

Interfacial Synthesis and Characterization of Random and Segmented Block Bisphenol A–Tetrabromobisphenol A Copolycarbonates

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SYNOPSIS

The chain sequence architecture of bisphenol A–tetrabromobisphenol A copolycarbonates depends on the process employed to prepare them. An interfacial process involving a single-step phosgenation produces a segmented block copolymer, contrary to previous assumptions. An interfacial two-step phosgenation process allows the preparation of random copolycarbonates. In each process the control of the pH of the aqueous phase of the two phase reaction mixture is required to achieve complete comonomer conversion to copolymer and to obtain the desired sequence architecture. The chain sequence architecture of these copolycarbonates can be estimated by examination of their Fourier transform infrared spectra. The relative bandwidth of the carbonate stretching band is roughly proportional to the copolycarbonate number average sequence length, allowing the facile distinction between block and random copolymers. The number average sequence lengths of these copolycarbonates were quantified by carbon-13 NMR spectroscopy. These analyses showed that the one-step phosgenation process yields segmented block copolycarbonates having number average sequence lengths from about 4 to 9, and the two-step phosgenation process produces random copolycarbonates having sequence lengths from 1.6 to 2. The distribution of the aromatic carbon triads of these random copolymers shows them to have an alternate-segmented block architecture, which is consistent with the synthesis conditions, rather than a statistically random distribution of comonomer segments. Dynamic mechanical analysis of two of these copolycarbonates shows a dependence of their low temperature secondary transitions on the copolymer sequence structure. A segmented block copolycarbonate, having a number average sequence length of about 4, displays two distinct peaks in its $\tan \delta$ curve at temperatures corresponding to those transitions observed in the respective homopolymers. The $\tan \delta$ curve of a random copolycarbonate shows a single low temperature secondary transition midway between those of the homopolymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Bisphenol A polycarbonate (BA PC) is a widely used engineering thermoplastic utilized for its optical clarity, high toughness, and moderately high heat distortion temperature.¹ Numerous copolycarbonates (coPCs), based on BA and assorted other diphenols, have been prepared in order to improve upon the properties of the homopolymer.^{1–4} Among the most widely studied are the halogenated BA

coPCs, which have better ignition resistance properties and higher glass transition temperatures (T_g). In particular, PCs and coPCs based on tetrabromobisphenol A (TBBA) have found use as ignition-resistance additives in BA PC.² As a result, the ability to prepare bisphenol A–tetrabromobisphenol A copolycarbonates (BA-TBBA coPCs) by variations on the standard interfacial BA PC process² is of significant technological importance.

Among the most significant characteristics of copolymers in general is their chain sequence architecture.⁵ Linear copolymers are classified as alternate, random, or block. Alternate copolymers have

an alternate placement of comonomer repeat units, while random copolymers have a statistical distribution of comonomers in the copolymer chain. These structures give homogeneous materials having an average of the properties of the homopolymers obtained from the respective monomers. Block copolymers are composed of groups of comonomer units. Block copolymers are further characterized as diblock (A_nB_m), triblock ($A_nB_mA_n$), or segmented block [$(A_xB_y)_n$]. The properties of block copolymers are highly dependent on their chain sequence structure. In general, both block species contribute to the overall properties of these copolymers. The properties of segmented block copolymers approach those of random copolymers as the comonomer block lengths decrease. Phase separation may occur, which can also contribute to the block copolymer physical and chemical behavior.

Many articles and patents have addressed the synthesis of coPCs from diphenols and ortho-substituted diphenols. Most of these describe processes in which mixtures of comonomers, such as BA and TBBA,⁶⁻⁹ BA and tetrachlorobisphenol A (TCBA),¹⁰ and BA and various tetraalkyl-substituted diphenols,^{11,12} are phosgenated under interfacial conditions. These conditions are purported to yield either statistical or random copolymers, but, as shown by this study, these products are block coPCs. "Short block chains" are produced by the successive addition of BA during the phosgenation of an interfacial mixture containing TCBA.^{13,14} Coupling of BA oligocarbonates with TBBA,¹⁵⁻¹⁹ with TCBA,²⁰ or with tetraalkylbisphenol A derivatives²¹ necessarily only yields block copolymers.

Bischloroformates of diphenols can be used as intermediates in the synthesis of coPCs.²² Random or alternate copolymers are allegedly formed by the polycondensation of the bischloroformates of BA and TBBA,²³ and of BA bischloroformate with tetraalkyldiphenols,^{24,25} but the chain sequence architectures of these coPCs were not characterized. In any event, the separate preparation of the bischloroformates used in these processes limits their practical application.

In this study, the interfacial synthesis of 1:1 BA-TBBA coPCs having either random or segmented block sequence distributions was achieved. It is shown that the conventional one-step phosgenation of a mixture of the bisphenols produces segmented block coPCs rather than random coPCs, as previously assumed. Random coPCs can be produced by a two-step interfacial process involving phosgenation of TBBA and subsequent coupling with BA. These copolymers were analyzed by gel permeation

chromatography (GPC), viscometry, and differential scanning calorimetry (DSC). The chain sequence architecture of these coPCs was characterized by Fourier-transform infrared spectroscopy (FTIR), carbon-13 nuclear magnetic resonance spectroscopy (¹³C-NMR), and by dynamic mechanical analysis (DMA).

RESULTS AND DISCUSSION

Synthesis

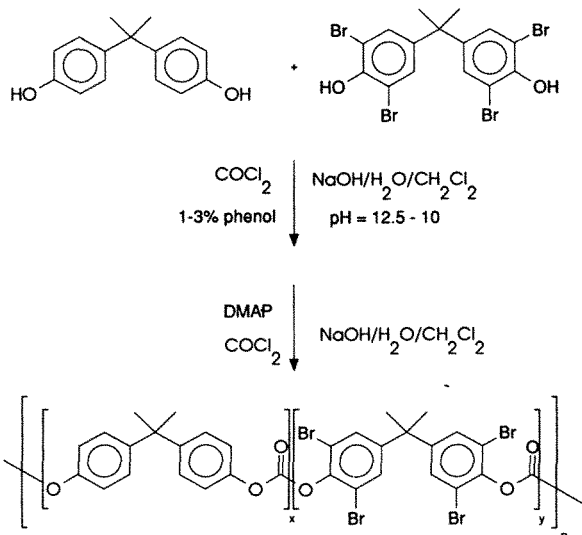
The standard interfacial process to produce BA PC involves phosgenation of a mixture of BA, a mono-phenol chain terminator (such as phenol), an organic solvent such as methylene chloride, water, and aqueous sodium hydroxide, to form a mixture of organic soluble oligomeric bischloroformates, followed by coupling of those oligomers in the presence of a tertiary amine catalyst.² Control of the pH of the aqueous phase as well as the type of tertiary amine catalyst employed proved important in the preparations of BA-TBBA coPCs. The one-step phosgenation processes described below entail a single phosgenation step prior to coupling, whereas the two-step phosgenation process involves phosgenation and phosgenation/coupling steps.

One-step Processes

BA PC can be prepared with complete BA conversion by interfacial phosgenation at an aqueous phase pH of 12.0–12.5 and triethylamine catalyzed coupling at the same aqueous phase pH.² Phosgenation of BA, TBBA, and 1–3 mol % (based on total comonomers) phenol chain terminator under these conditions gave a badly emulsified copolymer solution and significant amounts of unreacted TBBA.

The interfacial synthesis of high molecular weight TBBA PC requires the use of a lower aqueous phase pH of about 10 and certain types of substituted pyridine coupling catalysts, such as 4-*N,N*-dimethylaminopyridine (DMAP).²⁶ Thus, in order to prepare BA-TBBA coPCs with complete comonomer conversion and without emulsification, the key aspects of the processes to prepare the respective homopolymers were combined.²⁷ Equimolar amounts of BA and TBBA in the presence of 1–3 mol % phenol were phosgenated under interfacial conditions at about pH 12.5 to nearly complete comonomer conversion, then the pH was allowed to drop with added phosgene to pH 10 (Scheme 1).

At the lower pH level phosgene was added to



Scheme 1 One step phosgenation process for BA-TBBA CoPCs.

complete the conversion of TBBA to its bischloroformate derivative. Coupling of the mixture of oligomeric bischloroformates at pH 12.5 in the presence of DMAP gave a copolymer solution that did not emulsify and was free on unreacted comonomers. As will be shown below, the BA-TBBA coPC produced by this process is a segmented block copolymer.

