Synthesis of Aromatic Polyesters Based on Bisphenol A and Phthalic Acids. A New Preparative Process

C. Berti,* V. Bonora, and F. Pilati

Dipartimento di Chimica Applicata e Scienza dei Materiali, Università di Bologna, Viale Risorgimento 2, 40136 Bologna, Italy

M. Fiorini

Istituto di Merceologia, Università di Bologna, Piazza Scaravilli 2, 40126 Bologna, Italy

Received February 19, 1991

ABSTRACT: A new bulk process for the preparation of polyarylates, based on Bisphenol A and phthalic acids, is described. The two-stage process, useful for the synthesis of a variety of polyarylates, employs preformed Bisphenol A polycarbonate and dimethyl esters of phthalic acids. In the first stage, a mixture of oligomeric (ester–carbonate)s and dimethyl carbonate is obtained via catalyzed interchange reactions. The second stage involves the elimination, under vacuum, of dimethyl carbonate, which drives the equilibria of the reversible reactions to the formation of aromatic polyesters. Polyarylates can also be obtained starting from Bisphenol A bis(methyl carbonate) instead of the Bisphenol A polycarbonate. The process seems to be quite efficient and flexible, permits the use of commercial products as starting materials, and leads to volatile byproducts that are less toxic and hazardous than those derived from the presently used methods. High molecular weight polyarylates are obtained.

Introduction

Polyarylates constitute an important class of engineering polymers.[1,2] These materials, aromatic polyesters that formally derive from aromatic dicarboxylic acids and diphenols, can be prepared by solution reaction between dicarbonyl dichlorides and bisphenols or by polycondensation in the melt (from activated monomers). Neither method is exempt from problems; when the former process is used, problems derive from the preparation, purification, and storage of the diacid chloride, from the large amount of solvent required (when operating on an industrial scale), and from the generally low solubility of these polymers, which prevents the attainment of high molecular weights.[1,2] In melt polycondensation the problems derive from the high melting points of these polymers, which normally exceed 300–350 °C, and mainly from the fact that at least one monomer must be derivatized to enhance its reactivity, e.g., by acetylation[2] or silylation[3-5] of the hydroxy groups or by the transformation of the carboxylic groups in phenyl esters.[2]

In this report we present a new two-stage melt process for the synthesis of polyarylates based on Bisphenol A and phthalic acids.[6] In the first stage, catalyzed reversible interchange reactions between carbonate groups and ester groups lead to the formation of a mixture containing oligomeric (ester–carbonate)s and the highly volatile dimethyl carbonate as a byproduct. In the second stage, the dimethyl carbonate is completely removed under vacuum, which drives the equilibria of the reversible process toward the formation of high molecular weight polyarylates. The formation of the dimethyl carbonate, which because of its high volatility is easily removed from the existing equilibrium, can be considered the driving force of the process.

Experimental Section

Materials. Bisphenol A polycarbonates (PC) (gift of Enimont), dimethyl terephthalate (DMT), and dimethyl isophthalate (DMI) (Aldrich Chemicals) were used, after drying, without further purification; titanium tetrabutoxide (Merck) was distilled under vaccum.

Bisphenol A Bis(methyl carbonate) (BPDC). An excess of methanol, in pyridine, was added to a solution of Bisphenol A bis(chloroformate), prepared according to Schnell and Bottenbruch,[7] and dissolved in CH_2Cl_2, under magnetic stirring. After 1 h the mixture was washed twice with 50 mL of 10% hydrochloric acid and twice with 50 mL of water. The organic phase was then dried over anhydrous sodium sulfate, and the solvent was evaporated in vacuo. The crude product was directly crystallized from cyclohexane and characterized by IR and NMR spectroscopy (yield 95%; mp 91 °C).

Syntheses of the Polyarylates. Polymerizations were carried out by a two-stage process in a 1.8-L stainless steel batch reactor, equipped with a paddle agitator (driven at 30 rpm) with a strain-gauge bridge mounted on the drive shaft to indicate the extent of the polymerization reaction. During polymerization, samples were taken from the bottom of the reactor.

