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Aliphatic Polyester Carbonate Copolymers: Enzymatic Synthesis and Solid-State Characterization

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ABSTRACT: *Candida antarctica* Lipase B (CALB), immobilized on Lewatit (Novozym 435), was used as catalyst to prepare a series of poly(butylene carbonate-*co*-butylene succinate) [poly(BC-*co*-BS)] copolymers. The polymers were synthesized by copolymerizations of diethyl carbonate (DEC), 1,4-butanediol (BD), and diethyl succinate (DES) at 70−80 °C under 2.0 mmHg pressure. Poly(BC-*co*-BS) with M_w up to 21 000 and polydispersity between 1.6 and 1.9 were obtained. By changing the monomer feed ratio, proportions of carbonate-to-ester repeating units in polymers were varied from 18:82 to 86:14. For example, poly(BC-*co*-14 mol % BS) and poly(BC-*co*-82 mol % BS) were prepared by using DEC/DES/BD feed ratios of 1.6:0.2:1 and 0.4:0.8:1, respectively. NMR analysis shows that copolymer carbonate and ester repeat units are *randomly* distributed along polymer chains. TGA, DSC, and WAXS were used to investigate the thermal properties and crystal structures of these copolymers. The synthesized, random, poly(BC-*co*-BS) copolymers are more thermally stable than poly(butylene carbonate) (PBC, decomposition temperature 338 °C) but less stable than poly(butylene succinate) (PBS, decomposition temperature 391 °C). Depending on composition, poly(BC-*co*-BS) copolymers vary from semicrystalline to near completely amorphous. The semicrystalline copolymers show only one crystal phase (either of the PBC type or the PBS type), indicating the inability of either crystal lattice to host foreign comonomer units. At particular copolymer compositions (∼70 mol % BC units), neither BC units nor BS units are able to organize into a crystal structure.

Introduction

Aliphatic polycarbonates and aliphatic ester−carbonate copolymers are hydrolyzable and have received considerable attention as potential materials for medical applications.[1] In particular, poly(butylene carbonate-*co*-butylene succinate) [poly(BC-*co*-BS)], with low BC unit content (<20 mol %), have recently been developed by Mitsubishi Gas Chemical Company[2] and form completely miscible blends with poly(L-lactide), another polymer widely used in the biomedical field.[3]

Our laboratory and others have reported enzyme-catalyzed routes to synthesize polycarbonates.[4] Recently, our group described the synthesis of nonfractionated, high molecular weight (M_w > 25 000) poly(hexamethylene carbonate), PHC, via condensation copolymerization between diethyl carbonate (DEC) and 1,6-hexanediol (HD).[5] Systematic changes in molar ratio of DEC to HD were used to control PHC end-group structure. In other words, by varying DEC content in reactions, PHC polymers were prepared with high ethyl carbonate or hydroxyl terminal groups. The companion paper[6] describes Novozym 435 (N435)-catalyzed synthesis of both poly(BC-*co*-BS) and poly(hexamethylene carbonate-*co*-hexamethylene adipate) [poly(HC-*co*-HA)] by reactions between DEC with corresponding diols and diesters. For poly(BC-*co*-BS) synthesis, performed by copolymerization of DEC/DES/BD (2:1:2 molar ratio) in diphenyl ether, the polymerization rate was highest at 80 °C. Poly(BC-*co*-BS) M_w reached 26 000, and M_w/M_n ranged from 1.7 to 2.0. Polymerization rates were relatively greater for poly(HC-*co*-HA), giving higher molecular weight copolymers (M_w up to 59 000) with lower polydispersity (M_w/M_n down to 1.5). The BC/BS unit ratios, calculated from proton resonance absorptions, were all nearly 50:50 mol/mol, and the copolymer repeat unit sequence distribution was random. By lowering the DEC content in the monomer feed, poly(BC-*co*-BS) with up to 96 mol % hydroxyl terminal groups was prepared.

In this paper, synthetic methods were explored to vary the copolymer composition so that a systematic set of poly(BC-*co*-BS) copolymers would, for the first time, be available. DES-to-BD composition was varied during terpolymerizations while fixing the DEC/(BD−DES) monomer feed ratio at 2:1. Effects of DES to BD feed ratio on the polymerization rate, polymer composition (repeat unit ratio), molecular weight averages, polydispersity, and end-group structure were determined. Additionally, studies were performed in order to prepare poly(BC-*co*-BS) diols with variation in copolymer composition. Then, solid-state characterization of poly(BC-*co*-BS) over a broad composition range was performed in order to investigate effects of composition on physical properties.

A series of poly(BC-*co*-BS) copolymers with BC/BS unit ratios of 86:14, 71:29, 50:50, 31:69, and 18:82 were prepared. Polymer molecular weights and microstructures were analyzed by gel permeation chromatography (GPC) and by proton (^{1}H) and carbon-13 (^{13}C) NMR spectroscopy, respectively. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and wide-angle X-ray diffraction measurements (WAXS) were employed to study the thermal stability, morphology, and crystal structures of copolymers. WAXS and DSC results of a commercial poly(butylene carbonate-*co*-butylene succinate) containing 10 mol % of BC units have been recently published by Qui et al.[7] However, to the best of our knowledge, no such data are available on poly(BC-*co*-BS)s with changing composi-

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tion. Results herein show that, by tuning poly(BC-*co*-BS) composition through selection of appropriate reaction conditions, poly(carbonate-*co*-esters) with desired physical properties can be obtained. Furthermore, this new series of poly(BC-*co*-BS) polyols represent important new macromer building blocks for segmented polyurethane copolymer synthesis.