Two-step Process

To prepare a random BA-TBBA coPC, a new two-step phosgenation-phosgenation/coupling process was devised.²⁸ In the first step in this synthesis TBBA and 1–3 mol % phenol are phosgenated at pH 10 to complete TBBA conversion to form predominantly its bischloroformate (Scheme 2).

Then, a slurry of BA and aqueous sodium hydroxide is added and the mixture is agitated with a catalytic amount of DMAP while maintaining a pH of 12.5 to effect coupling of BA with TBBA bischloroformates. Competing with the coupling reaction is hydrolysis of TBBA bischloroformates, so the resulting reaction product is an emulsified mixture of BA, TBBA, and phenolic capped alternate BA-TBBA oligocarbonates. To complete the conversion of all of the phenolics to carbonates additional phosgene is added at pH 12.5 to 10.

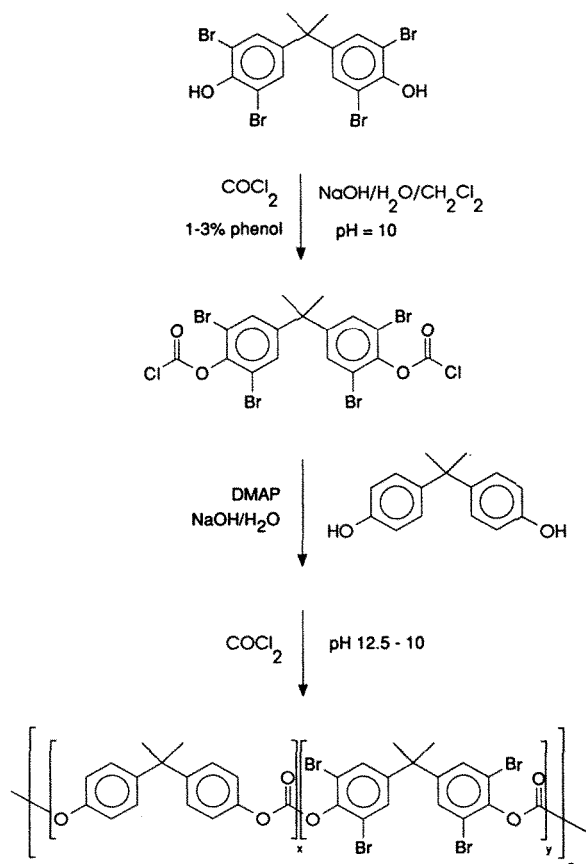
Two process factors contribute to optimizing the selectivity of the reaction of BA and TBBA bischloroformates to the alternate oligocarbonates. The presence of residual phosgene after phosgenation of TBBA will produce BA oligocarbonates with the

addition of BA. These oligomers increase the blockiness of the resulting coPC and can be eliminated at this step by purging the reaction mixture with nitrogen. To minimize the amount of TBBA bischloroformate hydrolysis upon addition of the BA slurry, no excess sodium hydroxide was employed.

Characterization

Molecular Weight and Glass Transition Temperature

The molecular weight of the BA-TBBA coPCs prepared by these two processes, estimated by GPC and intrinsic viscosity ($[\eta]$) measurements, as well as the glass transition temperatures (T_g) of these copolymers as determined by DSC, were evaluated as a function of phenol terminator level (Table I). CoPC molecular weight was controlled as expected for the mol % phenol terminator employed. For BA PC, the critical molecular weight (M_c), that at which many polymer properties such as T_g become nearly



Scheme 2 Two step phosgenation process for BA-TBBA CoPCs.

Table I Molecular Weight and T_g of BA-TBBA CoPCs

Process	% Phenol	M_w	M_n	M_w/M_n	T_g	$[\eta]$
Two-step	3.0	28,263	9,328	3.03	185	0.28
One-step	2.0	45,090	16,638	2.71	210	0.45
Two-step	2.0	44,568	21,955	2.03	207	0.40
One-step	1.5	57,133	19,939	3.04	209	0.47
One-step	1.0	101,246	45,402	2.23	215	0.65

invariant with increasing molecular weight, is at $[\eta] = 0.45$.²⁹ At 2% or less phenol terminator the coPC $[\eta]$ reaches that range and the coPC T_g becomes relatively constant, thus giving an estimate of the M_c of these copolymers. The average T_g of the higher molecular weight coPCs is about 210°C, midway between that of the respective homopolycarbonates, BA PC (155°C) and TBBA PC (265°C).

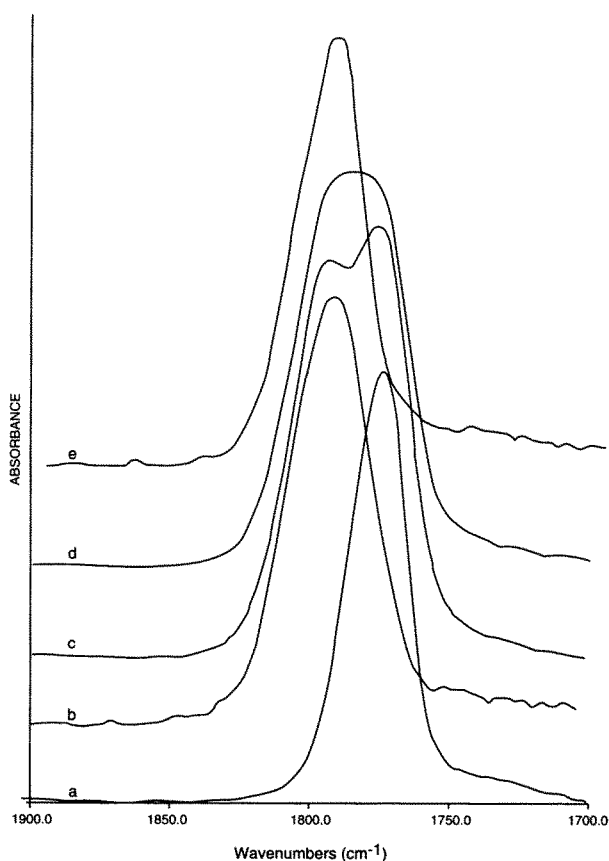


Figure 1 Carbonate band in the FTIR spectra of BA PC, TBBA PC, and BA-TBBA CoPCs. (a) BA PC; (b) TBBA PC; (c) 2 : 1 blend of BA PC and TBBA PC; (d) BA-TBBA coPC, one-step process; (e) BA-TBBA coPC, two-step process.

Carbonate Bandwidth by FTIR

FTIR analysis of the carbonate (CO_3) bandwidth of BA-TBBA coPCs provides an estimation of the relative comonomer sequence lengths. The frequency of the CO_3 absorption band is dependent on the *ortho* substituents of the diphenol precursor. The CO_3 bands of BA PC and TBBA PC appear at 1776 cm^{-1} and 1796 cm^{-1} , respectively [Fig. 1 (a,b)]. From expanded plots of the CO_3 region ($1700\text{--}1900\text{ cm}^{-1}$) the bandwidths at half-height were calculated and normalized with respect to BA PC (Table II). Considering the CO_3 bandwidth shift and the slightly broader band in TBBA PC (entry b), a completely alternate BA-TBBA coPC is expected to have a CO_3 band at 1785 cm^{-1} and a bandwidth of about 1.1. The presence of BA and TBBA CO_3 blocks in the coPC introduces absorptions at the homopolymer CO_3 frequencies and, thus, broadens the band of the copolymer in proportion to its sequence block length.

A 2 : 1 by weight blend of TBBA PC and BA PC (about equimolar) was analyzed by this FTIR method to model an ideal diblock coPC. The CO_3 band peaks at 1786 cm^{-1} and has a bandwidth almost twice that of BA PC [Fig. 1 (c) and Table II, entry c]. Each of the coPCs prepared by the two processes show CO_3 band peaks at 1786 cm^{-1} [Fig. 1 (d,e)].

