Synthesis of High Aspect Ratio Bisphenols and Polycarbonates Incorporating Bisaryl Units

David A. Boyles,*,† Tsvetanka S. Filipova,†,‡ John T. Bendler,§ Guy Longbrake,†,⊥ and Josiah Reams†,∥

Department of Chemistry and Chemical Engineering, South Dakota School of Mines and Technology, Rapid City, South Dakota 57701, and Physics Department, United States Naval Academy, Annapolis, Maryland 21402

Received July 8, 2004; Revised Manuscript Received September 30, 2004

ABSTRACT: Theoretical arguments linking monomer geometries to polymer fracture strengths and melt flow properties provide the rationale for design of a series of isomeric, high-aspect ratio bisphenols and new polycarbonates. An efficient synthesis of these monomers in addition to an optimal triphosgenation-based method for the synthesis of high molecular weight polycarbonates is presented. Preparation and polymerization of *o*-, *meta*-, and *p*-tetraaryl bisphenol A are reported, in addition to glass transition temperatures of the new polycarbonates. In accordance with expectations, the *p*- and *m*- isomers form ductile, amorphous high-heat films, while the *o*-isomer produces a relatively low-T_g brittle glass.

Introduction

For over 50 years, efforts to understand the molecular origin of bisphenol A polycarbonate's solid-state ductility have continued, although progress to date is limited and useful structural criteria to guide the design of new high impact polycarbonates are lacking. The remarkable success of bisphenol A−polycarbonate (BPA−PC) (Figure 1) derives from the versatility of its applications which are a function of its properties, including transparency, heat resistance, and excellent impact toughness. The present work is part of a program designed to elucidate the role played by overall monomer shape as a factor influencing ductility.

Ductility necessarily requires that stored elastic energy can be successfully released by diffuse nonlocal shear flow before craze formation and breakdown culminate in brittle failure. All glassy thermoplastics are ductile in compression and conversely, all glassy thermoplastics are brittle when the cavitational stress is sufficiently large relative to the shear stress, implying that ductility ultimately reflects the relative ease of shear flow vs the ease of crazing.[1,2] As is true in metals, shear flow in glassy thermoplastics requires solid-state atomic and molecular motions, and realization of this fact has spawned a host of studies characterizing local motions in polycarbonates,[3−6] especially the low-temperature dynamic mechanical γ process in BPA−PC and its homologues, in the expectation that the γ process is associated with if not responsible for polycarbonate's ductility and toughness.

However, systematic studies of both low-temperature motions and yield stresses σ_y of a wide variety of engineering thermoplastics suggest that the connection between the γ process and ductility is incomplete: (a) a facile low-temperature γ process is apparently necessary but not a sufficient condition for a particular polycarbonate to exhibit ductility;[5,7] (b) with modifications in chemical structure, room-temperature yield stresses of BPA-based thermoplastics[8] vary from a low of about 45 MN/m^2 (for BPA-formal) to a high of nearly 95 MN/m^2 (for tetramethyl BPA−PC), or an overall variation of approximately a factor of 2. In contrast, critical strains to initiate dry crazes ϵ_c in the same group of thermoplastics vary from a low of 0.5% (in BPA-formal) to a high of 2.9% (in BPA-arylate-carbonate copolymers) for an overall variation of nearly a factor of 6.[8] Thus, in this particular group of thermoplastics, ease of craze initiation shows nearly three times as large a variation with chemical structure modification as does the ease of yielding. It is likely, therefore, that the molecular factors which influence crazing contribute at least as much to mechanical toughness as does the dynamic mechanical γ process.

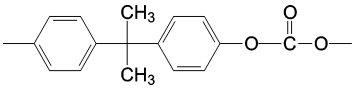


Figure 1. Molecular structure of bisphenol A−polycarbonate (BPA−PC).

Both theory and experiment indicate that the fracture strength of glassy polymers is strongly influenced by monomer geometry and chain flexibility. For example, Vincent[9,10] found from a study of synthetic fibers that the tensile brittle strengths of thermoplastics could be correlated with the molecular cross sectional areas (MCSA) of the polymer chains. In particular, he found that the smaller the MCSA of the chain, the greater was the brittle strength of the polymer. Vincent explained this finding by suggesting that thinner chains could pack more closely together, so that when a fracture surface is created in the glassy polymer more chains will pass through each element of the surface (per unit area) in the case of a thin chain than will do so for a thick chain. Since the difficulty of creating a fracture surface should increase as the number of chain backbones passing through the surface increases, thinner monomers (with higher backbone densities) should exhibit higher brittle strengths.

* Corresponding author. E-mail: David.Boyles@sdsmt.edu.
† South Dakota School of Mines and Technology.
‡ E-mail: Tsvetanka.Filipova@sdsmt.edu.
§ United States Naval Academy.
⊥ E-mail: guylongbrake@yahoo.com.
∥ E-mail: jreams1@juno.com.

10.1021/ma048616m CCC: $30.25
Published on Web 03/30/2005

A more recent and possibly more cogent argument for a relationship between monomer geometries and glassy polymer fracture strengths is provided by the discovery that the entanglement molecular weight of a polymer, M_e, is related by a power law to p, the packing length of the polymer species.[11,12] The packing length of a polymer is defined by [11,13]

$$p = \frac{M}{[\langle R^2\rangle_0 \rho N_a]} = \frac{V_C}{\langle R^2\rangle_0} = \frac{MCSA}{l_k} \quad (1)$$

where M is the molecular weight of the chain, N_a is Avogadro's number, $\langle R^2\rangle_0$ is the mean-squared unperturbed end-to-end distance, ρ is the density of the polymer, V_C is the chain volume, MCSA is the molecular cross sectional area of the chain, and l_k is the Kuhn segment length of the polymer. Equation 1 shows that p is a local quantity independent of molecular weight and that it is proportional to the molecular cross sectional area, MCSA. The relationship between p and M_e is given by[11]

$$M_e = \rho N_a n_t^2 p^3 \quad (2)$$

where n_t (approximately a constant equal to 21) corresponds to the number of entanglement strands in a cube having the dimensions of the tube diameter, d_t. Though the packing length−M_e relation of eq 2 was established from melt and solution properties,[11,12] it is generally agreed that a polymer glass inherits its entanglement structure from the melt, so that eq 2 should also hold below the glass transition T_g. Equations 1 and 2 imply a connection between the chain packing length p and glassy state toughness. Craze strengths are known to be proportional to entanglement densities.[14] Craze extension ratios decrease and craze fibril diameters increase as the entanglement molecular weight M_e decreases, and therefore (according to eq 1) crazes should become tougher as the chains become thinner.[14−16]

The present article reports the synthesis of high aspect ratio (and therefore low MCSA and low p) bisphenols containing one or more bisaryl units and the polycarbonates made from these materials. The present research is part of a broader study to explore the hypothesis that small packing length (or small MCSA) polycarbonates will display improved ductility and toughness. Mechanical properties of these new materials will be reported separately.