Experimental Section

Materials. Diphenylmethane was purchased from Aldrich Chemical Co. and was used as received. Sources of all monomers, other solvents, and the enzyme catalyst N435 (*Candida antarctica* Lipase B (CALB) physically adsorbed within the macroporous resin Lewatit VPOC 1600) used herein are given in the companion paper.[6]

Instrumental Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300 spectrometer or a Bruker AVANCE 500 spectrometer. The chemical shifts reported were referenced to internal tetramethylsilane (0.00 ppm) or to the solvent resonance at the appropriate frequency. The number- and weight-average molecular weights (M_n and M_w, respectively) of polymers were measured by gel permeation chromatography (GPC) using a Waters HPLC system. All other details of the GPC method used are described in the companion paper.[6] Thermogravimetric analysis (TGA) was carried out using a TA Instruments TGA2950 thermogravimetric analyzer from room temperature to 600 °C, with a heating rate of 10 °C/min, under nitrogen purge. Differential scanning calorimetry (DSC) was performed with a TA Instruments Q100 DSC equipped with a LNCS low-temperature accessory. The temperature scale was calibrated with high-purity standards. DSC heating scans were performed in the temperature range from −100 to 160 °C, in a helium atmosphere, at 20 °C/min. Controlled cooling at 10 °C/min, as well as quench cooling, was applied between heating runs. Glass transition temperatures (T_g) were taken at the midpoint of the stepwise specific heat increment. Crystallization temperatures (T_c) and melting temperatures (T_m) were taken at the peak maximum of exotherm and endotherm, respectively. In cases where multiple endotherms are present, the temperature of high-T peak was taken as T_m. DSC was also used in the temperature-modulated mode (TMDSC), with heating rate = 2 °C/min, oscillation amplitude = 0.5 °C, and oscillation period = 40 s. Wide-angle X-ray diffraction measurements (WAXS) were carried out at room temperature with a PANalytical X'Pert PRO diffractometer equipped with an X'Celerator detector (for ultrafast data collection). A Cu anode was used as X-ray source (K radiation: $\lambda = 0.154\ 18$ nm, 40 kV, 40 mA), and 1/4° divergence slit was used to collect the data in 2θ range from 2° to 60°. After subtracting the diffractogram of an empty sample holder from the experimental diffraction curve, the amorphous and crystalline contributions in the resulting diffractogram were calculated by a fitting method using the WinFit program. The degree of crystallinity (χ_c) was evaluated as the ratio of the crystalline peak areas to the total area under the scattering curve.

N435-Catalyzed Terpolymerization of Diethyl Carbonate (DEC), Diethyl Succinate (DES), and 1,4-Butanediol (BD). Copolymerizations of DEC and DES with BD were performed either in solution or in bulk, in a parallel synthesizer. Vacuum control (±0.2 mmHg) during reactions was achieved by using a vacuum regulator. Reactions were conducted using various DEC/DES/BD monomer feed ratios (see Tables 1 and 2). Information on the range of reaction conditions studied (temperature, time, pressure) are provided in Tables 1 and 2. Further details of the polymerization method are described in the companion paper.[6]

Synthesis and Purification of Poly(BC-*co*-BS) Copolymers Used for Solid-State Characterizations. Except for modifications to the method given below, the experimental procedure follows that described in the companion paper.[6] Monomer feed molar ratios of DEC to DES to BD were 1.7:0.15:1, 1.4:0.3:1, 0.6:0.7:1, and 0.3:0.85:1. Reactions with 0.6:0.7:1 and 0.3:0.85:1 DEC/DES/BD ratios were performed at 80 °C in diphenyl ether (140 wt % vs total monomer). Reactions with 1.7:0.15:1 and 1.4:0.3:1 DEC/DES/BD ratios were performed in diphenylmethane (50 wt % vs total monomer) at 70 and 80 °C, respectively. All reactions at these four monomer ratios took place at 600 mmHg for 22 h during first stage oligomerization and thereafter at 2 mmHg for 52 h during second stage polymerization. Reaction temperature was maintained same during both stages. After completion of copolymerizations, reaction mixtures were dissolved in chloroform, and the resultant solutions were filtered to remove the enzyme catalyst. Filtrates with polymer products were concentrated under vacuum, and the resulting solutions were added dropwise to stirring methanol to precipitate copolymers. Products were isolated by filtration, washed on the filter pads with methanol three times, and dried at 50 °C under vacuum for 24 h.

Table 1. Effects of Monomer Ratio on Terpolymerization of DEC, DES, and BD

						end group (mol %)	
entry	DEC/DES/BD (molar ratio)	BC/BS ratio	M_w	M_n	M_w/M_n	−OH	−OC(O)OEt + −COOEt
1	1.6:0.2:1[a]	80:20	21200	13100	1.6	44	56
2	1.2:0.4:1[a]	61:39	16300	9200	1.8	42	58
3	1.0:0.5:1[a]	50:50	20200	11600	1.7	31	69
4	0.8:0.6:1[a]	40:60	18300	9800	1.9	33	67
5	0.4:0.8:1[a]	22:78	15800	8200	1.9	23	77
6	0.8:0.2:1[b]	70:30	2300	1000	2.1	99	1
7	0.6:0.4:1[b]	49:51	6500	3700	1.8	97	3
8	0.4:0.6:1[b]	31:69	7800	4300	1.8	95	5
9	0.2:0.8:1[b]	14:86	3700	2200	1.7	70	30
10	*0.2:0.8:1*[c]	*14:86*	*7300*	*3800*	*1.9*	*100*	*0*

[a] Reaction conditions: in diphenyl ether (140 wt % vs total monomer); 10 wt % N435 (vs total monomer); first stage oligomerization: 80 °C, 600 mmHg, 18 h; second stage polymerization: 80 °C, 2.0 mmHg, 53 h. [b] Reaction conditions: bulk reaction; 23 wt % N435 vs BD; first stage oligomerization: 80 °C, 600 mmHg, 22 h; second stage polymerization: 80 °C, 2.0 mmHg, 27 h. [c] Comparative example: same conditions as used for entry 9, but in diphenylmethane (70 wt % vs total monomer) solution.