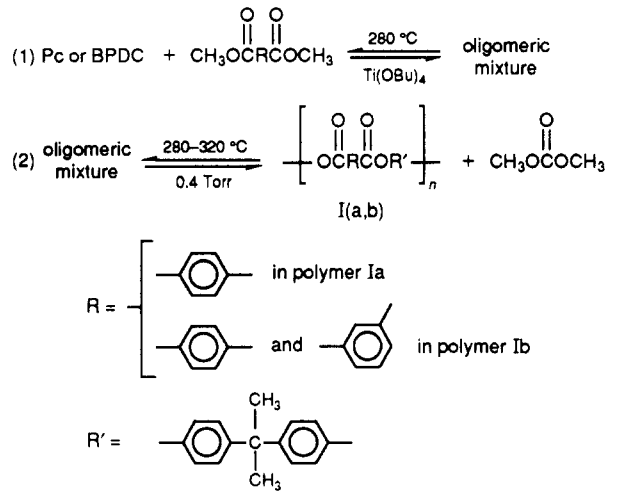
Synthesis of Ia. PC (244.0 g, 0.960 mol of repeating unit), DMT (268.0 g, 1.381 mol), and $Ti(OBu)_4$ (1.1 g, 3.2 mmol) were introduced into the reactor, under nitrogen atmosphere. During the first stage the mixture was allowed to react for 1 h at 280 °C in the closed reactor under stirring, and then the dimethyl carbonate formed was continuously distilled out at atmospheric pressure (50 mL collected in 2 h). Finally, in the second stage, polymerization was completed at reduced pressure (0.4 Torr); the temperature was raised to 320 °C, and these conditions were maintained for 1 h before extrusion of the polymer from the reactor. A pale yellow polymer, with inherent viscosity 0.94 dL/g (in phenol–1,1,2,2-tetrachloroethane (60/40 w/w) at 30 °C), was obtained.

Synthesis of Ib. PC (244.0 g, 0.960 mol of repeating unit), DMT (134.0 g, 0.691 mol), DMI (134.0 g, 0.691 mol), and $Ti(OBu)_4$ (1.1 g, 3.2 mmol) were poured into the reactor, and the process was carried out as described for the synthesis of Ia (40 mL of dimethyl carbonate collected during the first stage). A pale yellow polymer, with intrinsic viscosity 0.89 dL/g (in chloroform at 30 °C) and molecular weight 53 000 (from GPC peak), was obtained.

Synthesis of Ia (Starting from the Monomers). BPDC (1.7 g, 4.942 mmol), DMT (1.05 g, 5.412 mmol), and $Ti(OBu)_4$ (2.0×10^{-2} g, 0.059 mmol) were introduced into a glass tube (i.d. 3 cm) and heated in a silicone oil bath. The temperature of the mixture, at atmospheric pressure, was raised from 150 to 240 °C in 1.5 h, and these conditions were maintained for 1 h. During this stage, 0.3 g of dimethyl carbonate and 6.0×10^{-2} g of dimethyl terephthalate were eliminated. In the second stage, carried out under vacuum (0.4 Torr), the temperature was increased up to 320 °C and the system was kept at these conditions for 2 h. A pale yellow polymer, with inherent viscosity 0.90 dL/g

0024-9297/91/2224-5269$02.50/0

Scheme I



(in phenol–1,1,2,2-tetrachloroethane (60/40 w/w) at 30 °C), was obtained.

Measurements. Viscosities were measured with an Ubbelohde viscometer thermostated at 30 °C. ^{1}H NMR spectra were recorded on a Varian XL-200 spectrometer (chemical shifts are in parts per million downfield from TMS). IR spectra were recorded as thin films, from solution, on NaCl cells, by means of a Bruker IFS 48 FT-IR spectrometer. Molecular weights were determined by GPC analysis using a calibration plot constructed with polystyrene standards. The GPC measurements were carried out with a Perkin-Elmer Series 2 liquid chromatography instrument using a set of one Mixed plus two 10^3-Å PL gel columns (300 × 7.5 length/i.d., in mm). The GPC operating conditions consisted of a tetrahydrofuran mobile phase, a flow rate of 1.0 mL/min, and a sample size of 20 μL of 0.1% solution. GC–mass spectroscopy was carried out by using an HP 59970 workstation, formed by an HP 5790 mass detector and by an HP 5890 gas chromatograph equipped with a methylsilicone capillary column.