Historically, considerable effort has been directed toward the synthesis of modified polycarbonates with *larger* packing lengths and *smaller* aspect ratios than BPA−PC, in particular those from bisphenols with bulky side group substitutions at the isopropylidene unit.[6,7] These common bisphenols have tended toward sphericity, rather than elongation, giving them relatively lower aspect ratios. Consequently, these bulky bisphenols have resulted in polycarbonates which were invariably less ductile than BPA−PC. In contrast, the relatively high aspect ratio bisphenol "tetraaryl BPA" (TABPA)—so named by us as it is an analogue of BPA having four aryl rings rather than the two found in bisphenol A—has been synthesized[17,18] and appears to be an attractive prototype of a new class of high aspect ratio, small packing length p monomers, although the original synthesis was laborious and difficult to scale up. The molecular structure of the polycarbonate formed from TABPA is shown in Figure 2.

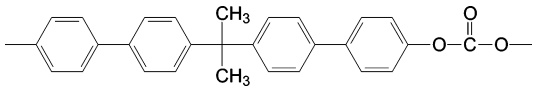


Figure 2. Molecular structure of tetraaryl bisphenol A−polycarbonate (TABPA−PC).

TABPA (bis[4-(4-hydroxyphenyl)phenyl]propane) was first synthesized from bisphenol A by Bendler et al.[17,18] in a process that utilized the Stille[19] cross-coupling reaction. Interfacial and solution polycondensation of TABPA with BPA and phosgene to prepare copolycarbonates (coPCs) was also reported. These copolycarbonates contained approximately 25−75 mol % of TABPA units and were ductile with glass transition temperatures 30−40 °C higher than that of BPA−PC .

More recently, palladium-catalyzed cross-coupling reactions have enjoyed favor for the construction of C_{aryl}−C_{aryl} bonds.[20] The Suzuki[21] reaction, for example, uses an organoboronic acid as one reaction partner. TABPA itself has recently been synthesized by such a modified Suzuki procedure using a diarylborinic acid and Fu's[22] catalyst system, resulting in a higher yielding synthesis for this particular monomer.[23] Distinct drawbacks of this method, however, included the tedious preparation of a commercially unavailable and unstable diarylborinic acid, its difficult separation from the contaminating arylboronic acid and its anhydride byproducts, and the use of an expensive, liganded Suzuki procedure requiring strict exclusion of both oxygen and water.

We report below a facile three-step route for the synthesis of bis[4′-(4-hydroxyphenyl)phenyl]propane (TABPA) applicable also to its *o*- and *m*-isomers, the key step being a ligandless Suzuki aryl coupling reaction which proceeds in aqueous media.[24] Polycondensation results of TABPA with different dihydroxydiaryl compounds using triphosgene to prepare copolycarbonates by solution and interfacial methods are also reported. Preliminary results indicate that polymers formed from the *p*- and *m*- isomers are ductile, while those from the *o*-isomer are brittle, in accordance with theoretical expectations.

Experimental Section

Materials. 2,2′-Diphenylpropane (99%), [bis(trifluoroacetoxy)iodo]benzene PhI($OCOCF_3$)$_2$ (97%), iodine (99.5%), palladium(II)acetate ($Pd(OAc)_2$) (99.9%), potassium carbonate (K_2CO_3) (99+%), 3-methoxyboronic acid (*m*-$CH_3OPhB(OH)_2$) (95%), 2-methoxyboronic acid (*o*-$CH_3OPhB(OH)_2$) (95%), triphosgene (98%), benzyltriethylammonium chloride ($BnNEt_3Cl$) (99%), sodium hydroxide (NaOH) (97%), bisphenol A (99+%), and 4,4′-(hexafluoroisopropylidene)diphenol (HFBP) (97%) were purchased from the Aldrich Chemical Co. and used as received. 4-Methoxyphenylboronic acid (*p*-$CH_3OPhB(OH)_2$) (95%, Optima Chemical Group, LLC), pyridine hydrochloride (Py.HCl) (97+%, Avocado), and 2,2′-(4-hydroxyphenyl)-1,1-dichloroethylene (BPC) (98%, Chemical Synthesis & Engineering Laboratory GE) were used as received without further purification. All solvents were dried and purified by standard procedures.

Instrumentation. IR spectra were determined on a BIO−RAD FT-40 spectrophotometer, using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were recorded with a GE-QE300 operating at 300 or 75 MHz, respectively. ^{1}H and ^{13}C chemical shifts were reported as δ values (ppm) relative to $CDCl_3$ (7.24) or DMSO-d_6 (2.49). Elemental analyses were obtained from Midwest Microlab, LLC, Indianapolis, IN. Reactions were monitored by thin-layer chromatography (TLC) performed on Kieselgel 60 F_{254}, 0.2 mm plates (Merck) with visualization under UV light (254 or 366 nm).

Molecular weights were determined using a Shimadzu HPLC instrument comprised of an LC-10AD pump, SIL-10AF autosampler, with an injection volume of 50μL, followed by two PL gel 5um Mixed-D columns in series maintained at 35 °C in a Shimadzu CTO-10A column oven. All polymer samples were prepared in HPLC-grade THF at concentrations at or near 1 mg/mL, and the flow rate was maintained at 1 mL/min. Degassed HPLC-grade THF served as mobile phase for polymer characterization. Detection was by a Wyatt miniDawn light scattering photometer followed in-line by a Wyatt Optilab DSP differential refractive index detector at 690 nm. Astra software was used for data collection and calculation of absolute molecular weights.

Synthesis of 2,2-Bis(4-iodophenyl)propane, I—BPA, 2. A suspension of 2,2′-diphenylpropane (29.40 g, 149.8 mmol), iodine (38.10 g, 150.1 mmol), and $PhI(OCOCF_3)_2$ (68.80 g, 160.0 mmol) in tetrachloromethane (600 mL) was stirred at 50−55 °C for 1 h. After cooling to room temperature, the suspension was concentrated under reduced pressure. The cloudy white residue was recrystallized from ethanol (53.70 g, 80.02%) giving white needles. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.56−7−59 (d, J = 8.6 Hz, 4H, Ar*H*), 6.92−6.96 (d, J = 8.6 Hz, 4H, Ar*H*), 1.61 (s, 6H, CH_3). Anal. Calcd for $C_{15}H_{14}I_2$: C, 40.21; H, 3.15; I, 56.64. Found: C, 40.10; H, 3.12; I, 56.53.

Synthesis of Bis[4′-(4-methoxyphenyl)phenyl]propane, 3. I−BPA (31.40 g, 70.08 mmol) and p-$CH_3OPhB(OH)_2$ (22.80 g, 150.0 mmol) were dissolved in acetone (100 mL). A solution of K_2CO_3 (58.00 g, 419.7 mmol) in water (100 mL) was then added, and the reaction mixture was stirred 5 min to gentle reflux. After evacuation and flushing with argon, $Pd(OAc)_2$ (5 mg, 0.02 mmol) was added, and the suspension was heated 6 h under reflux and positive argon pressure. Upon cooling to room temperature, the crude product was extracted with methylene chloride (4 × 200 mL) and washed with water (2 × 100 mL) and brine (1 × 150 mL). The combined organic layers were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was recrystallized from ethanol to afford the title compound (27.40 g, 95.70%) as white crystals, mp 198−200 °C. IR (KBr, cm^{-1}): 3025, 2972, 2958, 2836, 1606, 1581, 1520, 1497, 1385, 1365, 1289, 1248, 1183, 1037, 826. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.46−7.53 (m, 8H, Ar*H*), 7.30−7.33 (d, J = 8.6 Hz, 4H, Ar*H*), 6.94−6.97 (d, J = 8.7 Hz, 4H, Ar*H*), 3.84 (s, 3H, OCH_3), 1.74 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.0 (*C*−OCH_3), 149.2 (Ar*C* quat.), 138.1 (Ar*C* quat.), 133.5 (Ar*C* quat.), 128.1 (Ar*C*H), 127.3 (Ar*C*H), 126.4 (Ar*C*H), 114.2 (Ar*C*H), 55.4 (O*C*H_3), 42.6 (Ar−*C*$(CH_3)_2$−Ar), 30.8 (*C*H_3). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.11; H, 6.90.