Table 2. Molecular Characterization and Molecular Weight Distribution of Homopolymers (PBS and PBC) and Poly(BS-*co*-BC) Copolymers

product	DEC/DES/BD (molar ratio)	product yield [a] (%)	M_w	M_n/M_w
PBC[b]			14 700	1.6
poly(BC-*co*-14 mol % BS)[c]	1.7:0.15:1	90	18 300	1.7
poly(BC-*co*-29 mol % BS)[d]	1.4:0.3:1	92	20 900	2.0
poly(BC-*co*-50 mol % BS)[e]		95	59 400	2.1
poly(BC-*co*-69 mol % BS)[f]	0.6:0.7:1	94	19 700	1.6
poly(BC-*co*-82 mol % BS)[f]	0.3:0.85:1	95	18 800	1.7
PBS[b]			32 000	2.3

[a] Product yield is determined by the quantity of precipitated product obtained relative to the theoretical value assuming 100% conversion of monomers. [b] Synthesis of the homopolymers is described in the companion paper. The polymers were isolated and purified via reprecipitation in $CHCl_3$/CH_3OH mixture. [c] Reaction conditions: in diphenylmethane (50 wt % vs total monomer); 10 wt % N435 (vs total monomer); first stage oligomerization: 70 °C, 600 mmHg, 22 h; second stage polymerization: 70 °C, 2.0 mmHg, 52 h. [d] Reaction conditions: as in footnote *c*, except that the reaction temperature was 80 °C. [e] This random copolymer was prepared via transesterification between PBC and PBS (see companion paper for details) and purified via reprecipitation in $CHCl_3$/CH_3OH mixture. [f] Reaction conditions: in diphenyl ether (140 wt % vs total monomer); 10 wt % N435 (vs total monomer); first stage oligomerization: 80 °C, 600 mmHg, 22 h; second stage polymerization: 80 °C, 2.0 mmHg, 52 h.

Results and Discussion

Effects of Monomer Feed Ratio on Terpolymerizations of DEC with DES and BD. Studies were performed to explore the synthesis of poly(BC-*co*-BS) with compositions other than 50:50 mol/mol BC to BS units. Molar ratios of DEC to DES to BD in the monomer feed included 1.6:0.2:1, 1.2:0.4:1, 1.0:0.5:1, 0.8:0.6:1, and 0.4:0.8:1. Thus, the DEC/(BD − DES) ratio (i.e., the ratio of DEC to the difference BD − DEC) was maintained at 2:1, while the ratio of DES to BD was varied. Experiments were conducted in diphenyl ether using 10 wt %

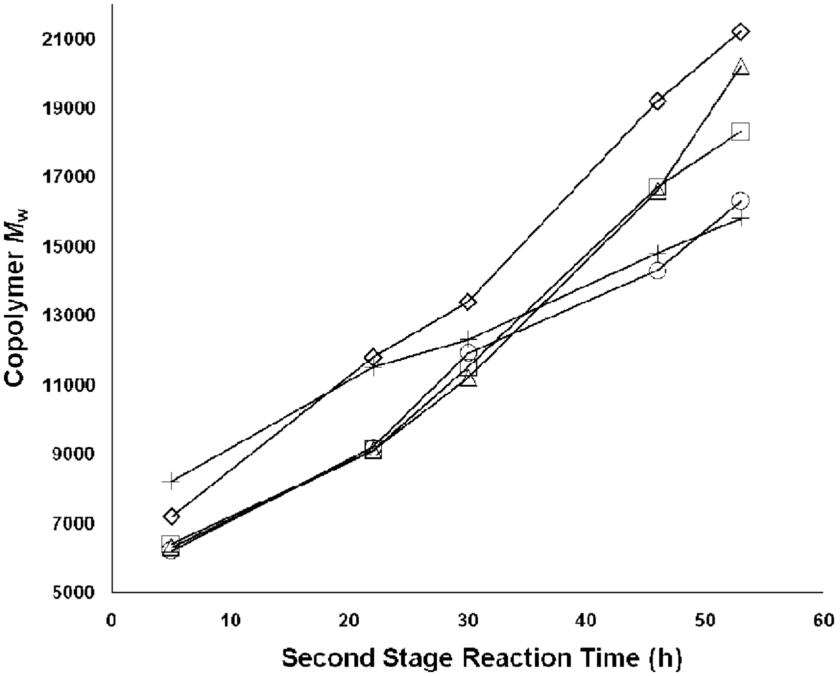

Figure 1. Effects of DES/BD ratio on terpolymerization of DEC and DES with BD in diphenyl ether (polymerization conditions: 2:1 DEC/(BD − DES), 80 °C, 2.0 mmHg pressure): 0.2:1 DES/BD (◇), 0.4:1 DES/BD (○), 0.5:1 DES/BD (△), 0.6:1 DES/BD (), 0.8:1 DES/BD (+).

N435 (vs total monomer) at 80 °C. The pressure and reaction time were 600 mmHg for 18 h during the first stage oligomerization and 2.0 mmHg for 53 h during the second stage polymerization. Figure 1 displays polymer chain growth vs polymerization time for copolymerizations conducted with different DES to BD feed ratios. Changes in the DES/BD ratio resulted in no substantial effects on the polymerization rate. In all cases, M_w increased continuously throughout terpolymerization reactions. Polydispersities (M_w/M_n) of synthesized poly(BC-*co*-BS) copolymers were between 1.6 and 1.9. For example, using 1.6:0.2:1 DEC/DES/BD, at 5, 22, 30, 46, and 53 h, the M_w and M_w/M_n (in parentheses) values were 7 200 (1.7), 11 800 (1.8), 13 400 (1.9), 19 200 (1.8), and 21 200 (1.6), respectively. Similarly, when the monomer feed was 0.8:0.6:1 DEC/DES/BD, at 5, 22, 30, 46, and 53 h, the M_w and M_w/M_n (in parentheses) values were 6400 (1.7), 9100 (1.8), 11 500 (1.8), 16 700 (1.7), and 18 300 (1.9), respectively. Table 1 (entries 1−5) gives polymer composition, molecular weight, polydispersity, and end-group structures for products obtained at the end of polymerizations where DEC/(BD − DES) was fixed at 2:1. Comparison of the monomer feed ratios ([BD − DES]/[DES]) and copolymer compositions (BC to BS units) shows that they are in excellent agreement (±2%). Thus, poly(BC-*co*-BS) composition is predetermined by selecting the desired monomer feed ratio. All products contained hydroxyl, ethyl carbonate, and ethyl ester terminal groups although their relative contents varied as a function of the monomer feed ratio (Table 1, entries 1−5).