Results and Discussion

Process from PC and DMT (Synthesis of Ia). The first stage of the two-stage process involves taking preformed Bisphenol A polycarbonate and DMT, 40% in excess (based on functional groups), and bringing them, in the presence of titanium tetrabutoxide, into the molten state at 280 °C under mechanical stirring.

We used a 40% excess of DMT to increase the rate of the interchange reactions between carbonate and ester groups and to avoid any stoichiometric imbalance that might occur, as a result of possible sublimation, before a high molecular weight is reached.

The catalyst titanium tetrabutoxide was chosen for its well-known efficiency in the activation of ester–carbonate interchange reactions.[8,9] The presence of the catalyst in the system is necessary. Indeed, under the same process conditions, but without catalyst, no distillation of dimethyl carbonate was obtained (see below). During this step, interchange reactions between the carbonate groups present in the polymer and the ester groups of DMT lead to the complete degradation of PC with the formation of a mixture of oligomeric (ester–carbonate)s and dimethyl carbonate (Scheme I). The strain-gauge bridge mounted on the drive shaft of the reactor showed a considerable decrease in the viscosity of the system. After 1 h of reaction the dimethyl carbonate formed was distilled off at atmospheric pressure (50% of the theoretical amount).

In the second stage the process is completed under vacuum (0.4 Torr) while the temperature is increased up to 320 °C (reaction 2 of Scheme I). The residual part of the dimethyl carbonate and the excess DMT are removed during this step. Small amounts of Bisphenol A,

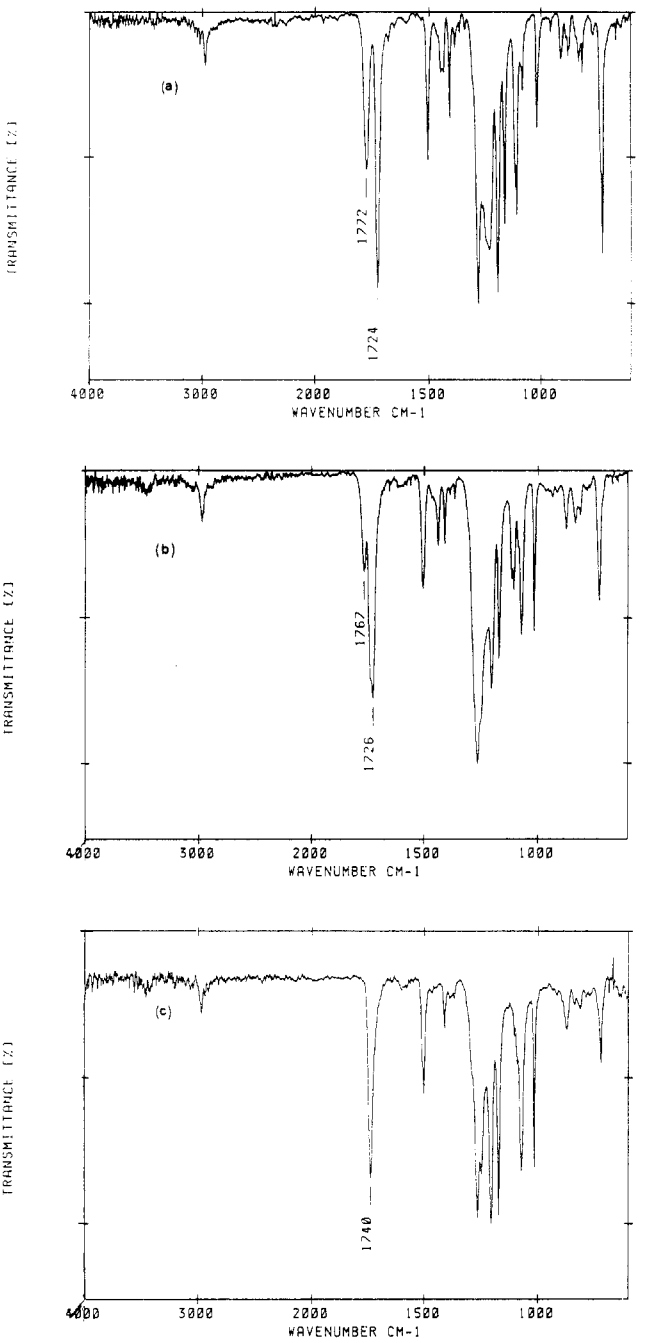


Figure 1. IR spectra of samples taken during the process from PC and DMT: (a) initial mixture; (b) sample extruded during the first stage; (c) crude final polymer.

