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Branching by Reactive End Groups. Synthesis and Thermal Branching of 4-Hydroxybenzocyclobutene/*p-tert*-Butylphenol Coterminated Bisphenol A Polycarbonates

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ABSTRACT: Long chain branched bisphenol A polycarbonates (BA PC's) were prepared by use of a combination of thermally reactive 4-hydroxybenzocyclobutene (BCB-OH) and the nonreactive *p-tert*-butylphenol (PTBP) chain terminators. These two monophenols react under interfacial conditions at similar rates to provide a statistical distribution of coterminated PC's having molecular weights controlled by the total amount of coterminators. Heating these materials to 300 °C causes branching and/or cross-linking depending on the value of X_{BCB}, thereby separating the polycondensation and branching processes and allowing greater degrees of branching than possible by random branching during polycondensation. At $X_{BCB} < 0.55$ the BCB-OH/PTBP BA PC's branch without cross-linking. The poly-BCB products formed upon the thermal branching of these PC's are the same as those observed in cross-linked BCB terminated BA PC's. The nongel value of X_{BCB} is that expected for a thermally reacted BCB functionality of 2.6, which is the same as that estimated for cross-linked BCB PC's. Based on the statistical distribution of the chain ends and the functionality of the poly-BCB products, BCB-OH/PTBP BA PC's having X_{BCB} values of 0.50 have a minimum of 0.45 number fraction branched chains. The M_w and polydispersity of branched BCB-OH/PTBP BA PC's depend on their initial molecular weight and increase with X_{BCB}. The M_w's for each composition converge to large values (∼100 000 Da) near the gel point, after which the M_w's of the soluble fractions decrease. The T_g's of these polymers scale inversely with M_n rather than M_w. Film toughness also trends with M_n. Films of branched BCB-OH/PTBP BA PC's having $M_n > \sim 2M_e$ are relatively tough and flexible, while those having lower M_n's, regardless of M_w, are relatively brittle. The melt viscosities of branched BCB-OH/PTBP PC's are very high at low shear rates, as expected from their high M_w's, but decrease dramatically with increasing shear rates to values approaching those of conventional linear and randomly branched PC's. Such high zero-shear viscosity, which is indicative of high melt strength, and large shear sensitivity suggests that these new materials could display significant improvements in melt processing by techniques such as blow molding, thermoforming, injection molding, and extrusion.

Introduction

Reactive end groups on bisphenol A polycarbonates (PC's) allow for significant structural changes in this condensation polymer that are not accessible by direct synthetic routes. We have previously investigated the thermal cross-linking of PC's having benzocyclobutene (BCB),[1] maleimide,[2] and (meth)acrylate[3] reactive end groups and have evaluated some properties of the resultant network polymers as a function of cross-link density. Remarkable improvements in the solvent resistance, surface hardness, and ignition resistance of PC are obtainable by its transformation from a thermoplastic to a thermoset material.

There is obviously also high interest in improving the properties of PC through structural modifications while maintaining its thermoplastic nature. Commercially offered branched PC's have improved melt rheological properties, namely melt strength and shear sensitivity, compared to their linear analogues and are manufactured by incorporation of a trifunctional comonomer in the PC polycondensation process.[4] The constraints on the amount of trifunctional comonomer that can be used while precluding cross-linking and the polydispersity (≥2) resulting from this step-growth process only allow up to 25% of the chains (number fraction) to be branched.[5] These factors obviously limit the degree to which random branching can be used to provide the above rheological improvements.

Another approach to branching employs a combination of reactive and nonreactive chain terminators wherein a linear reactive precursor polymer is formed in the polymerization step, and the branched derivative is obtained by subsequent reaction of the end groups. This strategy to branching results in distinct structures and conceivably higher degrees of branching without cross-linking compared to random branching. Demonstrations of this approach have been reported for BCB terminated polystyrenes[6,7] and PC's,[8] but studies of the range of branching that can be obtained without cross-linking and of the properties of these novel polymers have not appeared. In this work a series of PC's coterminated by the thermally reactive 4-hydroxybenzocyclobutene (BCB-OH) and the nonreactive *p-tert*-butylphenol (PTBP) were prepared and thermally reacted to investigate the limits of branching without cross-linking with changing initial chain molecular weight and coterminator ratios. Additionally, the thermal and rheological properties of the resultant branched PC's were briefly examined.