Synthesis of Bis[4′-(3-methoxyphenyl)phenyl]propane, 4. A procedure similar to that described for **3** was followed using I−BPA (0.90 g, 2.0 mmol), m-$CH_3OPhB(OH)_2$ (0.67 g, 4.4 mmol), K_2CO_3 (1.66 g, 12.0 mmol) and $Pd(OAc)_2$ (1.5 mg). The suspension was heated for 3 h under reflux and positive argon pressure. After usual workup, the residue was recrystallized from ethanol to afford the title compound (0.55 g, 67%) as tan crystals, mp 125−6 °C. IR (KBr, cm^{-1}): 3061, 3024, 2970, 2930, 1606, 1581, 1558, 1479, 1433, 1385, 1365, 1268, 1211, 1119, 875, 832, 778, 696. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.53 (d, J = 8.4 Hz, 4H, Ar*H*), 7.31−7.36 (m, 6H, Ar*H*), 7.16−7.18 (d, J = 7.7 Hz, 2H, Ar*H*), 7.12 (s, 2H, Ar*H*), 6.86−6.89 (d, J = 8.2 Hz, 2H, Ar*H*), 3.85 (s, 3H, OCH_3), 1.75 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0 (*C*−OCH_3), 149.9 (Ar*C* quat.), 142.5 (Ar*C* quat.), 138.5 (Ar*C* quat.), 129.8 (Ar*C*H), 127.3 (Ar*C*H), 126.9 (Ar*C*H), 119.7 (Ar*C*H), 112.8 (Ar*C*H), 112.6 (Ar*C*H), 55.4 (O*C*H_3), 42.8 (Ar−*C*$(CH_3)_2$−Ar), 30.9 (*C*H_3). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 84.01; H, 6.93.

Synthesis of Bis[4′-(2-methoxyphenyl)phenyl]propane, 5. A procedure similar to that described for **3** was followed using I−BPA (1.00 g, 2.23 mmol), o-$CH_3OPhB(OH)_2$ (0.74 g, 4.9 mmol), K_2CO_3 (1.85 g, 13.4 mmol) and $Pd(OAc)_2$ (2 mg). The suspension was heated 6 h under reflux and positive argon pressure. After usual workup, the product was obtained (0.83 g, 91%) as white crystals, which were pure enough to be used as such in the next step, mp 180−2 °C. IR (KBr, cm^{-1}): 3062, 3025, 2932, 2834, 1596, 1581, 1514, 1486, 1436, 1397, 1360, 1260, 1234, 1109, 1028, 836, 761. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50−7.53 (d, J = 8.4 Hz, 4H, Ar*H*), 7.31−7.36 (m, 6H, Ar*H*), 7.16−7.18 (d, J = 7.7 Hz, 2H, Ar*H*), 7.12 (s, 2H, Ar*H*), 6.86−6.89 (d, J = 8.2 Hz, 2H, Ar*H*), 3.85 (s, 3H, OCH_3), 1.75 (s, 6H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.6 (*C*−OCH_3), 149.3 (Ar*C* quat.), 135.8 (Ar*C* quat.), 130.5 (Ar*C* quat.), 131.0 (Ar*C*H), 129.2 (Ar*C*H), 128.5 (Ar*C*H), 126.7 (Ar*C*H), 120.4 (Ar*C*H), 111.2 (Ar*C*H), 55.6 (O*C*H_3), 42.7 (Ar−*C*$(CH_3)_2$−Ar), 30.9 (*C*H_3). Anal. Calcd for $C_{29}H_{28}O_2$: C, 85.26; H, 6.91. Found: C, 85.01; H, 6.92.

Synthesis of Bis[4′-(4-hydroxyphenyl)phenyl]propane, *p*-TABPA, 6. Bis[4′-(4-methoxyphenyl)phenyl]propane, **3**, (8.17 g, 20.0 mmol) and Py.HCl (23.10 g, 199.9 mmol) were added to a beaker and slowly heated to 220−230 °C with stirring. Three 5 g portions of Py.HCl were added over the course of the reaction. The temperature was held at 220−230 °C for 1 h. The resultant viscous, dark, reddish-brown liquid was poured with stirring into 500 mL of water. The solid was collected by filtration and recrystallized from aqueous ethanol. The final product p-TABPA (7.15 g, 94.0%) was fine white crystals, mp 237−239 °C. IR (KBr, cm^{-1}): 3530, 3300−2600, 3020, 2972, 2964, 1609, 1596, 1524, 1498, 1436, 1390, 1380, 1244, 1227, 1174, 1108, 1080, 823. ^{1}H NMR (300 MHz, DMSO-d_6): δ 9.50 (br.s. 2H, exchangeable with D_2O, O*H*), 7.40−7.46 (m, 8H, Ar*H*), 7.22−7.25 (d, J = 8.3 Hz, 4H, Ar*H*), 6.77−6.80 (d, J = 8.3 Hz, 4H, Ar*H*), 1.64 (s, 6H, CH_3). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.4 (*C*−OH), 148.8 (Ar*C* quat.), 137.9 (Ar*C* quat.), 131.2 (Ar*C* quat.), 128.1 (Ar*C*H), 127.4 (Ar*C*H), 126.1 (Ar*C*H), 116.2 (Ar*C*H), 42.4 (Ar−*C*$(CH_3)_2$−Ar), 30.8 (*C*H_3). Anal. Calcd for $C_{27}H_{24}O_2$: C, 85.23; H, 6.36. Found: C, 85.16; H, 6.35.

Solution Polycondensation of Homopolycarbonate PC *p*-TABPA, (Table 1, Entry 2). p-TABPA (0.38 g, 1.0 mmol) was dissolved in 1.5 mL of pyridine and the solution was cooled to 0 °C. A solution of triphosgene (0.124 g, 0.418 mmol) in methylene chloride (3 mL) was added dropwise, and the reaction mixture was vigorously stirred at 0−5 °C for 15 min. The solution became viscous and saturated with pyridine−hydrochloride during this time and was subsequently allowed to warm spontaneously to room temperature. After reaching room temperature, the suspension was stirred for 4 h. A 5% aqueous hydrochloric acid solution (10 mL) was used to neutralize the reaction mixture. The polymer was extracted with methylene chloride (3 × 20 mL) and washed with water (3 × 20 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated. The viscous residue was poured into methanol, whereupon the polymer precipitated and was filtered with subsequent washing with methanol. The polymer was dissolved in methylene chloride and reprecipitated from methanol. The white pure polymer was dried at 100 °C under vacuum for 24 h (0.38 g, 93% yield). IR (KBr, cm^{-1}): 3029, 2967, 2871, 1773, 1610, 1595, 1520, 1495, 1394, 1386, 1228, 1188, 1162, 1005, 821. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59−7.63 (m, 4H, Ar*H*), 7.48−7.51 (m, 4H, Ar*H*), 7.33−7.36 (m, 8H, Ar*H*), 1.75 (s, 6H, CH_3).