Bisphenol A mono(methyl carbonate), Bisphenol A bis(methyl carbonate) (BPDC), and methyloxycarbonyloxy-1,4-phenyleneisopropylidene-1,4-phenyleneoxycarbonyl-1,4-phenylenecarbonyloxymethyl were detected in the solid part of the distilled fraction (GC–mass spectroscopy analysis).

The process was followed by IR and NMR spectroscopy on samples extruded at various times as the reaction progressed. IR and NMR spectra are presented in Figures 1 and 2, respectively.

The IR spectrum of the sample extruded during the first stage shows important structural changes (Figure 1b). A new infrared absorption at 1767 cm^{-1}, attributable to the formation of the aromatic–aliphatic carbonate group,[10] was detected along with the broadening of the phthalate ester group band at 1724 cm^{-1}. The IR spectra of samples extruded in the second stage show the progressive dis-

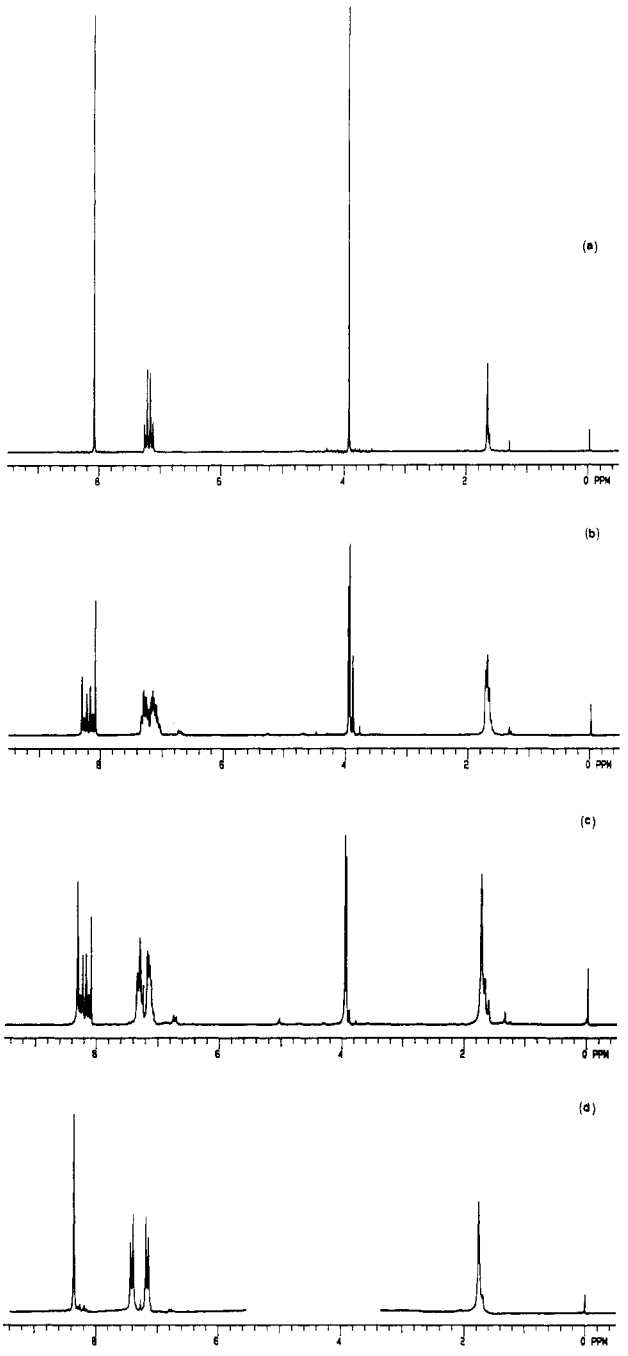


Figure 2. ^1H NMR spectra of samples taken during the process from PC and DMT (recorded from deuteriochloroform solution for a–c and from 1,1,1,3,3,3-hexafluoro-2-propanol–CD_2Cl_2 (1/3) for d): (a) initial mixture; (b) sample extruded during the first stage; (c) sample extruded during the second stage; (d) crude final polymer.