Table II Relative Carbonate Bandwidths of BA PC, TBBA PC, and BA-TBBA CoPCs

Entry	Sample	Process	Rel. CO_3 Bandwidth
a	BA PC	—	1.0
b	TBBA PC	—	1.2
c	TBBA PC/BA PC blend	—	1.9
d	BA-TBBA coPC	One-step	1.7
e	BA-TBBA coPC	Two-step	1.4
f	BA-TBBA coPC	Two-step	1.6
g	BA-TBBA coPC	Solution	1.6

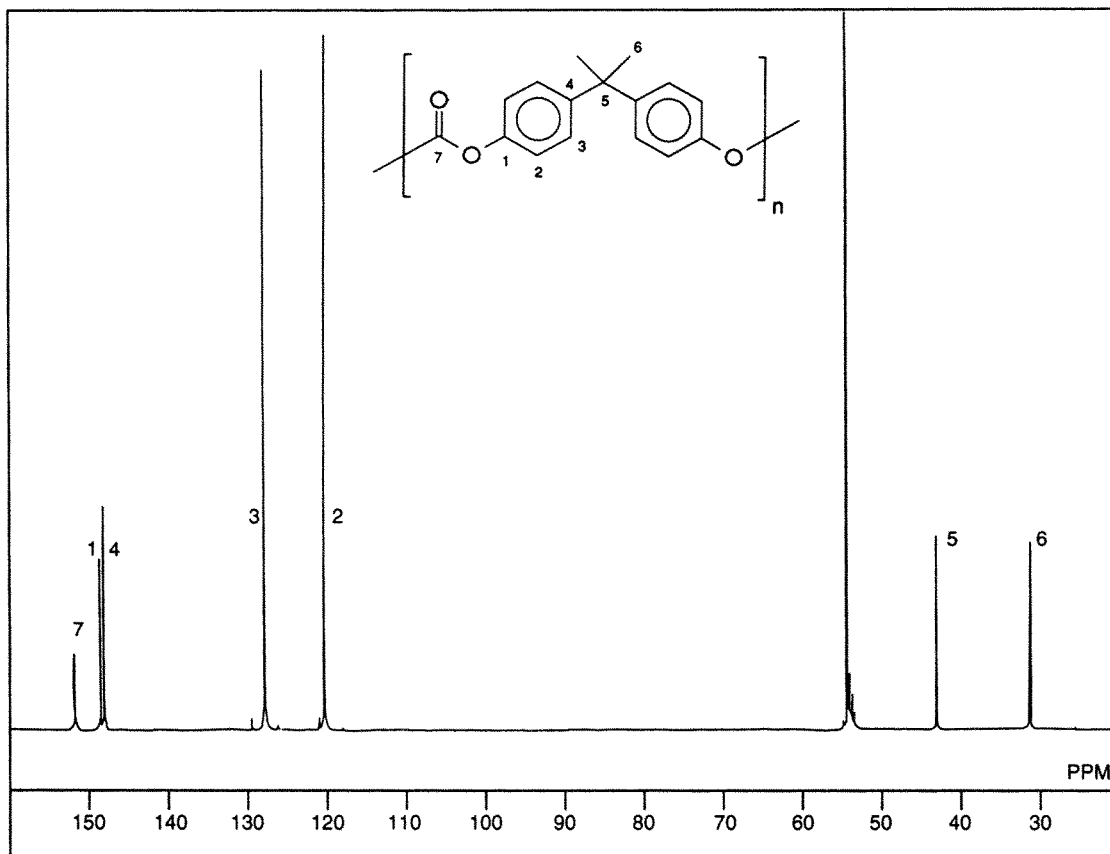


Figure 2 ^{13}C NMR spectrum of BA PC.

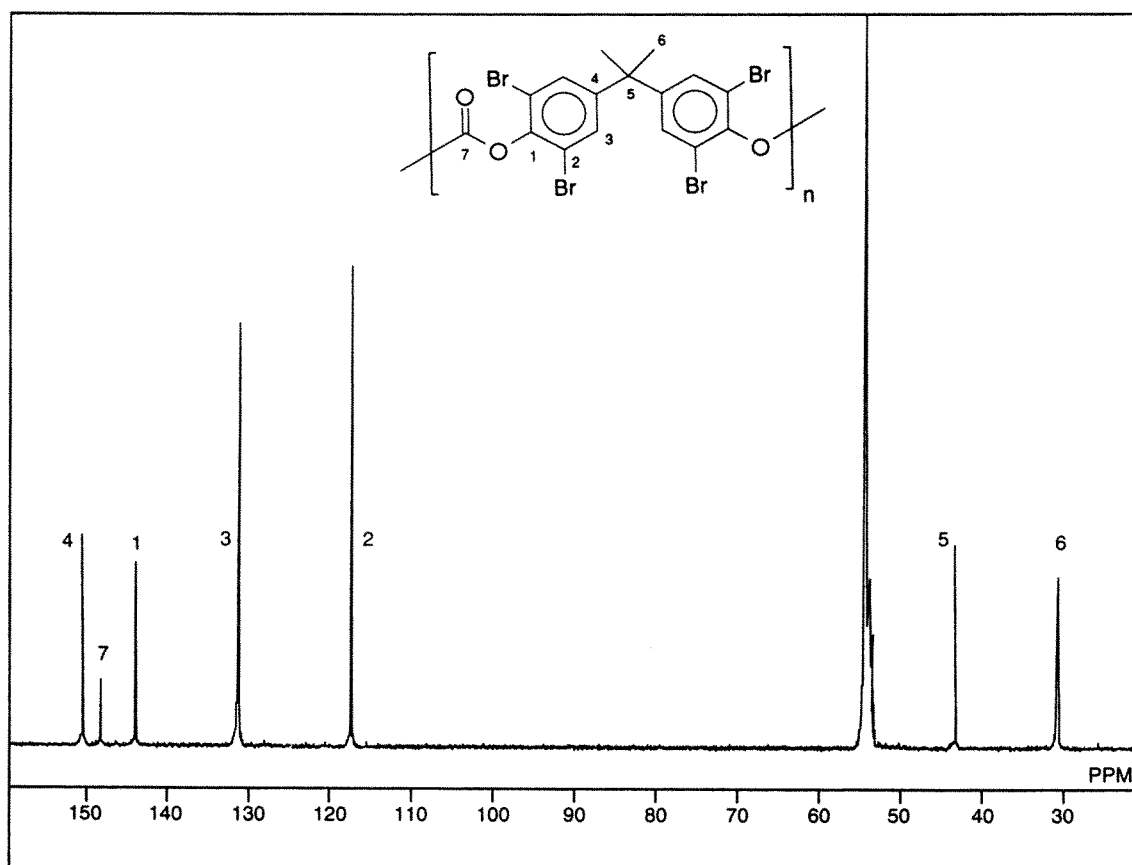


Figure 3 ^{13}C NMR spectrum of TBBA PC.

Table III ^{13}C NMR Spectrum Assignments for BA PC and TBBA PC

Carbon No.	BA PC Chemical Shift (ppm)	TBBA PC Chemical Shift (ppm)
1	148.8	143.8
2	120.5	117.3
3	127.9	131.2
4	148.4	150.4
5	42.9	43.3
6	31.1	30.7
7	152.2	148.1

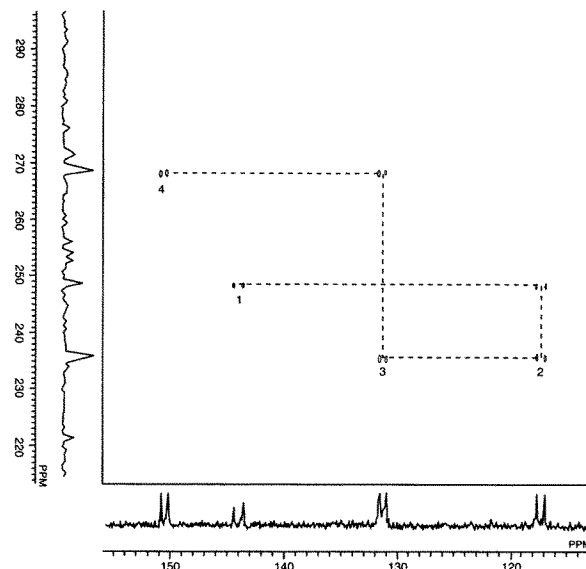
The CO_3 bandwidth of the one-step coPC (entry d) is nearly as broad as that of the PC blend, indicating a relatively blocky sequence architecture. The two-step coPC (entry e) shows an intermediate CO_3 bandwidth which suggests a more random comonomer distribution. A two-step process coPC prepared without nitrogen purging of excess phosgene (entry f) shows a broader CO_3 bandwidth, indicating a more blocky sequence structure. For comparison, a BA-TBBA coPC prepared by the solution phosgenation process (phosgenation of the comonomers in pyridine/dichloromethane, entry g),³⁰ which is expected to produce a random copolymer, shows a CO_3 bandwidth in between that of the two interfacially prepared coPCs.