Solution Polycondensation of coPC (Table 1, Entries 7—12). BPA was used as comonomer. The copolymers PC p-TABPA−BPA were prepared with triphosgene as described above. IR (KBr, cm^{-1}): 3036, 2968, 2872, 1775, 1604, 1597, 1496, 1466, 1394, 1364, 1227, 1187, 1162, 1005, 822. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59−7.62 (d, J = 8.1 Hz, 4H, Ar*H*), 7.48−7.51 (d, J = 8.1 Hz, 4H, Ar*H*), 7.31−7.35 (m, 8H, Ar*H*), 7.22−7.27 (m, 4H, Ar*H*), 7.17−7.19 (m, 4H, Ar*H*), 1.75 (s, 6H, CH_3), 1.68 (s, 6H, CH_3).

Solution Polycondensation of coPC (Table 1, Entries 15—17). HFBP was used as comonomer. The copolymers PC p-TABPA−HFBP were prepared with triphosgene as described above. IR (KBr, cm^{-1}): 3032, 2970, 2874, 1779, 1608, 1510, 1496, 1395, 1388, 1228, 1190, 1165, 1006, 969, 929, 822. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61−7.63 (d, J = 8.4 Hz, 4H, Ar*H*), 7.49−7.51 (m, 4H, Ar*H*), 7.45−7.47 (m, 4H, Ar*H*), 7.32−7.36 (m, 12H, Ar*H*), 1.76 (s, 6H, CH_3).

Solution Polycondensation of coPC (Table 1, Entries 19—21). BPC was used as comonomer. The copolymers PC

Table 1. Yields and Properties of Polycarbonates Prepared by Solution Polycondensation of *p*-TABPA and Various Diols

PC	diol 1, 1 mol	diol **2**, 1 mol	actual mole ratio diol **1** to diol **2**, %	triphosgene, mol	Py, mL	yield, %	M_w, g/mol	M_n, g/mol	PDI	T_g, °C
1		BPA	100	0.30	3.5	84	47 430	31 610	1.5	150.61
2[a]	*p*-TABPA		100	0.42	1.5	93				173.97
3	*p*-TABPA	BPA	49.7/50.3	0.34	0.75	89	6141	3875	1.6	148.46
4	*p*-TABPA	BPA	49.1/50.9	0.34	1	90	9170	6867	1.3	151.83
5	*p*-TABPA	BPA	51.1/48.9	0.34	1.5	83	6105	3543	1.7	144.21
6	*p*-TABPA	BPA	54.9/45.1	0.34	3.5	37	3133	2347	1.3	149.93
7	*p*-TABPA	BPA	49.7/50.3	0.42	0.75	95	14 500	8640	1.7	171.94
8	*p*-TABPA	BPA	50.2/49.8	0.42	1.5	89	13 700	8636	1.6	161.14
9	*p*-TABPA	BPA	50.2/49.8	0.42	3.5	87	14 370	9934	1.4	166.23
10[a]	*p*-TABPA	BPA	71.0/29.0	0.42	3.5	93				161.37
11	*p*-TABPA	BPA	25.8/74.2	0.42	3.5	93	20 710	14 690	1.4	160.51
12	*p*-TABPA	BPA	17.1/82.9	0.42	3.5	97	19 280	11 300	1.7	149.66
13		HFBP	100	0.42	3.5	86	40 800	27 620	1.5	157.63
14	*p*-TABPA	HFBP	47.7/52.3	0.37	3.5	57	3520	2537	1.4	137.87
15	*p*-TABPA	HFBP	47.3/52.7	0.42	3.5	84	8847	6107	1.4	153.99
16	*p*-TABPA	HFBP	24.9/75.1	0.42	3.5	91	16 170	12 140	1.3	153.86
17	*p*-TABPA	HFBP	14.8/85.2	0.42	3.5	95	19 480	12 020	1.6	160.18
18		BPC	100	0.47	3.5	89	48 990	34 440	1.4	162.54
19	*p*-TABPA	BPC	45.6/54.4	0.42	3.5	94	6251	4518	1.4	138.25
20	*p*-TABPA	BPC	31.5/68.5	0.42	3.5	91	18 520	12 350	1.5	165.95
21	*p*-TABPA	BPC	17.3/82.7	0.42	3.5	97	18 980	12 560	1.5	164.27

[a] Not all dissolved, cloudy solution.

Table 2. Yields and Properties of Polycarbonates Prepared by Interfacial Polycondensation of *p*-TABPA and Various Diols

PC	diol **1**, 1 mol	diol **2**, 1 mol	actual mole ratio diol **1** to diol **2**, %	triphosgene, mol	yield, %	M_w, g/mol	M_n, g/mol	PDI	T_g, °C
22		BPA	100	0.30	93	110 900	72 520	1.5	152.85
23	*p*-TABPA[a]		100	0.40	91				175.77
24	*p*-TABPA	BPA	38.9/61.1	0.34	96	26 910	17 450	1.5	176.37
25	*p*-TABPA	BPA	27.2/72.8	0.34	97	46 690	30 140	1.5	169.75
26	*p*-TABPA	BPA	16.4/83.6	0.34	96	134 130	69 560	1.9	159.12
27	*p*-TABPA	BPA	10.1/89.9	0.34	97	91 040	56 690	1.7	165.68
28		HFBP	100	0.30	92	26 600	10 440	2.2	134.78
29	*p*-TABPA	HFBP	56.4/43.6	0.42	95	30 290	15 860	1.9	188.23
30	*p*-TABPA	HFBP	26.8 /73.2	0.42	87	11 910	4683	2.5	168.13
31	*p*-TABPA	HFBP	23.2/76.7	0.42	97	13 360	6357	2.1	156.47
32		BPC	100	0.42					141.07
33	*p*-TABPA	BPC	51.7/48.3	0.42	94	29 940	14 740	2.0	160.40
34	*p*-TABPA	BPC	29.2/70.8	0.42	97	27 530	17 250	1.6	166.86
35	*p*-TABPA	BPC	28.7/71.3	0.42	91	91 080	53 020	1.7	169.73

[a] Not all dissolved, cloudy solution.

p-TABPA−BPC were prepared with triphosgene as described above. IR (KBr, cm^{-1}): 3035, 2968, 2872, 1775, 1603, 1592, 1496, 1390, 1367, 1226, 1185, 1161, 1005, 974, 888, 861, 822. ^1H NMR (300 MHz, $CDCl_3$): δ 7.60−7.63 (d, J = 8.0 Hz, 4H, Ar*H*), 7.48−7.51 (d, J = 8.0 Hz, 4H, Ar*H*), 7.33−7.35 (m, 12H, Ar*H*), 7.27−7.30 (m, 4H, Ar*H*), 1.75 (s, 6H, CH_3).