Synthesis of Poly(BC-*co*-BS) Diols Using 1:1 DEC/(BD − DES) Ratio. Poly(BC-*co*-BS) diols may be useful intermediates for producing specialty polyurethanes and other high molecular weight segmented copolymers. As described in the companion paper,[6] by using a 1:1 DEC/(BD − DES) monomer feed ratio (0.5:0.5:1 DEC/DES/BD), a copolymer with nearly equimolar contents of BC and BS units was prepared with 96 mol % hydroxyl terminal units. Since a key objective in this work is preparation of poly(BC-*co*-BS) with different BC/BS compositions, and given the importance of polymeric diols as precursors for segmented copolymers such as polyurethanes, a study was performed where the DEC/(BD − DES) ratio was fixed at 1:1, but the DES-to-BD monomer feed ratio was varied. In order to decrease diffusion constraints and thereby prepare poly(carbonate-*co*-esters) of higher molecular weight (e.g., $M_n > 10\,000$), terpolymerizations described above and most studies in the companion paper[6] were performed in diphenyl ether. However, since commercial polyols often have molecular weights below 3000, in this paper terpolymerizations to prepare poly(BC-*co*-BS) polyols were performed in bulk. Monomer feed ratios used and corresponding M_n and M_w/M_n values are given in Table 1, entries 6−9. Values of M_n ranged from 1000 to 4300, and end-group hydroxyl contents for entries 6, 7, and 8 are 99, 97, and 95, respectively. The BC-to-BS contents of copolymers in entries 6−9 were lower than corresponding DEC/DES monomer feed ratios. This is explained by loss of DEC, due to its high volatility, during first stage oligomerizations. For these low molecular weight polymers, the distribution of BC and BS units along chains could not be quantitatively determined due to overlap of carbon-13 resonances at 25.0−25.3 ppm between end-group ($-CH_2\mathit{CH}_2\mathit{CH}_2CH_2OH$) and main-chain repeat units ($-OCH_2\mathit{CH}_2\mathit{CH}_2CH_2O-$) (see companion paper[6] for details on unit distribution analysis). However, it is likely that the repeat units are randomly distributed since the reaction conditions are similar to those of the DEC/DES/BD terpolymerization in diphenyl ether or diphenylmethane solution, which yields random copolymers as discussed in the following section.

The relatively low terminal hydroxyl content (70%) of poly(BC-*co*-86 mol % BS) (Table 1, entry 9) is believed to result from crystallization and phase separation of this copolymer from the reaction mixture (see thermal properties in following sections). In order to overcome product solidification, the terpolymerization using 0.2:0.8:1 DEC/DES/BD was performed under the same conditions as in the bulk reaction above, except by using diphenylmethane (70 wt % vs total monomer) as solvent. Addition of diphenylmethane to reactions resulted in monophasic solutions throughout polymerizations that prohibited polymer precipitation and crystallization. As a result, poly(BC-*co*-86 mol % BS) of higher molecular weight ($M_n = 3800$ vs 2200) with nearly quantitative incorporation of hydroxyl terminal units was obtained (Table 1, entry 10).

Table 3. Structures of Poly(BC-*co*-BS) Copolymers

	BC–BS + BS–BC		BC–BC		BS–BS	
sample	measd[c]	calcd[d]	measd[c]	calcd[d]	calcd[d]	measd[c]
poly(BC-*co*-14 mol % BS)[a]	0.27	0.24	0.69	0.74	0.04	0.02
poly(BC-*co*-50 mol % BS)[b]	0.5	0.5	0.25	0.25	0.25	0.25
poly(BC-*co*-69 mol % BS)[a]	0.43	0.43	0.08	0.09	0.49	0.48
poly(BC-*co*-82 mol % BS)[a]	0.3	0.3	0.03	0.03	0.67	0.67

[a] Synthesized via polycondensation of DEC, DES, and BD. [b] Synthesized via transesterification of PBC with PBS. [c] Measured from the ^{13}C NMR spectra (the method is described in the companion paper). [d] Calculated for a random A–B copolymer, distribution of diad X–Y = $f_X \times f_Y$ (X and Y independently equal to A or B; f_X and f_Y are molar fractions of corresponding repeating units X and Y in the polymer chains).

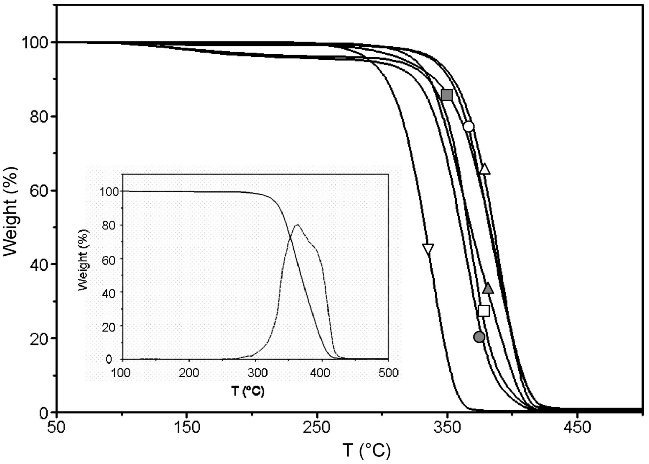

Figure 2. Thermogravimetric curves of: PBS (△), PBC (▽), poly(BC-*co*-82 mol % BS) (■), poly(BC-*co*-69 mol % BS) (○), poly(BC-*co*-50 mol % BS) (▲), poly(BC-*co*-29 mol % BS) (□), and poly(BC-*co*-14 mol % BS) (●). Inset: magnification of thermogravimetric (—) and derivative (– –) curves of poly(BC-*co*-50 mol % BS).