Chain Sequence Architecture by Carbon-13 NMR

The chain sequence architecture of many types of copolymers is most thoroughly characterized by NMR spectroscopy.³¹ The ^{13}C NMR spectra of BA-TBBA coPCs reveals considerable detail about their chain microstructure from the splitting of carbonate dyads and aromatic carbon triads, and from the distributions of those triads.

The ^{13}C NMR spectra of BA PC and TBBA PC are shown to aid in the interpretation of the copolymer spectra (Figs. 2 and 3). The chemical shifts for each carbon atom of BA PC (Table III) are similar to those reported in a previous study.³² The bromine substituents in TBBA PC have the expected pronounced effects on its chemical shifts (Table III). The assignments for TBBA PC were confirmed by an off-resonance spectrum, which showed a doublet for C-3 (131.2 ppm), and by a two-dimensional connectivity experiment that shows the relative positions of the quaternary aromatic carbon atoms (Fig. 4).

The ^{13}C NMR spectra of the two types of BA-TBBA coPCs (Figs. 5 and 8) are complicated by

**Figure 4** Two-dimensional ^{13}C NMR spectrum of TBBA PC.

both the presence of both comonomer units and, because the bisphenols contain two aromatic rings each, the formation of unsymmetrical comonomer

Table IV ^{13}C NMR Spectrum Assignments for BA-TBBA CoPCs

Carbon No.	Chemical Shift (ppm)
7aa	152.16
4bba	150.42
4bbb	150.37
4aba	150.07
4abb	150.03
7ab	149.80
1ba	148.82
1aa	148.82
4baa	148.74
4bab	148.68
4aaa	148.36
4aab	148.30
7bb	148.14
1ab	144.07
1bb	143.81
3bb	131.18
3ab	131.06
3ba	128.03
3aa	127.91
2aa	120.49
2ba	120.28
2bb	117.28
5b	43.29
5a	42.89
6a	31.05
6b	30.66

segments. The splitting of each type of carbon resonance varies from monads to triads, and the assignments follow from the homopolymer spectra (Table IV). The nomenclature used to describe these copolymer resonances employs the carbon number and a letter code, wherein "a" denotes a BA unit and "b" denotes a TBBA unit. The monad resonances are denoted by a single letter. Two letters, such as 7ab, are required to describe those resonances that appear as three dyads. Triad resonances are denoted using three letters, such as 4bba, wherein the second letter denotes the left-hand ring of the comonomer unit and the other letters refer to the types of flanking comonomer units. The symmetrical triads, like 4bab, have degenerate resonances, but the unsymmetrical triads, such as 4bba and 4abb, are resolved.

The ^{13}C NMR spectrum of the one-step BA-TBBA coPC shows resonances arising mainly at the chemical shifts of the respective homopolymer units (Fig. 5), confirming the blocky character of this copolymer. Weak resonances do appear for alternate coPC segments which are used as described below to quantify the chain sequence architecture. In con-

trast, the ^{13}C NMR spectrum of the two-step BA-TBBA coPC is much more complex, due to the large proportion of alternate coPC segments (Fig. 8).

The key resonances to consider in the interpretation of the sequence architecture of BA-TBBA coPCs appear in the downfield region of their spectra (Figs. 6, 7, 9, 10). The carbonate carbons (C-7) are split into three dyads (7aa, 7ab, and 7bb), and the aromatic carbons *para* to the carbonate bond (C-4) are split into eight triads (4aaa, 4aab, etc.) for both the BA- and the TBBA-centered resonances. As shown in the expanded spectra, the C-7 dyad resonances are well resolved, but only the BA-centered C-4 triad resonances are sufficiently resolved for peak integration. For this reason the integrals and/or peak heights of only these resonances are utilized in the chain sequence calculations.

The number average sequence length, n , of each block of a copolymer can be calculated from any order multiplets observed in its spectrum from the number, N , of each type of multiplet.³¹ The number of dyads N_{aa} , etc., give n_a and n_b (the subscript indicating the copolymer block type) as shown in eqs. (1) and (2). Analogously, n is calculated from the

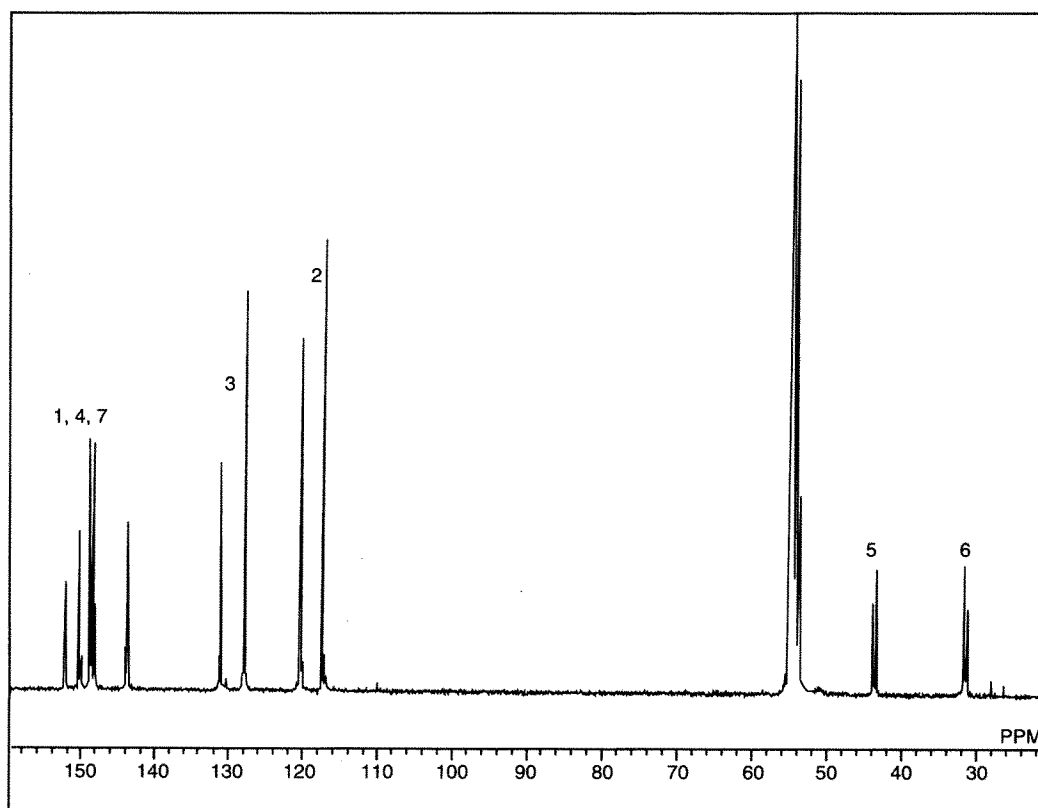


Figure 5 ^{13}C NMR spectrum of BA-TBBA CoPC, one-step process.