Interfacial Polycondensation of Homopolycarbonate PC *p*-TABPA (Table 1, Entry 23). A solution of *p*-TABPA (0.38 g, 1.00 mmol) and 1 N aqueous NaOH (4 mL) was prepared and cooled to 0−5 °C. Triphosgene (0.12 g, 0.40 mmol) and $BnNEt_3Cl$ (10 mg) were dissolved in methylene chloride (10 mL), and the solution was added to aqueous 1 N NaOH immediately. Both phases were then rapidly stirred at 0−5 °C for 15 min and at 10−15 °C for 45 min. The organic phase was separated, washed with water (4 × 50 mL) and poured into methanol (200 mL), and the precipitated polymer was filtered. The polymer was dissolved in methylene chloride, filtered and reprecipitated from methanol (91% yield). Finally, the polycarbonate was dried at 100 °C under vacuum for 24 h.

Interfacial Polycondensation of coPC (Table 2, Entries 22—27, 29—31, and 33—35). BPA, HFBP and BPC were used as monomers. The copolymers PC *p*-TABPA−BPA, PC *p*-TABPA−HFBP, and PC *p*-TABPA−BPC were prepared with triphosgene as described above.

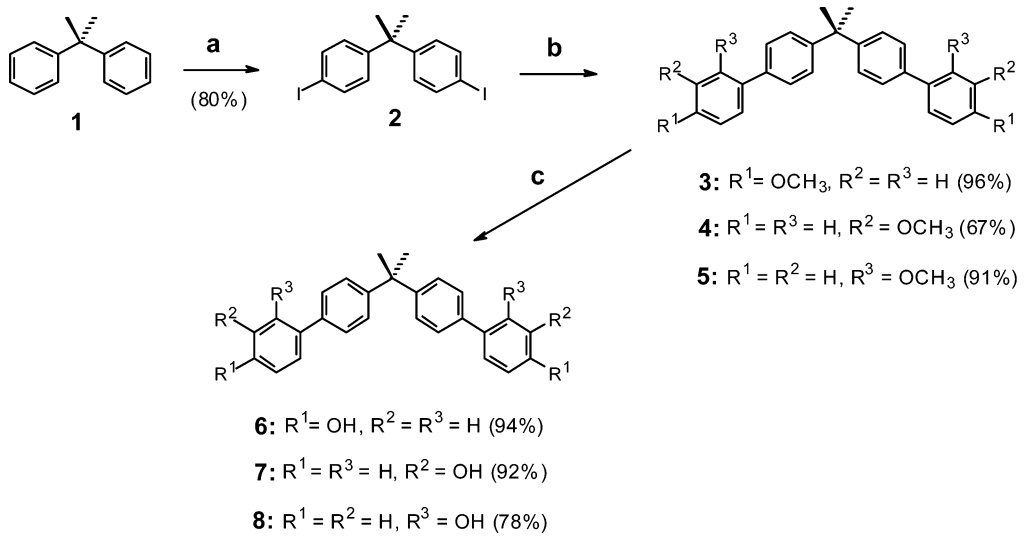
All homopolycarbonates (Table 2, entries **23**, **24**, **29**, **33**) and coPCs (Table 2, entries **23**−**28**, **30**−**32**, **34**−**36**) obtained by interfacial polycondensation were found, via comparison, to be identical with the corresponding PCs obtained from solution polycondensation (IR and ^1H NMR).

Results and Discussion

Synthesis of TABPA Monomers. The synthesis of the desired TABPA monomers was achieved in three steps from commercially available 2,2′-diphenylpropane (Scheme 1).

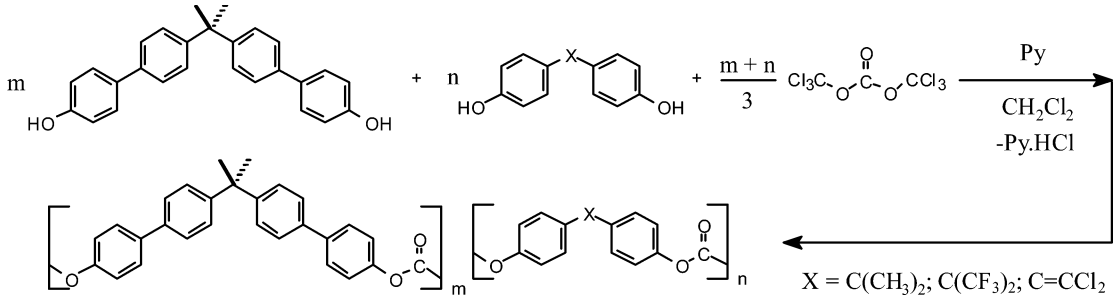
Facile iodination of 2,2′-diphenylpropane with PhI-$(OCOCF_3)_2$/iodine in carbon tetrachloride solution[24] gave I−BPA, **2**, in good yield (80%). Monomers **6**−**8** were prepared from commercially available methoxyarylboronic acids, $CH_3OArB(OH)_2$. The method of Wallow[25] was used to effect the coupling reaction of I−BPA with 2.2 equiv of *p*-$CH_3OArB(OH)_2$ precursor. Anhydrous K_2CO_3 (2.5 equiv) as base and $Pd(OAc)_2$ were mixed in an acetone−water solvent system. The reaction proceeded smoothly under reflux in argon atmosphere for 48 h to afford the desired Suzuki product **3** in 70% yield. The coupling product **3** in Scheme 1 was obtained in excellent yield in 6 h using 5 equiv of anhydrous K_2CO_3 and 2.2 equiv of *p*-$CH_3OArB(OH)_2$. In similar manner the *m*- and *o*-methoxyphenylboronic acids were used to synthesize the *m*- and *o*-isomers **4** and **5** in good yield and purity.

Scheme 1. Synthesis of TABPA Monomers[a]



[a] Key: (**a**) I_2, $PhI(OCOCF_3)_2$, CCl_4, 50−55 °C, 1 h; (**b**) *p*-$MeOPhB(OH)_2$, $Pd(OAc)_2$, K_2CO_3, acetone/water, reflux, 6 h for **3**; *m*-$MeOPhB(OH)_2$, $Pd(OAc)_2$, K_2CO_3, acetone/water, reflux, 3 h for **4**; *o*-$MeOPhB(OH)_2$, $Pd(OAc)_2$, K_2CO_3, acetone/water, reflux, 6 h for **5**; (**c**) Py·HCl, 215−220 °C, 1 h for **6** and **7**; 30 min for **8**.