appearance of the carbonate band, and in the IR spectrum of the final extruded polymer only one band at 1740 cm^{-1} is present in the region from 1700 to 1800 cm^{-1} (Figure 1c). This band is typical of an aromatic–aromatic ester group,[10] and the overall spectrum is identical with the spectrum of poly(Bisphenol A terephthalate) obtained by interfacial polymerization.[11]

The NMR analysis of the samples also is of particular interest. In the region between 8 and 8.4 ppm, typical of the terephthalic unit, the NMR spectrum of the sample extruded in the first step, before distillation of the dimethyl carbonate (Figure 2b), clearly shows the appearance in the mixture of terephthalic ester moieties substituted by one or two aromatic groups (determining an apparent quartet and a singlet, respectively, in the spectrum). The analysis of this part of the spectrum was facilitated by data reported in the literature for similar polymers,[10,12] and in particular our results are in complete agreement with the data reported by Guinlock et al.[13] regarding a detailed study on Bisphenol A–neopentyl glycol–terephthalic acid copolyester in which terephthalate moieties analogous to ours were present.

In the region of Bisphenol A aromatic protons (7.0–7.5 ppm) a multiplet is present instead of the AA'BB' system typical of the PC spectrum. Also in the region of aliphatic protons there are important changes due to modifications in the surroundings of the methyl groups present in the Bisphenol A moieties and in the methyl ester groups; the original singlets (at 1.68 and 3.95 ppm, respectively) are split into multiplets (Figure 2b). The NMR spectra of samples extruded during the second step (Figure 2c) of the process are similar, but the relative peak intensities differ. In particular, in the region between 8 and 8.4 ppm there is a progressive increase in the peak of the symmetrical aromatic substituted terephthalaic unit centered at 8.35 ppm. There is also an important relative reduction in the intensitty of the peak in the range of 3.5–4.0 ppm due, mainly, to the elimination from the system of the methyl units as dimethyl carbonate and DMT.

Lastly, the NMR spectrum of the final polymer (Figure 2d), recorded in 1,1,1,3,3,3-hexafluoro-2-propanol–CD_2Cl_2 (1/3 v/v) because the polyarylate is no longer soluble in $CHCl_3$, is identical with the spectrum of an authentic sample of poly(Bisphenol A terephthalate), obtained by interfacial polymerization.[11]

All these data clearly indicate the occurrence of interchange reactions and the elimination of methyl moieties. The progress of reactions is also shown by the progressive appearance of terephthalic ester units substituted by two aromatic groups up to the formation of the pure polyarylate.

The formation of aliphatic carbonates, by interchange reactions, in the modification or in the synthesis of polymers has already been reported;[14,15] Sweeny observed the elimination of ethylene carbonate with the formation of a residual polymer, identified as bisphenol A polycarbonate, when alternating poly(carbonate ethylene glycol)–Bisphenol A copolymer was heated at 280 °C in vacuo.[14] More recently, the synthesis of aromatic polycarbonates by self-condensation of aromatic diol bis(alkyl carbonate)s through the removal of dialkyl carbonate has been patented.[15] However, the formation of the dialkyl carbonates, described in these reports, occurs through interchange reactions between carbonate groups and still leads to polycarbonates. Instead, in our process the formation of the dimethyl carbonate derives from exchange reactions involving both carbonate and ester groups, and the final polymer is a polyester. To our knowledge, this is the first example reported for the synthesis of polyarylates.

Exchange reactions are expected to be reversible, and to prove the reversibility of the process, we reacted the poly(Bisphenol A terephthalate) with an excess of dimethyl carbonate in the presence of titanium tetrabutoxide in a closed system. Under these conditions we observed the degradation of the polyarylates, which led to a mixture containing carbonate–ester oligomers, similar to that obtained starting from BPDC and DMT (see below). We were able to reobtain the starting polyester by heating this mixture under vacuum (however, DMT must be added to avoid stoichiometric imbalance due to sublimation).

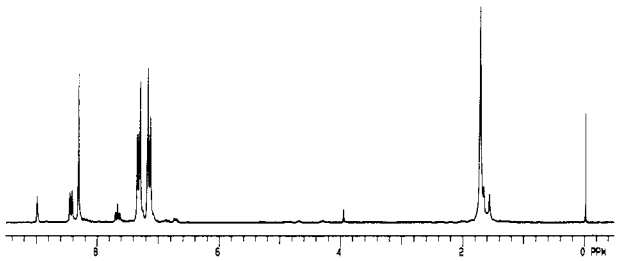


Figure 3. ^{1}H NMR spectrum of the crude polymer Ib (recorded from deuteriochloroform solution).