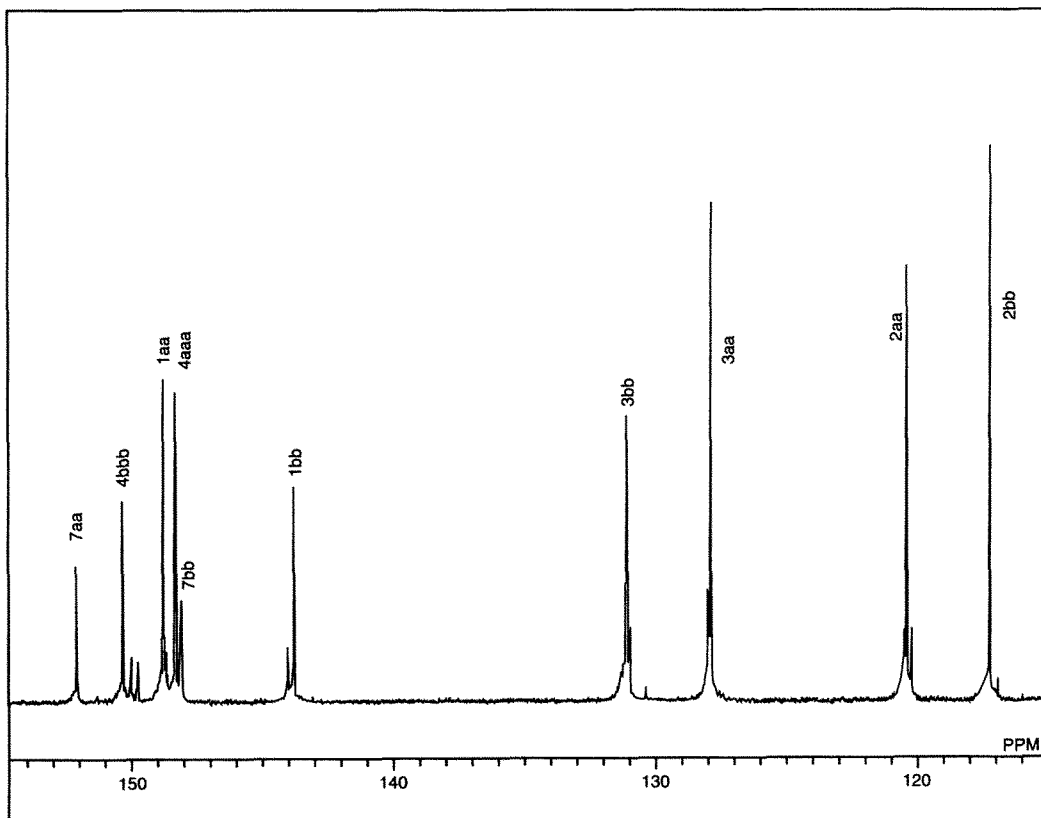


Figure 6 ^{13}C NMR spectrum of BA-TBBA CoPC, one-step process (downfield expanded).

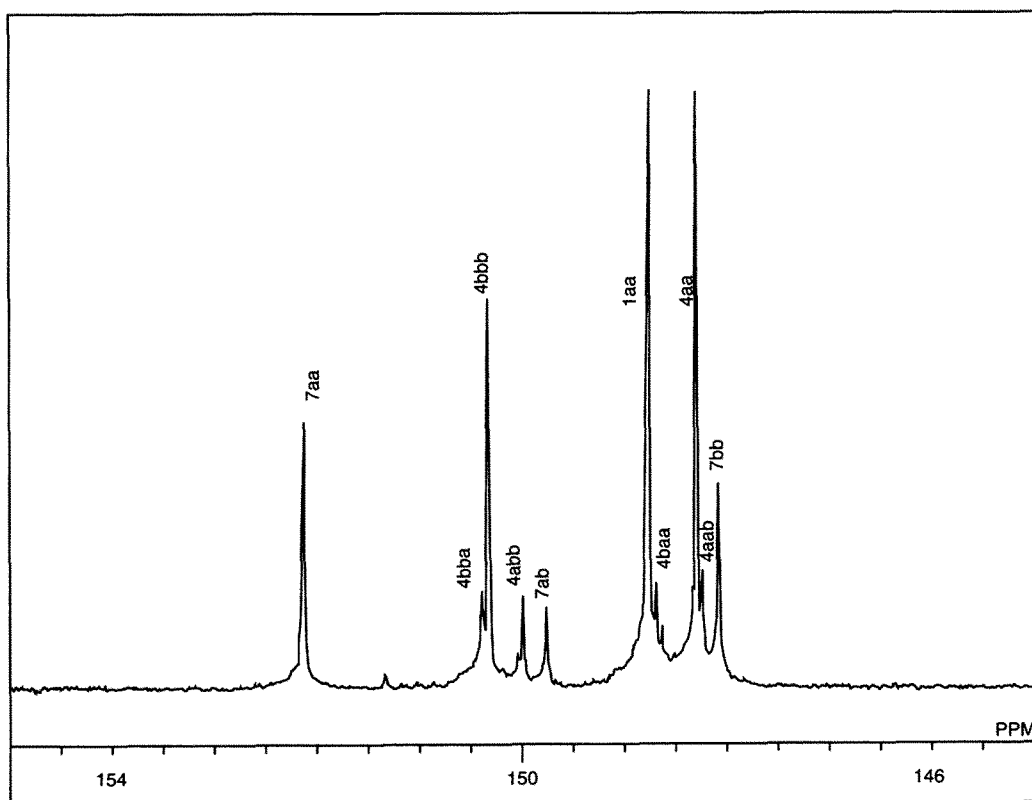


Figure 7 ^{13}C NMR spectrum of BA-TBBA CoPC, one-step process (downfield expanded).

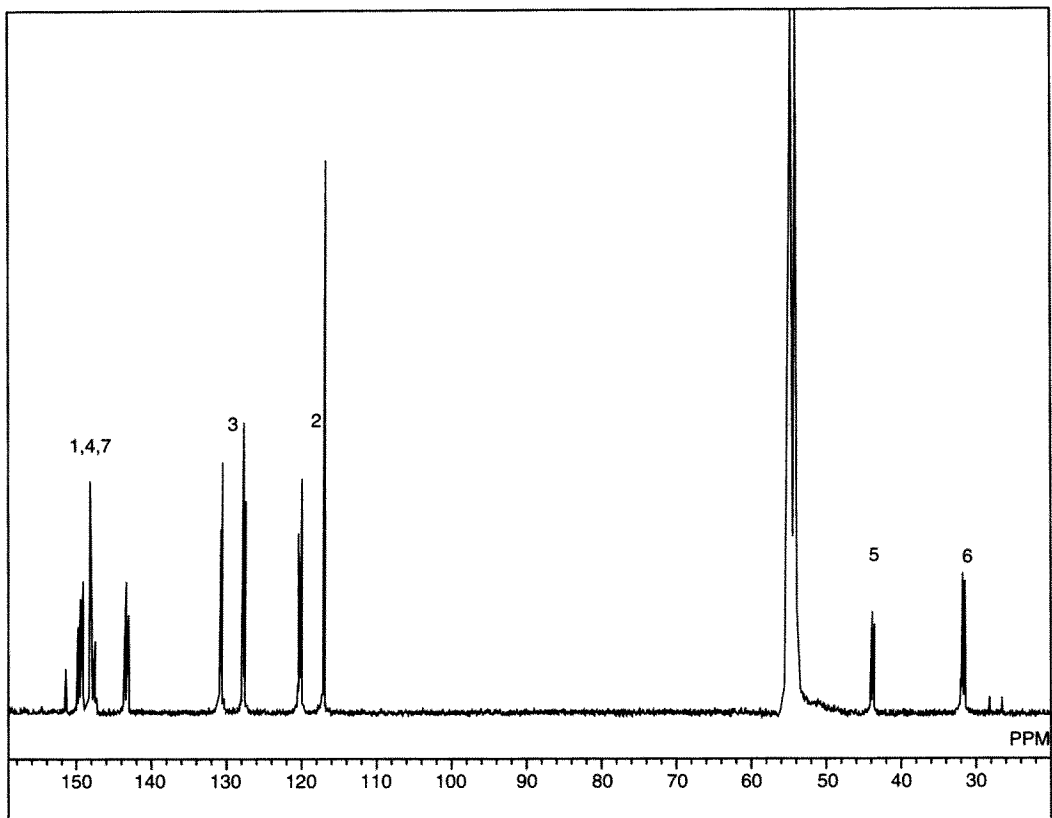


Figure 8 ^{13}C NMR spectrum of BA-TBBA CoPC, two-step process.