Scheme 2. Synthesis of Copolycarbonates by Solution Polycondensation



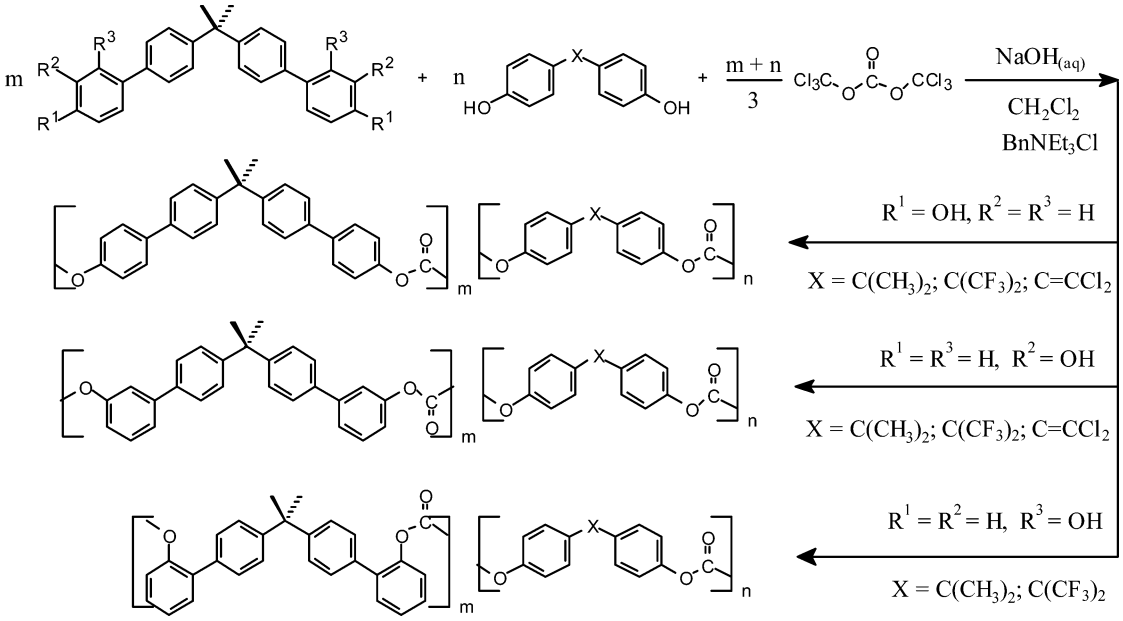
The reactions were monitored by TLC. The *meta* isomer **4** required 3 h reaction time, whereas the *ortho* isomer **5** required 6 h for completion, with the latter reaction giving higher yields. IR and NMR spectroscopy confirmed the structure of compounds **3**−**5**. The ^1H NMR spectrum exhibited two singlets at 1.75 ppm, assigned to the protons of the geminal methyl groups, and a singlet at 3.84 ppm, assigned to the protons of the methoxy group.

Subsequent demethylation of **3**, **4** and **5** to compounds **6**, **7** and **8**, respectively, was performed using Py·HCl.[26] Thus, the dimethoxy-substituted compounds **3**−**5** were treated with Py·HCl at 230 °C, affording the desired *o*-, *m*-, and *p*-tetraaryl BPA isomers in excellent yields. Spectroscopic data were in agreement with the structure of compounds **6**, **7**, and **8**. The infrared spectra indicated a broad absorption band at 3500−3200 cm^{-1} from the OH stretch. ^1H NMR spectra showed a broad singlet at 9.50 ppm for the same group. ^{13}C NMR spectra were also consistent with the assigned structures, exhibiting a methyl carbon at 30.8 ppm, the quaternary isopropylidene carbon at 42.5 ppm, four quaternary aromatic carbons and four secondary aromatic carbons for compound **6** and six secondary aromatic carbons for compounds **7** and **8**. We have applied this practical sequence to the preparation of up to 200 g of monomer **6**.

Polymer Synthesis. Several processes for the preparation of aromatic PCs have been reported, including the Schotten−Baumann reaction of phosgene and an aromatic diol in an amine-catalyzed interfacial condensation reaction,[27] direct reaction of phosgene with a bisphenol solution containing a tertiary amine,[28] and base-catalyzed transesterification of a bisphenol with a monomeric carbonate such as diphenyl carbonate.[29] We employed both solution and interfacial polycondensation methods for the monomers described above. While BPA−PC is commercially prepared using phosgene gas, the literature indicated that relatively high molecular weight PCs can also be obtained using more convenient triphosgene on a laboratory scale.[30−33] Sun et al.,[30] utilized triphosgene to prepare thermotropic liquid crystalline polycarbonates although viscosity data only was reported, making it difficult to ascertain the molecular weights of the materials. Likewise, Marks, et al.,[31] synthesized randomly branched polycarbonates utilizing triphosgene obtaining molecular weights M_w in the range of 16 300 to 75 900 g/mol with polydispersity indices (PDI) ranging from 2.5 to 6.6. Also, Eiffler et al.,[32] disclosed a triphosgene procedure with reported polycarbonate molecular weights of M_n = 13 450 g/mol and M_w = 45 670 g/mol. Our solution polymerizations utilized pyridine and methylene chloride as acid scavenger and solvent, respectively. The general reaction route and the structures of polycarbonates are depicted in Scheme 2.

Solution polycondensation was performed with a 50/50 molar ratio of *p*-TABPA and BPA monomers using various amounts of triphosgene and pyridine to ascertain optimal reaction conditions. Triphosgene was varied from 0.30 to 0.47 mol, and the pyridine was varied from 0.75 to 3.5 mL. Results are summarized in Table 1.

Scheme 3. Synthesis of Copolycarbonates by Interfacial Polycondensation



Extraction of the reaction mixture with methylene chloride, followed by a water wash, and precipitation into methanol afforded polymeric materials as white powders. A second reprecipitation afforded polymers in 37−95% yield with M_w from 3133 to 14 500 g/mol and PDI from 1.3 to 1.7. During workup, the byproduct pyridine hydrochloride dissolved in water, and decomposition of the chloroformate-pyridine complex at both ends of the polymer chain occurred. The molecular weight and yield of the polymers show a marked dependence on the amount of triphosgene and pyridine. Polycondensation with 0.42 mmol of triphosgene and 1 mmol of diols and pyridine in the range of 0.75−3.5 mL gave the best results. In the case of entry **9** (Table 1), a copolymer with a moderate molecular weight (M_w = 14 370 g/mol) was obtained which displayed a narrow size exclusion chromatography (SEC) curve and a PDI of 1.4. A series of copolycarbonates was prepared from *p*-TABPA with BPA (Table 1, entries **10**−**12**), HFBP (Table 1, entries **14**−**17**), and BPC (Table 1, entries **19**−**21**) under the reaction conditions used for synthesis of the copolymer in entry **9**. The molar ratio of diols was varied from 75/25 to 15/85. Thus, a reaction of 75 mol % of *p*-TABPA and 25 mol % of BPA afforded PC entry **10** in 93% yield. The copolymer was slightly soluble after heating in methylene chloride, chloroform, chlorobenzene, *o*-dichlorobenzene, or THF. Levels of *p*-TABPA greater than 75 mol % gave essentially insoluble materials, possibly of high molecular weight polymers since the homopolymer of *p*-TABPA was also insoluble. For this reason further copolymers in this study were prepared using not more than 50 mol % of *p*-TABPA monomer.

The coPCs were soluble in methylene chloride, chloroform, chlorobenzene, or *o*-dichlorobenzene, and films could be cast from solvent. Only the homopolymer of *p*-TABPA, entry **2,** and copolymer entry **10** were poorly soluble in all common organic solvents, although they could be dissolved in larger quantities of methylene chloride, as was necessary during reaction workup. The chemical structure of the polymers was confirmed by FTIR and ^{1}H NMR spectroscopy. The IR spectra of the polymers exhibited strong absorption bands at 1776 ± 3 cm^{-1}, the region assigned to the stretching vibration of C=O groups, and 1228, 1186, 1162 cm^{-1}, the regions assigned to the ether groups. All are characteristic absorptions of the aromatic polycarbonate system. Quantification of ^{1}H NMR signal intensities indicated that monomer incorporation into the polymers was close to the feed ratio. The ^{1}H NMR spectra revealed that the incorporation of *p*-TABPA and BPA, easily detectable by sharp signals at 1.75 and 1.68 ppm, respectively, were 71.0% and 29.0% (feed ratio of 75−25), 50.2% and 49.8% (feed ratio of 50−50), 25.8% and 74.3% (feed ratio of 25−75). The ^{1}H NMR spectra of PC entries **15**−**17** and PC entries **19**−**21** also indicated equimolar incorporation of the two monomers, which is reasonable for polycondensation in an organic reaction medium.