Synthesis of Poly(BC-*co*-BS) for Solid-State Characterizations. For solid-state property studies, a series of poly(BC-*co*-BS) copolymers with BC-to-BS unit ratios of 86:14, 71:29, 31:69, and 18:82 were prepared and purified using corresponding DEC/DES/BD monomer molar ratios of 1.7:0.15:1, 1.4:0.3:1, 0.6:0.7:1, and 0.3:0.85:1, respectively (see Table 2). Reaction conditions for copolymer synthesis are summarized in Table 2 footnotes. All copolymerizations at the four monomer ratios were initially performed in diphenyl ether to obtain polymer products with desirable molecular weights. However, subsequent analysis of products showed that while poly(BC-*co*-BS) copolymers with ≥50 mol % BS unit contents could readily be separated from diphenyl ether via reprecipitation in chloroform/methanol, we were unsuccessful in removing residual diphenyl ether (∼10–20 wt %) from poly(BC-*co*-14 and 29 mol % BS) copolymers owing to their high affinity to this solvent. This problem was solved by using diphenylmethane in place of diphenyl ether. Thus, by performing polymerizations in diphenylmethane, solvent-free poly(BC-*co*- 29 and 14 mol % BS) copolymers were successfully prepared. Copolymers with 29, 69, and 82 mol % BS units were prepared in sufficiently high molecular weights ($M_w \geq$ 15 000) by conducting reactions at 80 °C. However, poly(BC-*co*-14 mol % BS) synthesis was performed at 70 °C in order to obtain the copolymer in sufficiently high molecular weight for subsequent solid-state analyses. Furthermore, the companion paper[6] describes a transacylation reaction between preformed PBC and PBS that gave high molecular weight random poly(BC-*co*-50 mol % BS). Since this material was already in hand, it was used as the 50 mol % copolymer instead of initiating efforts to prepare a new 50 mol % product by copolymerization of a suitable DEC/DES/BD comonomer molar ratio.

To remove low molecular weight impurities and solvent, poly(BC-*co*-BS) products were precipitated in methanol (see Experimental Section). In all cases, yields of precipitated polymers were greater than 90% (Table 2). With the exception of poly(BC-*co*-50 mol % BS) that was synthesized via PBC–PBS transesterification[6] and shows higher molar mass (Table 2), reference homopolymer and copolymer M_w values ranged from 14 700 to 32 000, and their M_w/M_n were from 1.6 to 2.3. It is interesting to note that from purely qualitative observations it appears that poly(BC-*co*-29 mol % BS) exhibits remarkable adhesive properties toward various surfaces, such as stainless steel, glass, and natural wood. As described in the companion paper,[6] N435-catalyzed solution copolymerization of DEC and DES with BD, as well as transesterification between PBC and PBS, formed random poly(BC-*co*-BS) copolymers. Table 3 shows the distributions of diad structures for poly(BC-*co*-14 mol % BS), poly(BC-*co*-50 mol % BS), poly(BC-*co*-69 mol % BS), and poly(BC-*co*-82 mol % BS) copolymers. To quantitatively determine the repeat-unit sequence or arrangement of BC and BS units along copolymer chains, distributions of diad structures for statistically random copolymers at corresponding BC/BS unit ratios were calculated. Experimental results of diad distributions, measured by ^{13}C NMR absorptions, are in good agreement with those theoretically calculated for statistically random copolymers data (Table 3). Hence, random copolymers were formed regardless of BC or BS unit content in polymer chains, and comparisons of solid-state properties are based on random structures of these copolymers.

Thermal Characterization. Figure 2 compares thermogravimetric curves of poly(BC-*co*-BS) copolymers with those of reference PBC and PBS homopolymers. Both PBC and PBS degrade in a single step centered at 338 and 391 °C, respectively. Lower thermal stability of the polycarbonate is attributed to thermally induced decarboxylation reactions.[8] The weight change observed between room temperature to 200 °C, associated with loss of absorbed water, is lower than 0.1% in PBC and 0.6% in PBS. This result indicates slightly higher hydrophilicity of PBS than PBC and is consistent with the different ratio of polar to apolar groups in the molecular structures of the two polymers (COO/CH_2 is 1:3 and 1:4 in PBS and PBC, respectively). Both homopolymers are completely decomposed at 600 °C.

The main weight loss of all copolymers in Figure 2 lies between those of the two homopolymers. This observation suggests that the insertion of butylene succinate units in PBC chains hinders to some extent the degradation mechanism of PBC and that copolymerization with ester units may be used to raise the thermal stability of polycarbonates. Copolymers rich in BC units (71 and 86 mol %) present an additional broad degradation step, centered at 150 °C, which corresponds to a weight loss of around 4% and is tentatively attributed to residual diphenylmethane, the solvent used in the synthesis of these copolymers (Table 2). This attribution is corroborated by NMR evidence of diphenylmethane traces (1–2%) in both samples. In Figure 2, an inset shows a magnification of the thermogravimetric curve of poly(BC-*co*-50 mol % BS), where a peculiar dual degradation behavior is observed (see derivative curve). It is worth noting that, although the higher temperature step occurs in the temperature range of plain PBS degradation, NMR analysis (Table 3) rules out the presence of PBS blocks in this copolymer. The origin of the observed dual degradation behavior in poly(BC-*co*-50 mol % BS) remains unclear. All copolymers are completely decomposed at 600 °C.

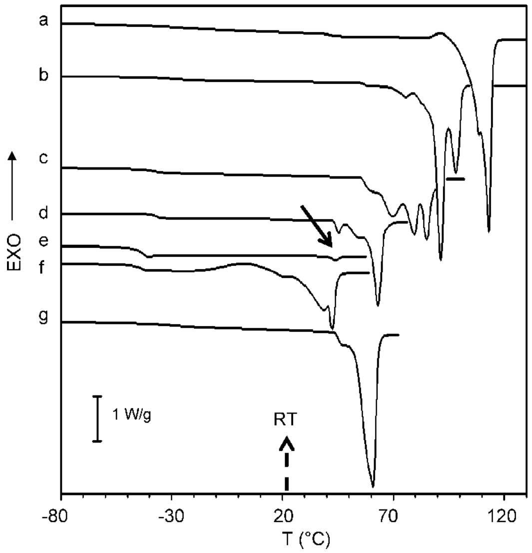

Figure 3. First DSC heating scans of PBS (a), poly(BC-*co*-82 mol % BS) (b), poly(BC-*co*-69 mol % BS) (c), poly(BC-*co*-50 mol % BS) (d), poly(BC-*co*-29 mol % BS) (e), poly(BC-*co*-14 mol % BS) (f), and PBC (g). The small melting endotherm of poly(BC-*co*-29 mol % BS) is indicated by the solid arrow. The broken arrow marks room temperature (RT).