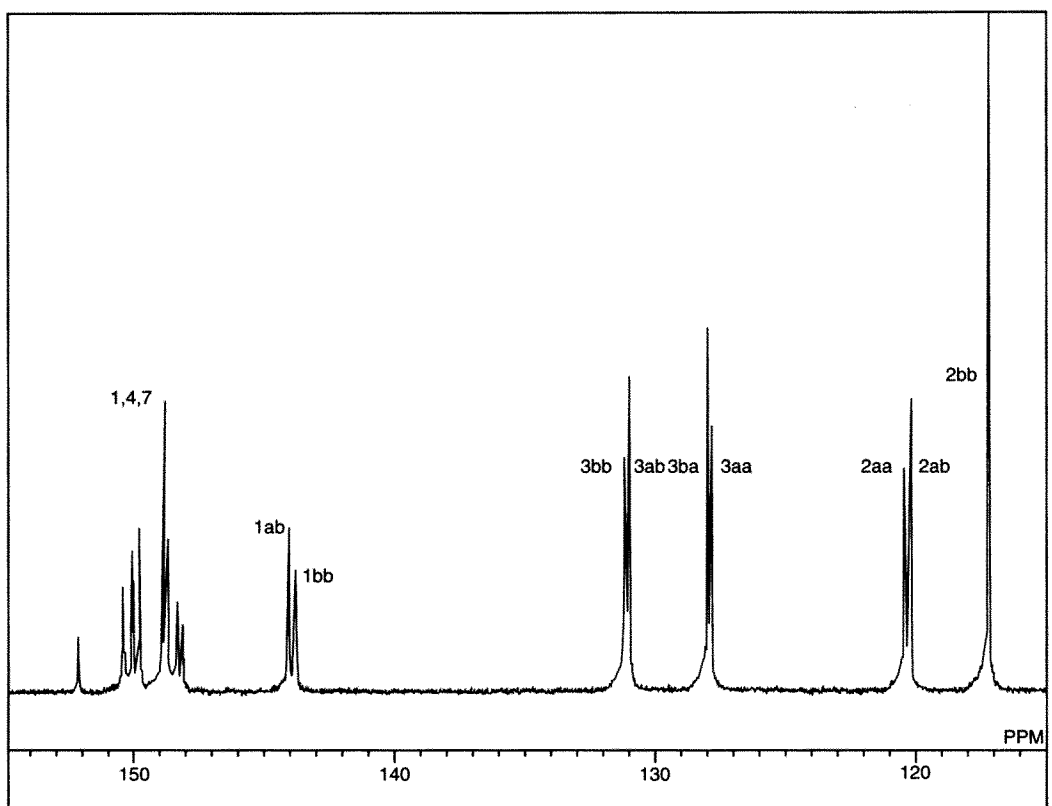


Figure 9 ^{13}C NMR spectrum of BA-TBBA CoPC, two-step process (downfield expanded).

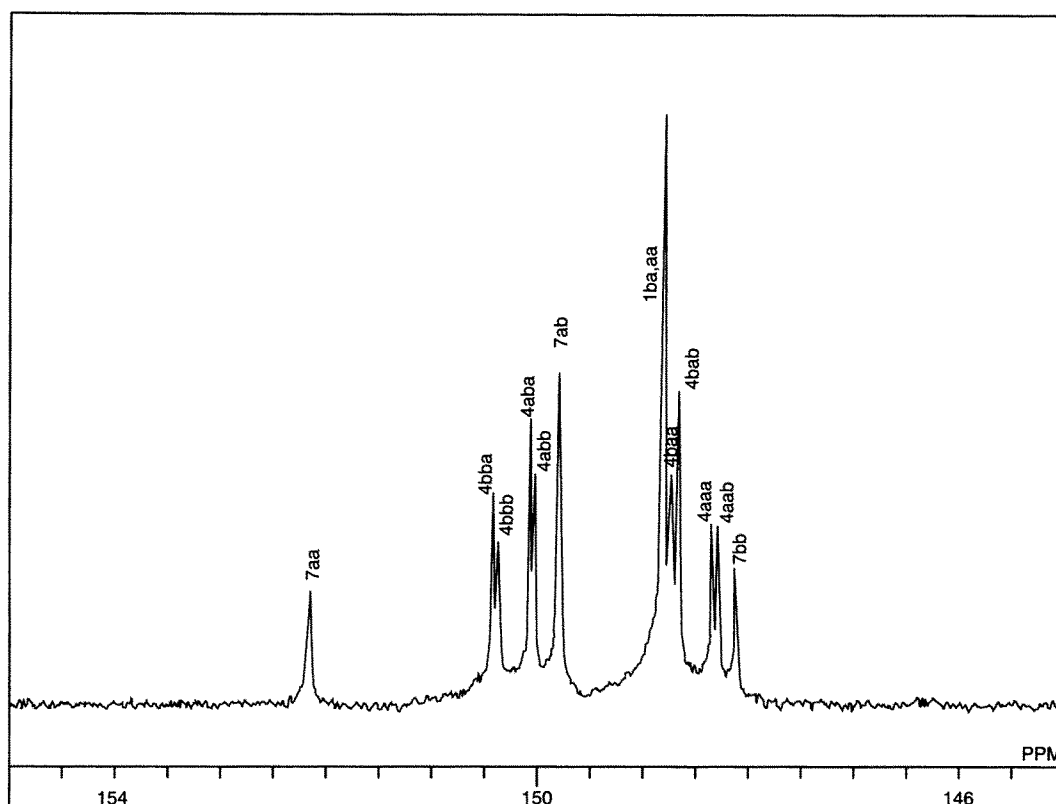


Figure 10 ^{13}C NMR spectrum of BA-TBBA CoPC, two-step process (downfield expanded).

number of triads of each block by eqs. (3) and (4), where N_{aab} represents the sum of the aab and baa triads, and so on for the other triads. Alternate, random, and block copolymers have n values of 1.0, 2.0, and > 2.0 , respectively. However, more detail about the chain microstructure of copolymers having about the same number average sequence lengths can be learned from the distribution of the triad resonances.

$$n_a = \frac{N_{aa} + 0.5N_{ab}}{0.5N_{ab}} \quad (1)$$

$$n_b = \frac{N_{bb} + 0.5N_{ab}}{0.5N_{ab}} \quad (2)$$

$$n_a = \frac{N_{bab} + N_{aab} + N_{aaa}}{N_{bab} + 0.5N_{aab}} \quad (3)$$

$$n_b = \frac{N_{aba} + N_{bba} + N_{bbb}}{N_{aba} + 0.5N_{bba}} \quad (4)$$

The number average sequence lengths of the one-

step and the two-step BA-TBBA coPCs calculated from the carbonate dyad integrals and peak heights confirms the segmented block and random sequence architecture of these copolymers (Table V). The n values determined from the peak integrals and the heights agree fairly well, as do the n_a and n_b averages, which should be equivalent for these 1 : 1 copolymers. The n_a values are considered more representative because the 7bb dyad appears on the tail of a C-4 triad, making its quantification less reliable. It is interesting to note the larger segment length of the highest molecular weight coPC prepared by the one-step process (entry a), a result that can be attributed to the formation of higher molecular weight BA oligocarbonates in the first phase of this process. The two-step coPC (entry d) has a sequence length midway between that of alternate and random copolymers, whereas that prepared without the N_2 purge of excess phosgene (entry e) has a more random architecture. The solution process coPC (entry f) also has a number average sequence length of a random copolymer.

Analysis of the C-4 BA centered triad peak heights (used because the integrals proved inaccur-

Table V Dyad Distributions from C-13 NMR Spectra of BA-TBBA CoPCs

Entry	Process	M_w	Peak Integrals						Peak Heights							
			aa	ab	bb	N_a	N_b	n_a	n_b	aa	ab	bb	N_a	N_b	n_a	n_b
a	One-step	101,246	1.00	0.26	1.10	1.26	1.36	8.69	9.46	2.17	0.71	1.68	2.88	2.39	7.11	5.73
b	One-step	57,133	1.00	0.95	0.98	1.95	1.93	3.11	3.06	1.08	0.98	1.01	2.06	1.99	3.20	3.06
c	One-step	45,090	1.00	0.74	0.73	1.74	1.47	3.70	2.97	0.91	0.78	0.91	1.69	1.69	3.33	3.33
d	Two-step	44,568	1.00	3.59	0.80	4.59	4.39	1.56	1.45	0.57	1.81	0.51	2.38	2.32	1.63	1.56
e	Two-step	50,109	1.00	1.70	0.60	2.70	2.30	2.18	1.71	1.01	1.60	0.88	2.61	2.48	2.26	2.10
f	Solution	74,636	1.00	2.05	0.93	3.05	2.98	1.98	1.91	0.84	1.43	0.82	2.27	2.25	2.17	2.15

rate) gives similar number average sequence lengths for these coPCs (Table VI). The only significant difference in the two calculated results is for the highest molecular weight one-step coPC (entry a), which has about one-half the average block length calculated from its triads. For those coPCs that have a more random structure, the standard deviation, σ , of the BA-centered triads about their mean peak height reveals more detail about the copolymer microstructure. (These σ 's were calculated from the aaa, bab, and combined aab and baa triad distributions.) The solution process coPC has a σ as expected for a completely random distribution of triads (entry f). The more random of the coPCs prepared by the two-step process (entry e) has much lower σ .