Experimental Section

Chemicals. Chemicals used in this work are as previously reported,[1] except for PTBP (Schenectady Chemical Co.) and CALIBRE 200-3 (high molecular weight linear PC) and 603-3 (high molecular weight randomly branched PC) grade resins (Dow Chemical Co.) which were used as received.

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Analyses. Gel permeation chromatography (GPC-UV), reversed phase liquid chromatography (LC), differential scanning calorimetry (DSC), and parallel plate rheology testing (at 280 °C on pieces cut from compression molded plaques) were done as previously described.[1] GPC-LALLS (low-angle laser light scattering) was done using 5 TSK MicroPak H-series (3 GMH6, 1 G500H6, and 1 G400H8) columns at 30 °C and THF eluent at 1 mL/min. A HP 1047 differential refractive index (DRI) detector and a CMX-100 LALLS photometer operated at 100 mV incident power were connected in series. Values of $\delta n/\delta c$ were estimated from the DRI responses and sample concentrations. Gel content was determined by submersing the sample encased in a stainless steel wire mesh in dichloromethane for 18 h, collection of the insoluble fraction, and evaporation of the retained solvent in a 100 °C vacuum oven for 18 h.

Synthesis. The synthesis of BCB-OH/PTBP BA PC's was done using the total and relative amounts of coterminators stated in the text by the interfacial phosgenation of the monomer/terminator mixtures using previously described procedures.[1]

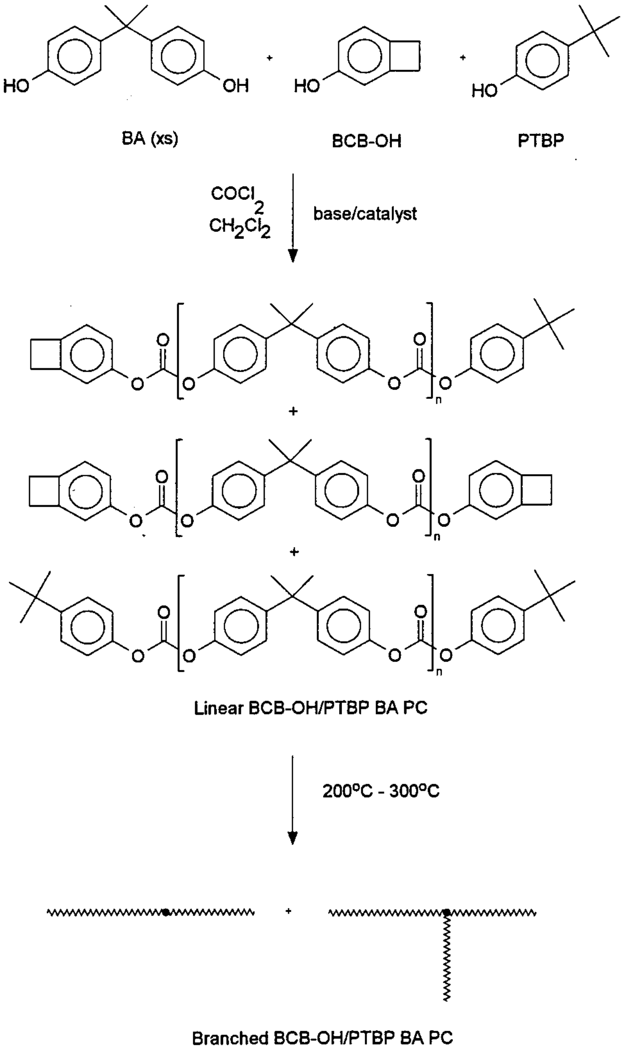
Branching and Molding. Low bulk density BCB-OH/PTBP BA PC's as recovered were dried under vacuum at $\sim$100 °C for 18 h and allowed to cool under N_2. For small sample branching studies portions of the polymer were compressed at room temperature into $\sim$1.25 in. × $\sim$0.125 in. disks using a Carver Press and sample cell. After a second drying as above the disks were placed in a 2 in. diameter aluminum dish and covered in a Petri dish. The dish and contents were purged with N_2 and placed in a N_2-purged Hewlett-Packard model 5890A gas chromatograph oven at 300 °C for 30 min. Compression moldings were prepared from $\sim$2.5 in. diameter disks prepared as discussed above and molded at 200−300 °C as previously described.[1]