Both homopolymers and copolymers investigated herein display a complex melting behavior as shown in Figure 3, where the DSC heating scans of as-purified samples (see Experimental Section) are reported. The only exception is copolymer poly(BC-*co*-29 mol % BS) which is almost completely lacking a crystal phase (see in Figure 3, curve e, the very small endotherm indicated by an arrow). It is worth noting that the temperature location of the melting process with respect to room temperature (RT in Figure 3) strongly affects the physical aspect of the analyzed materials: while PBS, PBC, and copolymers with BC units up to 50 mol % melt well above RT and are semicrystalline solids at RT, poly(BC-*co*-14 mol % BS) is waxy, owing to a fraction of poorly ordered crystals that start melting below RT (Figure 3, curve f). Finally, copolymer poly(BC-*co*-29 mol % BS), which is practically noncrystalline, is a sticky material at RT.

In order to investigate the crystallization process and to erase effects of thermal history on polymer morphology, the polymers were cooled from the melt at 10 °C/min and subsequently reheated at 20 °C/min. Selected crystallization and melting curves are shown in parts A and B of Figure 4, respectively, while Table 4 collects crystallization and melting data of the heating scan. The DSC results of the cooling run (selected curves) are reported in Figure 4A. The crystallization behavior of the homopolymers is quite different: while PBS (curve a) displays a sharp and intense crystallization peak ($\Delta H_c = 75$ J/g), PBC (curve g) shows a broad and much smaller exotherm ($\Delta H_c = 8$ J/g). Accordingly, only copolymers rich in BS units, i.e., poly(BC-*co*-69 mol % BS) and poly(BC-*co*-82 mol % BS), are seen to crystallize in the cooling experiments of Figure 4A ($\Delta H_c = 37$ J/g and $\Delta H_c = 63$ J/g, respectively). The cooling DSC scans of the noncrystallizing copolymers (i.e., those containing 50, 29, and 14 mol % BS) are not shown in Figure 4A.

In the reheating DSC heating scans of Figure 4B, the amorphous copolymers (curves d−f) show a well-defined glass transition around −40 °C. Poly(BC-*co*-50 mol % BS) also displays a very small exo/endothermal behavior ($\Delta H < 1$ J/g, Table 4), not appreciable in curve d of Figure 4B. The samples that develop crystallinity during the cooling run (see curves a−c and g in Figure 4A) show additional cold crystallization in subsequent heating scans (see exotherms in curves a−c and g of Figure 4B). Consequently, in these samples, the melting process observed in Figure 4B includes crystals formed during both cooling and subsequent heating, and indeed, the associated melting enthalpy (Table 4) roughly corresponds to the sum of the enthalpies of the two crystallization phenomena.

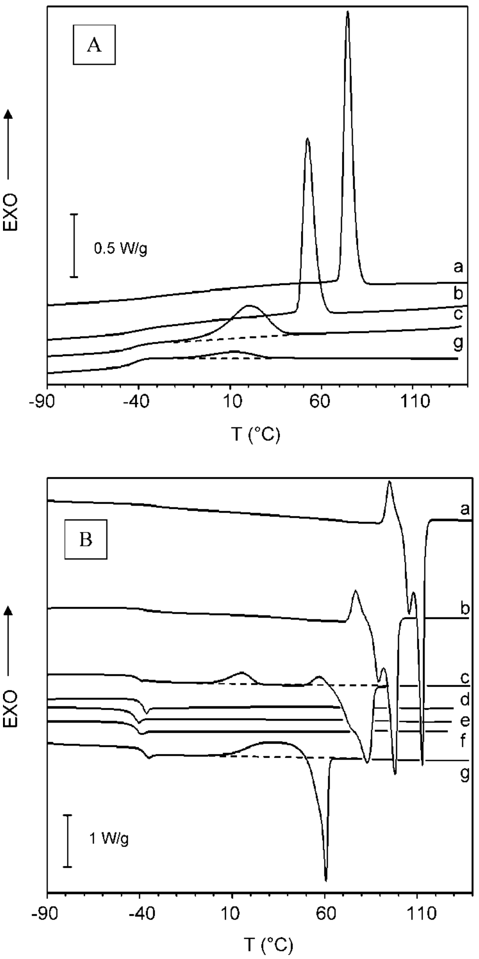

Figure 4. DSC scans (A: cooling from melt at 10 °C/min; B: subsequent heating at 20 °C/min) of PBS (a), poly(BC-co-82 mol % BS) (b), poly(BC-*co*-69 mol % BS) (c), poly(BC-*co*-50 mol % BS) (d), poly(BC-*co*-29 mol % BS) (e), poly(BC-*co*-14 mol % BS) (f), and PBC (g). Broken lines are used as guidelines to highlight the endo- and exothermal phenomena.

Table 4. Melting and Crystallization Data from DSC Heating Curves, after Cooling at 10 °C/min

sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PBC	33	26	61	34
poly(BC-*co*-14 mol % BS)[a]	–	–	–	–
poly(BC-*co*-29 mol % BS)[a]	–	–	–	–
poly(BC-*co*-50 mol % BS)	42	<1	69	<1
poly(BC*co*-69 mol % BS)	57	13	83	53
poly(BC-*co*-82 mol % BS)	77	7	98	67
PBS	95	9	113	79

[a] The two copolymers do not crystallize or melt.