Interpretation of these σ 's is aided by consideration of three model copolymers, random, alternate dyad, and alternate block, which each have a number average sequence length of 2.0 (Table VII). The random model copolymer (entry 3) has a statistical distribution of triads reflected by its σ of about 0.5 (Table VIII). The alternate dyad model copolymer (entry 2) has only aab type triads and, thus, has the largest σ . The minimum σ ($= 0$) is found for the alternate-block model copolymer (entry 1), which has a uniform distribution of triads. Referring to the BA-TBBA coPCs described above, the two-step coPCs have an alternate-block microstructure, which is consistent with the chemistry involved in

that process. The number average sequence lengths of two-step coPCs can vary above and below 2.0 due to the formation of greater or lesser relative amounts of alternate comonomer sequences as controlled by the process conditions. Also, the solution process yields a truly random coPC based on its triad distribution.

Dynamic Mechanical Analysis

Two BA-TBBA coPCs were examined by DMA to evaluate the effects of chain sequence architecture on the copolymer secondary relaxations. BA PC has a lowest temperature secondary transition at about -100°C ,³³ which is shifted to near $+100^\circ\text{C}$ in TBBA PC.³³ In the two-step coPC, which has an alternate-block microstructure, a single low temperature secondary transition at about $+25^\circ\text{C}$ is observed in the $\tan \delta$ curve of its DMA (Fig. 11). Two distinct secondary transitions are observed for the respective homopolymer blocks in the one-step coPC, which has a number average sequence length of about 4 (Fig. 12). Therefore, the molecular motions associated with these secondary transitions can be attributed to relatively short segment blocks, rather than to portions of a single repeat unit. This conclusion has been confirmed by much more detailed studies performed subsequent to this work by others.³⁴

Table VI Triad Distributions from C-13 NMR Spectra of BA-TBBA CoPCs

Entry	Process	M_w	aaa	aab	baa	bab	bbb	abb	bba	aba	N_a	N_b	n_a	n_b	σ
a	One-step	101,246	4.85	1.00	0.89	0.55	3.15	0.79	0.98	0.34	7.29	5.26	4.88	4.29	1.80
b	One-step	57,133	—	—	—	—	—	—	—	—	—	—	—	—	—
c	One-step	45,090	2.36	0.97	0.95	0.62	1.81	0.88	0.98	0.56	4.90	4.23	3.10	2.84	0.74
d	Two-step	44,568	0.92	0.74	1.00	1.83	0.59	1.11	0.93	1.75	4.49	4.38	1.66	1.58	0.04
e	Two-step	50,109	2.43	0.95	1.18	2.10	1.27	1.57	1.55	1.57	6.66	5.96	2.10	1.90	0.15
f	Solution	74,636	1.49	1.23	1.33	1.22	1.26	1.21	1.22	1.29	5.27	4.98	2.11	1.99	0.55

Table VII Model Copolymer Structures

Model No.	Model Type	Structure
1	Alternate-block	$-(ABABAAAABBBB)_n-$
2	Alternating dyad	$-(AABBAABBAABB)_n-$
3	Random	

CONCLUSIONS

The chain sequence architecture of bisphenol A-tetrabromobisphenol A copolycarbonates depends on the process employed to prepare them. An interfacial process involving a single step phosgenation produces a segmented block copolymer, contrary to previous assumptions. An interfacial two-step phosgenation process allows the preparation of random copolycarbonates. In each process the control of the pH of the aqueous phase of the two phase reaction mixture is required to achieve complete comonomer conversion to copolymer and to obtain the desired sequence architecture.

The chain sequence architecture of these copolycarbonates can be estimated by examination of their Fourier transform infrared spectra. The relative bandwidth of the carbonate stretching band is roughly proportional to the copolycarbonate number average sequence length, allowing the facile distinction between block and random copolymers. The number average sequence lengths of these copolycarbonates were quantified by carbon-13 NMR spectroscopy. These analyses showed that the one-step phosgenation process yields segmented block copolycarbonates having number average sequence lengths from about 4 to 9, and the two-step phosgenation process produces random copolycarbonates having sequence lengths from 1.6 to 2. The distribution of the aromatic carbon triads of these random copolymers shows them to have an alternate-segmented block architecture, consistent with the synthesis conditions, rather than a statistically random distribution of comonomer segments.

Dynamic mechanical analysis of two of these copolycarbonates shows a dependence of their low

temperature secondary transitions on the copolymer sequence structure. A segmented block copolycarbonate, having a number average sequence length of about 4, displays two distinct peaks in its $\tan \delta$ curve at temperatures corresponding to those transitions observed in the respective homopolymers. The $\tan \delta$ curve of a random copolycarbonate shows a single low temperature secondary transition midway between those of the homopolymer.

The physical and mechanical properties of bisphenol A-tetrabromobisphenol A copolycarbonates prepared by these routes will be reported in a future publication.

Experimental

General

Phosgenation reactions were carried out in a Class A fume hood. MDA tape was attached to the phosgenation reactor at various locations to detect phosgene leaks. Copolymerizations were performed in a 1 liter resin flask fitted with a mechanical stirrer, a stirring rod, a baffle, a thermometer, a pH electrode connected to a Fisher Model 650 pH meter/controller, a liquid inlet tube connected to a Masterflex peristaltic pump, and a dropping funnel filled with 50% aqueous sodium hydroxide (NaOH), a gas inlet-dip tube connected to a gas distribution apparatus fitted with N₂ and phosgene lines, and a gas outlet tube connected to a gas scrubber containing 20% aqueous sodium hydroxide and 5% TEA. The peristaltic pump and the pH meter were connected to a relay that allowed addition of NaOH at a pH set-point. The reactor was immersed in an ice bath to maintain its temperature below 30°C. Turbulent mixing was achieved at 800–1000 rpm.

Samples for DMA analysis were molded in a 3 × 2.5 × 1/16" mold at 307°C using a Tetrahedron MTP-14 compression molder. Specimens were cut to 2 × 0.5 × 1/16".

Chemicals

Bisphenol A (BA, PARABIS™, Dow Chemical Co.), tetrabromobisphenol A (TBBA, Great Lakes Chemical Co.), 90% phenol (Dow Chemical Co.), methylene

Table VIII Triad Distributions of Model Copolymers

Model	aaa	aab	baa	bab	bbb	abb	bba	aba	N _a	N _b	n _a	n _b	σ
1	2.00	1.00	1.00	2.00	2.00	1.00	1.00	2.00	6.00	6.00	2.00	2.00	0.00
2	0.00	3.00	3.00	0.00	0.00	3.00	3.00	0.00	6.00	6.00	2.00	2.00	2.83
3	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	4.00	4.00	2.00	2.00	0.47