The weight-average molecular weights of the series of copolycarbonates PC *p*-TABPA−BPA (Table 1, entries **9**−**12**), PC *p*-TABPA−HFBP (Table 1, entries **14**−**17**), and PC *p*-TABPA−BPC (Table 1, entries **19**−**21**) were 13 700 to 20 710 with a PDI in the range of 1.4−1.7, 8847 to 19 480 with a PDI of 1.3−1.6, and 6251 to 18 980 with a PDI of 1.4−1.5, respectively, determined by GPC. As seen from Table 1, increasing percentages of the comonomers BPA, BPC, and HFBP resulted in a proportional increase in the molecular weight of the copolymer, although polydispersity remained approximately constant at 1.3−1.7. The aforementioned increase in average molecular weight M_w associated with increased comonomer concentration was likely due to the increase in solubility of the resulting copolymers with BPA, BPC and HFBP in the polymerization process.

Liquid−liquid-phase transfer catalysis (PTC) polycondensation was used in order to obtain higher molecular weight polycarbonates. PTC polycondensation was simpler, required a shorter reaction time, and in the case of liquid−liquid systems, obviated the use of anhydrous solvents and reagents. The transport of the anionic species from aqueous medium into the organic medium was ensured by catalytic amounts of $BnNEt_3$-Cl as a lipophilic transfer agent.[34]

The general reaction route and the structures of polycarbonates thus obtained by PTC polymerization

Table 3. Yields and Properties of Polycarbonates Prepared by Interfacial Polycondensation of *m*- and *o*-TABPA and Various Diols

PC	diol **1**, 1 mol	diol **2**, 1 mol	actual mole ratio diol **1** to diol **2**, %	triphosgene, mol	yield, %	M_w, g/mol	M_n, g/mol	PDI	T_g, °C
36	*m*-TABPA[a]		100	0.42	90				125.95
37	*m*-TABPA	BPA	58.1/41.9	0.34	91	154 400	64 460	2.4	183.62
38	*m*-TABPA	BPA	41.0/59.0	0.34	97	70 840	39 600	1.8	150.32
39	*m*-TABPA	BPA	19.2/80.8	0.34	98	46 250	29 180	1.6	150.25
40	*m*-TABPA	HFBP	41.3/58.7	0.42	84	182 300	96 050	1.9	158.89
41	*m*-TABPA	HFBP	22.3/77.7	0.42	79	30 880	13 700	2.3	149.62
42	*m*-TABPA	HFBP	19.5/80.5	0.42	89	27 530	5588	4.9	143.47
43	*o*-TABPA		100	0.42	88	8067	3104	2.6	100.31
44	*o*-TABPA	BPA	29.6/70.4	0.34	98	15 890	11 730	1.4	129.61
45	*o*-TABPA	HFBP	33.1/66.9	0.42	83	12 190	9362	1.3	121.75

[a] Not all dissolved, cloudy solution.

are shown in Scheme 3. TABPA and corresponding monomers BPA, HFBP, and BPC were dissolved in aqueous 1 N NaOH. Methylene chloride containing $BnNEt_3Cl$ and triphosgene were added and the two-phase system was stirred for 1 h. When the polymer either precipitated from the methylene chloride solution or when gelation occurred, the organic layer was separated from the aqueous layer, and the methylene chloride solution was poured into cold methanol. Thus, the *p*-, *m*- and *o*-TABPA monomers were used to prepare a series of copolycarbonates. Maintaining the reaction temperature at 0−5 °C for 15 min and subsequently at 10−15 °C for 45 min with an optimal amount of triphosgene (0.30−0.42 mmol per 1 mmol of diols) produced 91−97% pure polycarbonates. The results of the interfacial polycondensation of TABPA isomers with various diols are summarized in Tables 2 and 3. With the exception of the *p*- and *m*-TABPA homopolymers, all of the PCs were soluble in chlorinated solvents or THF. The *p*- and *m*-TABPA homopolymers were at best only slightly soluble in these solvents.

The successful synthesis of PCs was confirmed by IR and ^{1}H NMR. All homopolycarbonates (Table 2, entries **22**, **23**, **28**, **32**) and coPCs (Table 2, entries **22**−**27**, **29**−**31**, **33**−**35**) obtained by interfacial polycondensation were identical with the corresponding PCs obtained from solution polycondensation (IR and ^{1}H NMR). The IR spectra of the isolated polymers exhibited the expected bands, specifically, a sharp CO-band at 1777 ± 4 cm^{-1}. The ^{1}H NMR spectrum of the *m*-TABPA homo- and copolymers displayed a singlet at 1.74 ppm, the shift assigned to isopropylidene protons of *m*-TABPA and a singlet at 1.67 ppm from the methyl protons of BPA (Table 3, entries **37**−**39**). The protons of the aromatic rings were shifted to a higher field compared with the *p*-isomer and appeared as multiplets at 7.47−7.51, 7.30−7.35, and 7.16−7.20 ppm.

Interpretation of structure−property relationships requires knowledge of the copolymer compositions and sequence distributions for the monomer units. Interfacial polycondensation of two different diols does not necessarily result in coPCs having either the composition of the feed ratio or a random sequence, as different solubilities and acidities of the OH groups may cause differences in monomer reactivity ratios. ^{1}H NMR spectra. indicated that the average incorporation of the monomer units in all the series in Tables 2 and 3 (TABPA−BPA, TABPA−HFBP, TABPA−BPC) was close to the feed ratio used. The ^{13}C NMR spectra of the two *p*-TABPA−BPA coPCs synthesized by solution (Table 1, entry **11**) and interfacial (Table 2, entry **25**) method were evaluated. The ^{13}C NMR spectra revealed that the carbonyl signals were sensitive to sequence effects, i.e., to diads. All three possible diads were resolved. The coPC **11** was found to be completely random (according to the deviation from random statistics given by: c = P{AB}/P{A}P{B} $c = 1$). The coPC **25** had a slight tendency toward blocking ($c = 0.9$).[35]

The molecular weights of coPCs prepared via interfacial polycondensation technique (Table 2) were much higher than the molecular weights of coPCs prepared by solution polycondensation. The results in Table 2 demonstrate that different proportions of monomers generally had an effect on the molecular weight of the resulting coPCs. The *p*-TABPA−BPA PCs were obtained in high yield with molecular weights in the range of 26 910−134 130 g/mol. The weight-average molecular weight increased as the percent of BPA monomer increased. The same behavior was observed in the *p*-TABPA−BPC PCs.