In order to clarify the complex melting processes observed in Figure 4B, the DSC technique was also used in temperature-modulated mode (TMDSC). As an example, Figure 5 shows TMDSC traces (heating rate 2 °C/min) of poly(BC-*co*-82 mol % BS) previously cooled from the melt at 10 °C/min (same cooling rate as that applied in the cooling runs of Figure 4A). The total (T) heat flow curve in Figure 5 shows complex exo/endothermal processes centered at temperatures T_1, T_2 and T_3. This behavior is the same as that shown by poly(BC-*co*-82 mol % BS) in Figure 4B (curve b), when the heating rate difference

Table 5. Temperature of the Peak Maxima from TMDSC Heating Scans after Cooling at 10 °C/min

sample	curve	$T_1{}^a$ (°C)	$T_2{}^a$ (°C)	$T_3{}^a$ (°C)
PBC	total	54	60	64
	reversible	53	60	64
	nonreversible	53	60	64
poly(BC-*co*-69 mol % BS)	total	61	77	86
	reversible		79	84
	nonreversible	62	78	87
poly(BC-*co*-82 mol % BS)	total	76	90	100
	reversible		92	99
	nonreversible	76	92	102
PBS	total	95	106	114
	reversible		108	114
	nonreversible	95	108	114

[a] Refer to Figure 5 for T_1, T_2, and T_3 definitions.

(2 °C/min in Figure 5 vs 20 °C/min in Figure 4B) is taken into account.

In addition to the total heat flow curve, the TMDSC technique also provides the component curves, i.e., the nonreversible (NR) and the reversible (R) heat flows (see corresponding curves in Figure 5). In the R curve, a multiple endotherm appears with peak temperatures T_2 and T_3. The NR curve, instead, shows two exothermal processes at T_1 and T_2, followed by an endothermal event at T_3. Since the total T curve is the mathematical sum of its R and NR components, the thermal events observed in the T curve of Figure 5 can be described as follows. At T_1, chain segments pertaining to the copolymer amorphous fraction assume ordered conformation and crystallize. More complex phenomena occur at T_2, where melting and recrystallization processes concomitantly occur, as revealed by an endotherm in R curve and exotherm in NR curve. Such rearrangements that imply melting of poorly ordered crystals and crystallization into larger and more perfect structures are commonly observed in polyesters.[9] Finally, the crystal population existing at $T > T_2$ melts at T_3. The TMDSC technique, which allows separation of different overlapping thermal phenomena, shows that in the total (T) curve a crystallization event is hidden behind the endotherm at T_2. Analogous MDSC results have been obtained for PBS, PBC, and poly(BC-*co*-69 mol % BS), i.e., the samples exhibiting multiple endotherms in Figure 4B, and their T_1, T_2, and T_3 data are collected in Table 5. In all analyzed samples, at T_2 endothermal (see reversible) and exothermal events (see nonreversible) coexist, indicating that in PBS, PBC, and their copolymers rich in BS units melting and recrystallization processes occur.

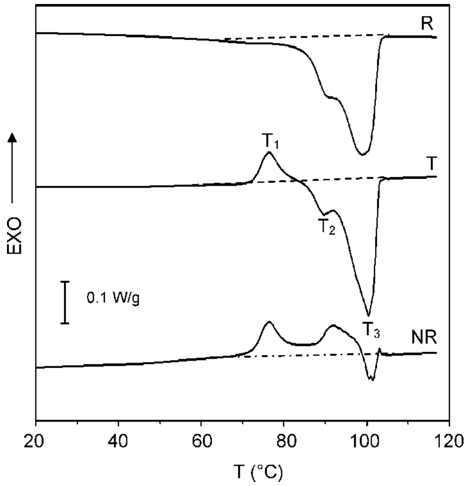

Figure 5. TMDSC heating traces of poly(BC-*co*-82 mol % BS); heating rate 2 °C/min, sample previously cooled from the melt at 10 °C/min. The three curves are total heat flow (T), reversible heat flow (R), and nonreversible heat flow (NR). Broken lines are drawn as guidelines to highlight the endo- and exothermal phenomena.

Table 6. Glass Transition Data from DSC Heating Curves after Quench Cooling

sample	T_g (°C)	ΔC_p (J/(g °C))
PBC	−38	0.56
poly(BC-*co*-14 mol % BS)	−43	0.60
poly(BC-*co*-29 mol % BS)	−44	0.65
poly(BC-*co*-50 mol % BS)	−39	0.58
poly(BC-*co*-69 mol % BS)	−42	0.65
poly(BC-*co*-82 mol % BS)	−34	0.28
PBS	−34	0.30

The present interpretation is corroborated by earlier work by Yoo[10] and Qui,[7,11]who proposed the melting and recrystallization model to explain multiple melting peaks observed in DSC thermograms of PBS crystallized under both isothermal and nonisothermal conditions. The same model was further invoked by Qui et al. to describe the thermal behavior of a commercial butylene succinate copolymer containing 10 mol % of butylene carbonate units[7] and in blends of PBS with poly(ethylene oxide).[12]

The glass-to-rubber transition of poly(BC-*co*-BS) copolymers was investigated by DSC on melt quenched samples. Table 6 lists values and corresponding heat capacity increments (ΔC_p). Analysis of ΔC_p data shows that, after quench cooling from the melt, most samples show values typical of completely amorphous polymers (ΔC_p around 0.6 J/(g °C)), while PBS and poly(BC-*co*-82 mol % BS) display lower ΔC_p values (ca. 0.3 J/(g °C)), showing that a fraction of the polymer is in the crystalline state. This result agrees with the high crystallizing ability of PBS and of PBS-rich copolymers discussed above. In Table 6, T_g values of all amorphous samples lies around −40 °C and seems to be uncorrelated with changes in copolymer composition, while the T_gs of the partially crystalline samples [PBS and poly(BC-*co*-82 mol % BS)] are slightly higher (−34 °C). It is well-known that in semicrystalline polymers, due to an anchoring effect of the crystal phase, the glass transition temperature increases compared to that of the fully amorphous polymer. It may be inferred, therefore, that the T_g of totally amorphous PBS might be close to that of amorphous PBC. The similarity of the two homopolymer T_g's might explain the observed lack of a clear composition dependence of glass transitions for poly(BC-*co*-BS) copolymers.

As concerns the remarkably different crystallization ability of PBS and PBC observed in Figure 4A, it is noteworthy that the melting temperature of PBS is about 50 °C higher than that of PBC (Table 4). Hence, the crystallization window of PBS is much wider than that of PBC, and in dynamic conditions the polyester crystallizes more easily than the polycarbonate. This behavior is evident both during slow cooling (10 °C/min, Figure 4A) and upon quenching (Table 6).