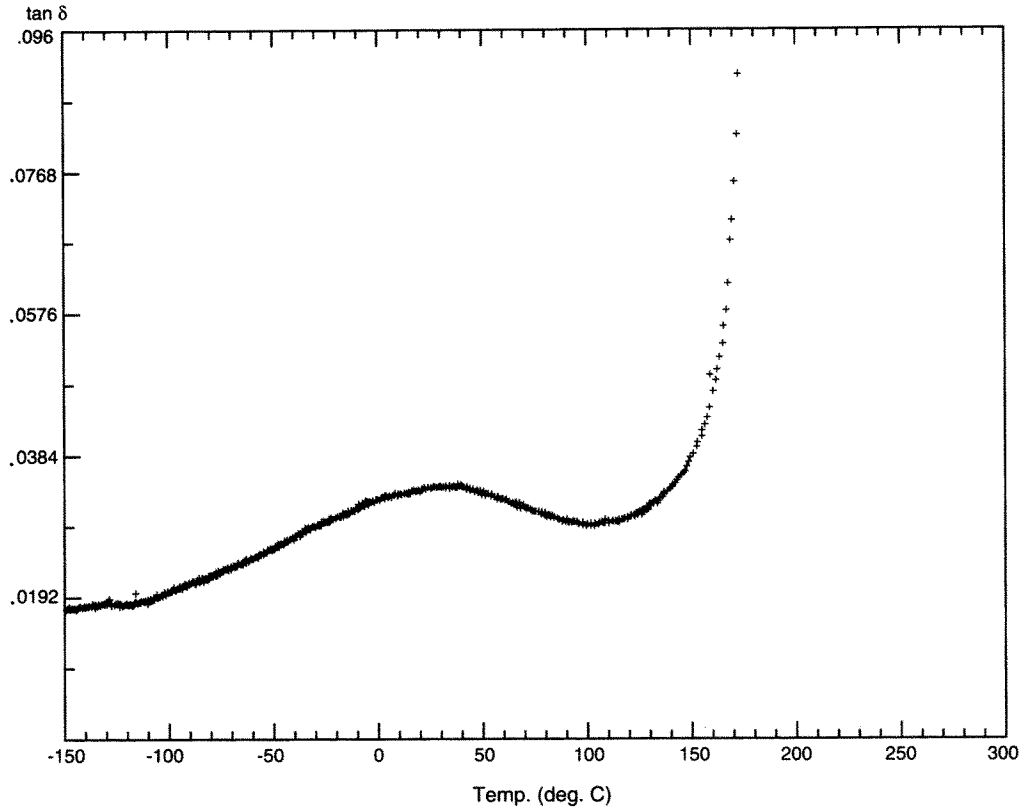


Figure 11 DMA of BA-TBBA CoPC, two-step process.

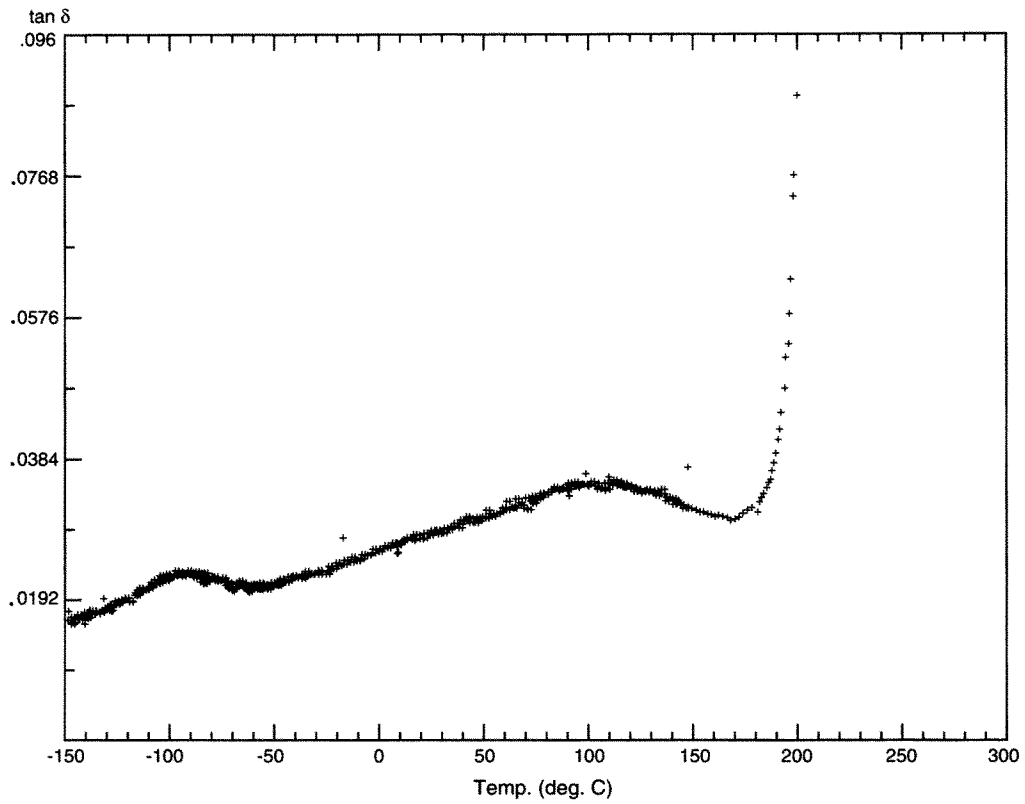


Figure 12 DMA of BA-TBBA CoPC, one-step process.

chloride (Dow Chemical Co., technical grade), 50 wt % aqueous sodium hydroxide (caustic, Fisher Scientific), triethylamine (TEA, Aldrich Chemical Co.), 4-*N,N*-dimethylaminopyridine (DMAP, Aldrich Chemical Co.), phosgene (5 lb cylinders from Matheson Gas Products), and tetrahydrofuran (THF, Fisher Scientific) were used as received.

Analytical

GPC analyses were done with a Hewlett Packard 1090 system fitted with a diode array UV detector and using two DuPont Zorbax PSM Bimodal-S columns (6.2 mm \times 25 cm) with 1 mL/min THF. A single broad molecular weight standard ($M_w = 30,000$; dispersity = 2.50) was used as the standard. FTIR spectra were recorded on a Digilab FX 60 FTIR spectrophotometer from methylene chloride polymer solution cast films on sodium chloride plates. Glass transition (T_g) data was obtained by differential scanning calorimetry (DSC) using a DuPont Model 912 Dual Sample Differential Scanning Calorimeter connected to a DuPont Model 2100 Thermal Analyst Controller and a heating rate of 20°C/min. T_g 's are reported as the inflection point of the heat flow curve. Viscosity measurements were made in a 50 mL Cannon-Ubbelohde viscometer immersed in a 25°C water bath. Dynamic mechanical analysis (DMA) was performed on a Rheometrics 7700 Dynamic Spectrometer with its torsional-rectangular fixture from -160°C to about 260°C (to sample failure) using an oscillatory frequency of 1 Hz and a strain of 0.05%.

One-step Phosgenation Process

The reactor was charged with 38.07 g (0.07 mol) TBBA, 15.98 g (0.07 mol) BA, 0.29 g, 90% phenol (0.26 g phenol, 0.0028 mol, 2.0 mol %, or other amounts as indicated above), 300 mL methylene chloride, and 400 mL deionized water. The pH of the mixture was increased to 12.5 by addition of NaOH with stirring under a N₂ purge. Then phosgene (30 g, 0.30 mol) was added at about 1 g/min while maintaining the pH at 12.5 with addition of NaOH. The pH of the mixture was decreased to 10 with phosgene, after which an additional 2 g of phosgene was introduced. The pH was then increased to 12.5 with NaOH and 0.40 g DMAP (3.04 $\times 10^{-4}$ mol, 0.2 mol %) and 100 mL methylene chloride were added. The pH of the mixture was maintained at 12–13 during 15 min of stirring with addition of NaOH, after which copolymerization was complete. The pH was decreased to about 9 with addition of phosgene, and the aqueous phase was

removed from the reactor with suction. The copolymer solution was washed successively with 1 N HCl and deionized water until neutral. The copolymer was recovered by evaporation of the methylene chloride or by addition of the solution to hot water.

Two-step Phosgenation Process

The reactor was charged with 38.07 g (0.07 mol) TBBA, 0.29 g 90% phenol (0.26 g phenol, 0.0028 mol, 2.0 mol %, or other amounts as indicated above), 300 mL methylene chloride, and 400 mL deionized water. The pH of the mixture was increased to 10 by addition of NaOH with stirring under a N₂ purge. Then phosgene (16 g, 0.16 mol) was added at about 1 g/min while maintaining the pH at 10 with addition of NaOH. The reactor was purged with N₂ with stirring for 45 min to remove excess phosgene. Then a slurry of 15.98 g BA (0.07 mol), 11.2 g NaOH (50%), and 50 mL deionized water, followed by 0.05 g DMAP (4.2 $\times 10^{-4}$ mol, 0.3 mol %) in 100 mL methylene chloride, were added. The pH of the mixture was maintained at 12.5 while stirring for 5 min. Phosgene (7 g, 0.07 mol) was added at pH 12.5, then the pH was decreased to 10 with phosgene and an additional 3 g phosgene was introduced, after which copolymerization was complete. The pH was decreased to about 9 with addition of phosgene, and the aqueous phase was removed from the reactor with suction. The copolymer solution was washed successively with 1 N HCl and deionized water until neutral. The copolymer was recovered by evaporation of the methylene chloride or by addition of the solution to hot water.

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