Results and Discussion

In this study of PC branching by reactive end groups the linear precursor polymers were first prepared and characterized and then were heated to effect reaction of the end groups. The amount of coterminators used to prepare these PC's is expected to affect the outcome in two ways. First, and obviously, the molecular weight of the reactive precursor BA PC is controlled by the total amounts of coterminators used in the polycondensation process. The amounts of either terminator and of total terminator used can be expressed as their molar ratio with respect to BA (termed m/m). Second, it is hypothesized that the degree of branching (or cross-linking) of the reactive PC is determined by both the molar ratio of the reactive terminator to the nonreactive one (herein expressed as mole fraction BCB, X_{BCB}) and the thermal reaction functionality of the reactive end group. To test these concepts, a series of moderate to low molecular weight BCB-OH/PTBP coterminated PC's were prepared having various X_{BCB}'s, and the results of their thermal reaction were examined.

Synthesis of Linear BCB-OH/PTBP BA PC's. Linear BCB-OH/PTBP BA PC's were prepared by interfacial phosgenation of BA, BCB-OH, and PTBP (Scheme 1). In this method phosgene is added to a mixture of dichloromethane and an aqueous solution of monomer and terminator sodium salts to produce chloroformate terminated oligocarbonate intermediates, which are subsequently coupled to yield the polymer using a catalytic amount of triethylamine.[1] In this process the two monophenols are expected to react at the same rate to form coterminated polymers having a statistical distribution of chain end groups. Thus, equimolar amounts of coterminators yield a product distribution of 50% coterminated polymer and 25% of each of the monoterminated polymers.

Scheme 1. Synthesis and Branching of BCB−OH/PTBP BA PC's



The molecular weight distributions of the linear BCB-OH/PTBP BA were determined by GPC-UV. Polymers having three different levels of total terminator (0.06, 0.10, and 0.20 m/m) and several levels of X_{BCB} (0.10−0.75) were prepared to examine the effect of initial polymer molecular weight and degree of functionality on the derived branched polymer (Table 1). The 0.06 m/m total terminator polymers were studied in the most detail. The ranges of molecular weight distributions obtained are within the normal variations observed in this lab scale method, and no trend with X_{BCB} is evident. LC analysis of the linear 0.03/0.03 m/m PC sample (0.06 m/m total terminator, $X_{BCB} = 0.50$) shows the expected mixture of cyclic, homoterminated, and coterminated oligomers (Figure 1). The first three eluting oligomers are well-resolved and illustrate the random nature of the termination reaction. The peak at about 5 min (a) is that for di-BCB carbonate,[1] at about 8 min (c) is di-PTBP carbonate,[9] and between these two at about 6.5 min (b) is presumably BCB-PTBP carbonate. These three peaks appear in roughly equal areas, which illustrates the equivalent reactivity of the two monophenols. The peak at about 10 min (d) is the cyclic oligomer having two BA segments.[10] After this oligomer the resolution of the several linear and cyclic *n*-mer peaks becomes inadequate for further interpretation.

Table 1. Analyses of Linear and Branched BCB-OH/PTBP BA PC's

	linear polymer			branched polymer							
	GPC-UV			GPC-UV			GPC-LALLS				
X_{BCB}	10^3M_n	10^3M_w	disp	10^3M_n	10^3M_w	disp	10^3M_n	10^3M_w	disp	% gel	T_g
				total terminator = 0.06 m/m							
0.10	7.8	20.2	2.6	8.8	23.0	2.6				0	150
0.20	8.3	20.0	2.4	7.7	24.6	3.2				0	150
0.30	9.8	20.7	2.1	8.6	30.0	3.5				0	152
0.40	7.3	20.0	2.7	9.8	35.5	3.6				0	155
0.50	7.6	22.4	2.9	16.0	70.6	4.4	18.4	135.1	7.0	0	158
0.51	8.0	22.7	2.8	15.9	76.1	4.8				0	158
0.52	7.8	23.4	3.0	16.8	90.5	5.4				0	158
0.53	7.4	23.4	3.1	16.5	86.4	5.2				0	158
0.54	7.7	22.6	2.9	16.1	93.6	5.8				0	159
0.55	7.7	22.5	2.9	16.5	100.6	6.1				0	159
0.55	7.5	19.2	2.6	7.2	72.5	10.1				13	
0.60	7.0	17.9	2.6	13.2	54.9	4.2				68	
0.65	6.8	17.3	2.5	10.7	44.5	4.2				83	
0.70	8.4	21.0	2.5	12.1	52.4	4.3				78	
0.75	8.2	20.7	2.5	10.6	51.9	4.9				91	
				total terminator = 0.10 m/m							
0.10	5.0	11.9	2.4	6.0	13.3	2.2				0	144
0.20	4.7	11.9	2.5	6.0	14.2	2.4				0	144
0.30	4.7	11.9	2.5	8.3	23.7	2.9				0	149
0.40	4.5	11.9	2.6	9.0	32.6	3.6				0	151
0.50	4.5	12.1	2.7	11.1	64.6	5.8	24.3	310.7	10.8	0	154
0.50	4.5	11.5	2.6	10.5	81.1	7.7				0	
0.55	4.3	11.9	2.7	8.1	90.6	11.3				45	155
0.60	4.2	11.6	2.8	13.0	67.2	5.2				63	151
				total terminator = 0.20 m/m							
0.10	2.7	6.2	2.3	3.4	7.3	2.2				0	128
0.20	2.6	6.2	2.3	3.9	9.4	2.5				0	132
0.30	2.6	6.3	2.5	4.4	12.7	2.9				0	136
0.40	2.3	6.1	2.7	5.6	25.2	4.5				0	141
0.50	2.3	6.0	2.6	6.6	59.1	8.9				0	144