Structural Characterization. The WAXS diffractograms of all polymers investigated in this work except poly(BC-*co*-29 mol % BS), which is poorly crystalline and sticky at room temperature, are collected in Figure 6. The two homopolymers show different WAXS patterns. PBS (curve a) shows main reflections at 18.9° (020), 21.1° (021), and 21.8° (110), in agreement with earlier publications,[7,10] while PBC's main reflections (curve g) appear at 15.9°, 20.4°, 20.9°, and 23.6°. To the best of our knowledge, no X-ray diffraction data are available in the literature for poly(butylene carbonate) to be compared with the present results. Because of the different patterns of PBS and PBC, it is easy to see in Figure 6 that copolymers with BS content above 50 mol % (curves b−d) crystallize in the PBS lattice, whereas poly(BC-*co*-14 mol % BS), curve f, shows reflections at the same positions as those of PBC. No coexistence of the two (PBS and PBC) crystal

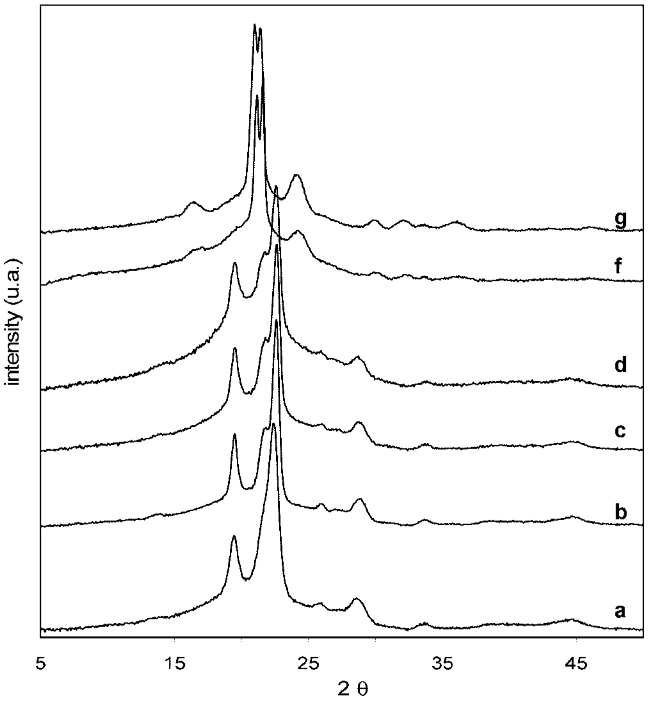

Figure 6. WAXS diffractograms of PBS (a), poly(BC-*co*-82 mol % BS) (b), poly(BC-*co*-69 mol % BS) (c), poly(BC-*co*-50 mol % BS) (d), poly(BC-*co*-14 mol % BS) (f), and PBC (g).

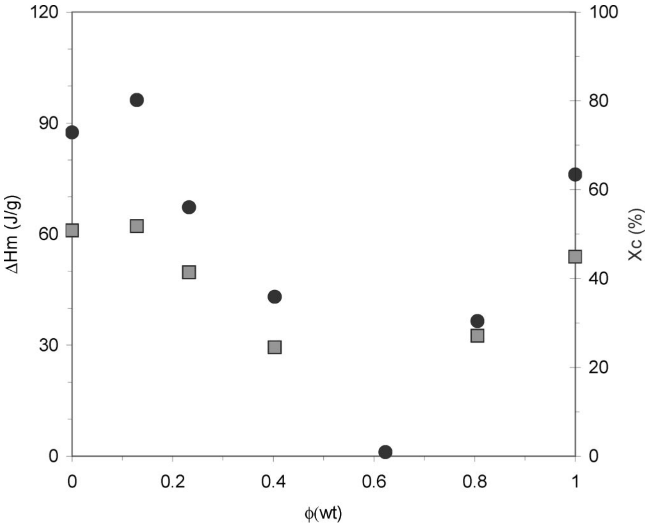

Figure 7. Melting enthalpy from the first DSC scan (ΔH_m, ●) and degree of crystallinity from WAXS diffractograms (χ_c, ■) as a function of copolymer composition (ϕ is the weight fraction of BC units).

phases appears in any diffractograms of Figure 6. This result supports the aforementioned conclusion that the complex thermal behavior of P(BC-*co*-BS) copolymers is associated with a single crystal phase undergoing multiple melting and crystallization processes.

Figure 7 shows a plot of the degree of crystallinity (χ_c, calculated from the WAXS patterns) and of the melting enthalpy (from the first DSC heating scan) as a function of composition. Since both ΔH_m and χ_c depend on the mass of the analyzed samples, copolymer composition is expressed on a weight basis. It is evident that with increasing BC unit content ΔH_m and χ_c follow an analogous trend characterized by a minimum around a BC content of 60 wt %, corresponding to the composition of the amorphous sample poly(BC-*co*-29 mol % BS). WAXS and DSC results both illustrate a behavior typical of random copolymers containing monomer units of two crystallizable homopolymers, which are unable to cocrystallize. Such copolymers are expected to lose their crystallizing ability at intermediate compositions.[13]

Conclusions

Synthesis of random poly(BC-*co*-BS) copolymers containing 18:82 to 86:14 BC/BS unit ratios was accomplished using a metal-free enzyme catalyst either via polycondensation of DEC and DES with BD or by transacylation reactions between preformed PBC and PBS homopolymers. By varying process-variables during polycondensation reactions methods were developed to effective regulate the end-group structures of copolymers, thereby enabling the preparation of predominantly hydroxyl-terminated macromers. Aliphatic poly(carbonate-*co*-ester) diols are potentially important intermediates for producing specialty polyurethanes and other high molecular weight, segmented copolymers. The synthesized copolymers possess higher thermal stability than PBC and are more thermally stable at higher ester unit contents. With changing composition, the poly(BC-*co*-BS) copolymers vary from rigid semicrystalline materials to near completely amorphous, sticky substances. Composition also affects the copolymer crystallizing ability, with BS-rich copolymers crystallizing faster than BC-rich ones. The composition parameter also determines the crystal phase (either PBC type or PBS type) that develops in the copolymers.

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