It was also noted that increased mole percent of *m*-TABPA monomer led to increasing molecular weight of coPCs (Table 3, entries **37**−**39** and **40**−**42**). Copolymers of BPA and HFBP with *m*-TABPA showed a dramatic increase in molecular weight as the mole percent of *m*-TABPA monomer was increased. Weight-average molecular weights ranged from 46 250 to 154 400 g/mol for *m*-TABPA−BPA coPCs and from 27 530 to 182 300 g/mol for *m*-TABPA−HFBP coPCs. These results are in contrast to the results for the *para* analogue. Unlike the distal aryl rings in the *para* analogue which experience free rotation having no effect on the directionality of the *p*-hydroxyl group, free rotation in both the *meta* and *ortho* analogues leads to a rotational continuum of possibilities for directionality of chain growth as well as differences in solid-state chain dynamics of the isomeric polymers.

The fact that the *ortho* analogue gave lower molecular weights—ranging from 8067 to 15 890 g/mol—than either the *meta* and *para* analogues, may be attributed to greater steric crowding in the vicinity of the hydroxyl group leading to hindered chain growth during the polymerization process. No evidence for cyclic oligomers in any of the purified polymers was noted by SEC. Comparison between films cast from isomeric *para* and *ortho* copolymers most similar in molecular weights and composition (Table 1, entries **11**−**12** and Table 3, entry **44**) showed distinct differences in film quality: the *para* formed tough films while the *ortho* formed relatively brittle films.

Conclusions

An efficient synthesis of the high aspect-ratio monomer bis[4′-(4-hydroxyphenyl)phenyl]propane and its

ortho and *meta* isomers has been achieved in three steps with high purity and an overall yield of 72−75%. Solution and interfacial polycondensations with triphosgene have been optimized and have proven successful in giving good incorporation of the new monomers into high molecular weight polycarbonates having narrow polydispersities, representing an improvement over previously reported triphosgenations. The satisfactory molecular weights obtained from the triphosgene method afforded clear and tough films which could be cast from concentrated solutions of the *meta* and *para* polymers. The availability of these new monomers and their polycarbonates affords a new series of compounds with which we are now able to further investigate the theoretical underpinnings prompting their design.

Our findings have implications for the determining influence of aspect ratios of bisphenol monomers not only on the ease of their polymerization to high molecular weight polycarbonates, but also on their ability to significantly influence entanglement molecular weights and segmental conformational chain motion in the three isomers studied. Monomer aspect ratio may therefore be a fundamental factor governing both molecular and macroscopic polymer properties. We are currently in the process of monomer and polymer scale-up for mechanical testing to study the effects of monomer size and shape.

Acknowledgment. The authors of this paper gratefully acknowledge support from the National Science Foundation (DMR-98-15957) and the Department of Defense-Army Research Office (DAAD19-01-1-0482). We thank Dr. Elizabeth Williams of GE for kindly allowing us to publish her ^{13}C NMR sequence distribution studies.

Supporting Information Available: Text giving synthetic procedures for the *meta* and *ortho* monomers and their polycarbonates and figures showing infrared as well as ^{1}H NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Ward, I. M. *Mechanical Properties of Solid Polymers*; John Wiley and Sons: New York, 1983.
(2) Kambour, R. P. *Macromol. Rev.* **1973**, *7*, 1.
(3) Boyer, R. F. *Polym. Eng. Sci.* **1968**, *8*, 161.
(4) Heijboer, J. *Br. Polym. J.* **1969**, *1*, 3.
(5) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54.
(6) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9421.
(7) Bendler, J. T. *Comput. Theor. Polym. Sci.* **1998**, *8*, 83.
(8) Kambour, R. P. *Polym. Commun.* **1983**, *24*, 292.
(9) Vincent, P. I. *Nature (Phys. Sci.)* **1971**, *233*, 104.
(10) Vincent, P. I. *Polymer* **1972**, *13*, 558.
(11) Fetters, L. J.; Lohse, D. J.; Graessley, W. W. *J. Polym. Sci., B: Polym. Phys.* **1999**, *37*, 1023.
(12) Fetters, L. J.; Lohse, D. J.; Milner, S. T.; Graessley, W. W. *Macromolecules* **1999**, *32*, 6847−6851.
(13) Heymans, N *Macromolecules* **2000**, *33*, 4226.
(14) Kramer, E. J. *Adv. Polym. Sci.* **1983**, *52/53*, 1.
(15) Brown, H. R. *Macromolecules* **2001**, *34*, 3720.
(16) Baljon, A. R. C.; Robbins, M. O. *Macromolecules* **2001**, *34*, 4200.
(17) Bendler, J. T.; Longley, J. C.; Schmidhauser, K. L. US Patent 5,281,689, 1994.
(18) Bendler, J. T.; Schmidhauser, J. C.; Longley, K. L. US Patent 5,319,149, 1994.
(19) Milstein, D.; Stille, J. K. *J. Am. Chem. Soc.* **1978**, *100*, 3636.
(20) Tsuji, J. *Palladium Reagents and Catalysts*; Wiley: Chichester, England, 1995.
(21) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. (c) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419.
(22) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5478.
(23) Hao, J.; Boyles, D. A. Presented at the 224th ACS National Meeting, Division of Organic Chemistry, Boston, MA, August 18−22, 2002.
(24) Merkushev, E. B.; Simarkhina, N. D.; Koveshnikava, G. M. *Synthesis* **1980**, 486.
(25) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *Org. Synth.* **1997**, *75*, 61.
(26) Lesiak, T.; Nowakowski, J. *J. Prakt. Chem.* **1981**, *323*, 684.
(27) (a) Schnell, H.; Bottenbruch, L.; Krimm, H. Belgian Patent 905141, 1945. (b) Schnell, H. *Angew. Chem.* **1956**, *68*, 633. (c) Schnell, H. *Ind. Eng. Chem.* **1959**, *51*, 157. (d) Morgan, P. W. *J. Polym. Sci., Part A* **1964**, *2*, 437.
(28) (a) Fox, D. W.; US Patent *3,144,432*, 1964. (b) Schnell, H. *Chemistry and physics of polycarbonates*, John Wiley: New York, 1964. (c) Moore, J. A.; Tannahill, T. *High Perform. Polym.* **2001**, *13*, 305.
(29) (a) Fox, D. W. (to General Electric Co.) Aust. Patent 221,-192, 1959. (b) Belg. Patent 532,543 to Farbenfabricken Bayer AG, 1954. (c) Kim, W. B.; Lee, J. S. *J. Appl. Polym. Sci.* **2002**, *86*, 937 and references therein. (d) Woo, B.; Choi, K. Y. *Ind. Eng. Chem. Res.* **2001**, *40*, 1312.
(30) (a) Sun, S. J.; Hsu, K. Y.; Chang, T. C. *Polym. J.* **1997**, *29*, 25. (b) Sun, S. J.; Liao, Y. C.; Chang, T. C. *J. Polym. Sci., Part A* **2000**, *38*, 1852.
(31) Marks, M. J.; Munjal, S.; Namhata, S.; Scott, D. C.; Bosscher, F.; De Letter, J. A.; Klumperman, B. *J. Polym. Sci., Part A* **2000**, *38*, 560.
(32) Eiffler, J.; Jueptner, G. A. US Patent 6,225,436, 2001.
(33) McCarthy, T. F.; Schwind, D. B.; Smith, G. C. US Patent 6,-153,721, 2000.
(34) Mijs, W. S. *New Methods for Polymer Synthesis*; Plenum Press: New York, 1992.
(35) The ^{13}C NMR data and analysis were performed by Dr. Elizabeth Williams of GE Global Research, Niskayuna, NY, who kindly gave permission for us to use them.

MA048616M