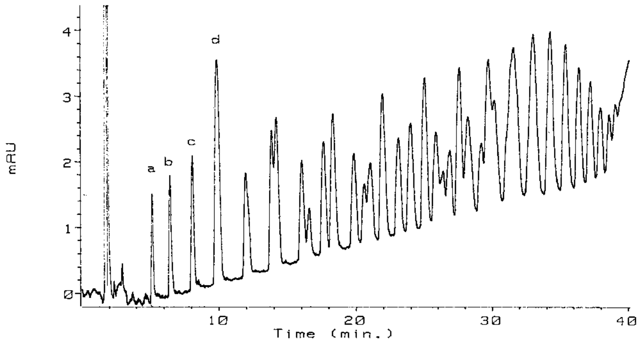


Figure 1. LC analysis of linear 0.03/0.03 m/m BCB-OH/PTBP BA PC.

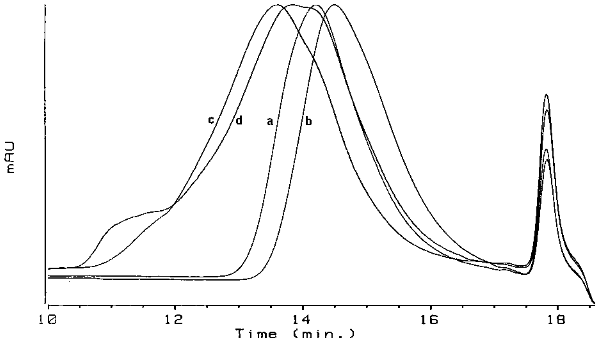


Figure 2. GPC-UV of linear and branched BCB-OH/PTBP BA PC's: (a) linear 0.03/0.03 m/m, (b) linear 0.05/0.05 m/m, (c) branched 0.03/0.03 m/m, and (d) branched 0.05/0.05 m/m.

Branching of BCB-OH/PTBP BA PC's. With heating to 300 °C for 20 min, BCB-OH/PTBP BA PC's branch and/or cross-link depending on X_{BCB}. The molecular weight, polydispersity, and, to a lesser degree, T_g of the branched polymers increase with X_{BCB} up to a value of 0.55, at which the onset of gel formation is observed (Table 1). Changes in the molecular weight distribution of two BCB-OH/PTBP BA PC's upon branching are illustrated by GPC-UV chromatograms (Figure 2). The linear 0.03/0.03 m/m sample (a) gives the higher molecular weight branched sample (c). Although the 0.05/0.05 m/m sample (b) has a lower molecular weight than the other linear polymer shown, the resultant branched sample (d) has the largest molecular weight and polydispersity (note the high molecular weight shoulder) by virture of its greater BCB end group concentration. Two polymers were prepared at $X_{\mathrm{BCB}} = 0.55$, and the sample having a lower molecular weight and polydispersity gelled slightly, while the other sample did not. A value of $X_{\mathrm{BCB}} = 0.55$ is therefore at or near the onset of gelation. The reason for the different results for the two samples having the $X_{\mathrm{BCB}} = 0.55$ was not proven, but it is likely due to a slightly higher BCB conversion for the gelled sample. At higher values of X_{BCB} the degree of gelation increases and, generally, the molecular weight of the soluble fraction decreases. As previously described, all BCB termination ($X_{\mathrm{BCB}} = 1.0$) gives cross-linked polymers having 100% gel and an increased T_g depending on cross-link density.[1] GPC-LALLS (Figures 3 and 4) was performed on two of the branched BCB-OH/PTBP BA PC samples and shows, as expected, a significantly higher molecular weight, particularly M_w, than indicated by GPC-UV (Table 1).