Process from PC and DMT–DMI (Synthesis of Ib). To check the flexibility of the process, we carried out the synthesis of copolyarylates using a mixture of DMT and DMI in a 1/1 molar ratio and PC. Again, in this case, the composition of the system throughout the entire process was followed using IR and NMR spectroscopy. The spectra confirm the same type of process evolution. The NMR spectrum of the final polymer (Figure 3) presents the same peaks found with an authentic sample obtained by interfacial synthesis, carried out following the method reported by Eareckson.[11] In particular, the presence of an equal number of terephthalic and isophthalic units was confirmed.

Process from Bisphenol A Bis(methyl carbonate) (BPDC) and DMT (Synthesis of Ia). The polymer Ia was also prepared by using BPDC, instead of the preformed polycarbonate, and DMT (10% in excess) in the presence of titanium tetrabutoxide. The reaction, carried out in a glass apparatus in two stages (see the Experimental Section), has the same evolution of the processes described above as demonstrated by the IR and NMR spectra of samples taken as the reaction progressed. The analysis of the spectra confirms the formation, in the first stage, of a mixture containing carbonate–ester oligomers and dimethyl carbonate (identical as far as the type of signals is concerned to that obtained starting from the polycarbonate) and, in the second stage, the formation of the polymer by the progressive elimination of the dimethyl carbonate and the excess DMT.

Conclusion

The new process described in this paper is a reversible melt process, useful for the preparation of polyesters[1] based on Bisphenol A and phthalic acids. It proceeds through interchange reactions between carbonate and ester groups, which give rise to a mixture containing oligomeric (ester–carbonate)s and dimethyl carbonate. In the polymerization step, carried out under vacuum, continuous removal of dimethyl carbonate is necessary in order to achieve high molecular weight polymers.

In our opinion, the use of commerical starting materials, the absence of hazardous and toxic byproducts, and the possibility of reaching high molecular weights without the employment of extreme reaction conditions (devolatizing extrusion, solid-state polymerization etc.) make the process quite interesting.

References and Notes

(1) Bier, G. *Polymer* **1974**, *15*, 527.
(2) Dean, B. D.; Matzner, M.; Tibbitt, J. M. In Polyarylates. *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, 1989; Vol. 5, p 317.
(3) Kricheldorf, H. R.; Schwarz, G. *Makromol. Chem.* **1983**, *184*, 475.
(4) Lieser, G.; Schwarz, G.; Kricheldorf, H. R. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1599.
(5) Imai, Y.; Oishi, Y. *Prog. Polym. Sci.* **1989**, *14*, 173.
(6) Italian patent pending.
(7) Schnell, H.; Bottenbruch, L. *Makromol. Chem.* **1962**, *57*, 1.
(8) Devaux, J.; Godard, P.; Mercier, J. P. *Polym. Eng. Sci.* **1982**, *22*, 229.
(9) Pilati, F.; Marianucci, E.; Berti, C. *J. Appl. Polym. Sci.* **1985**, *30*, 1267.
(10) Devaux, J.; Godard, P.; Mercier, J. P.; Touillaux, R.; Dereppe, J. M. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1881.
(11) Eareckson, W. M., III *J. Polym. Sci.* **1959**, *40*, 399.
(12) Hamb, F. L. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 3217.
(13) Gouinlock, E. V.; Wolfe, R. A.; Rosenfeld, J. C. *J. Appl. Polym. Sci.* **1976**, *20*, 949.
(14) Sweeny, W. *J. Appl. Polym. Sci.* **1961**, *5*, 15.
(15) Fukuoka, S.; Watanabe, T. Jpn Patent 01 04,617, 1989; *Chem. Abstr.* **1989**, *111*, 233914b.

Registry No. Ia (copolymer), 114994-29-5; Ia (SRU), 26659-32-5; Ib (copolymer), 85023-41-2; BPDC, 4824-74-2; (PC)(DMT) (copolymer), 85023-42-3; MeOH, 67-56-1; BP bis(chloroformate), 2024-88-6.