C.; Iyer, V. S., EU Patent 0 568 740 A1, 1992.
7. Sivaram, S.; Sehra, J. C.; Iyer, V. S.; Ravindranath, K., U.S. Patent 5 266 659, 1992.
8. Komiya, K.; Fukuoka, S.; Aminaha, M.; Hasegawa, K.; Hachiya, H.; Okamoto, H.; Watanabe, T.; Yondea, H.; Fukawa, I.; Donzano, T. ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; p 20.
9. Komiya, K.; Tomoyasu, K.; Fukuoka, S. JP Patent 05 178 979, 1993.
10. Kim, W. N.; Park, Ch. E.; Burus, Ch. M. J Appl Polym Sci 1993, 49, 1003.
11. Blass, E.; Langhammer, G. Plast Kautschuk 1967, 14, 248.
12. Sitaramaiah, G. J Polym Sci A 1965, 3, 2743.