The linear 0.10 and 0.20 m/m BCB-OH/PTBP BA PC's have the expected lower molecular weights compared to the above based on the increasing amount of chain terminators used. LC analyses (not shown) also indicate

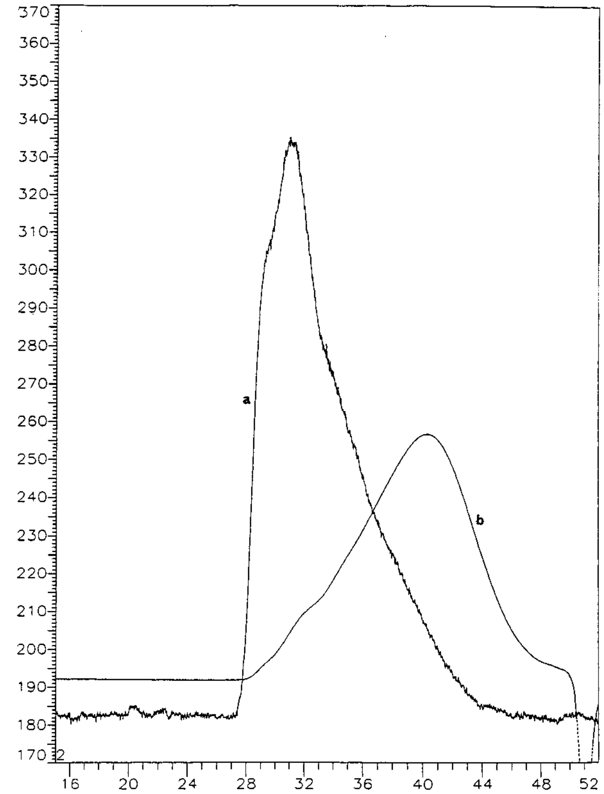


Figure 3. GPC-LALLS (a) and GPC-DRI (b) of branched 0.03/0.03 m/m BCB-OH/PTBP BA PC.

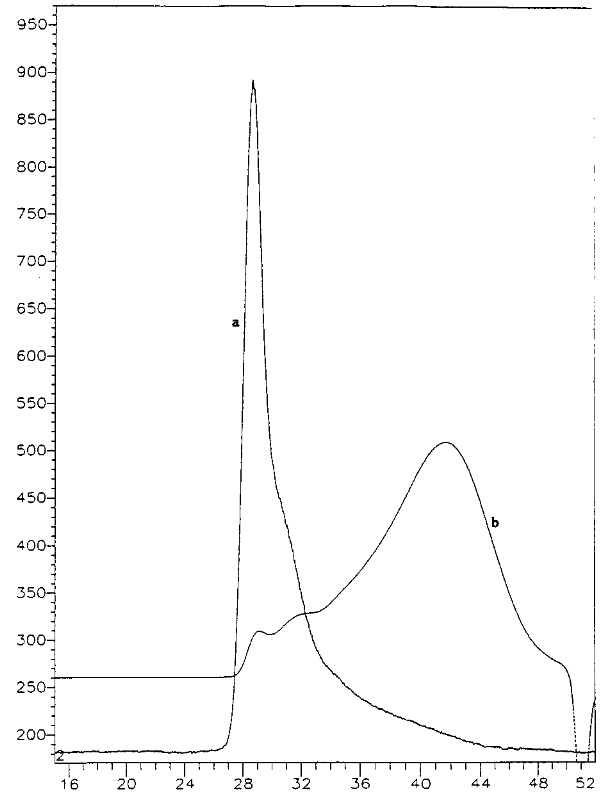


Figure 4. GPC-LALLS (a) and GPC-DRI (b) of branched 0.05/0.05 m/m BCB-OH/PTBP BA PC.

a random distribution of oligomers for these polymers. After heating, these samples also show increases in molecular weight, polydispersity, and T_g with X_{BCB}. The onset of gelation is the same ($X_{BCB} = 0.55$) as the 0.06 m/m polymers.

The T_g of branched BCB-OH/PTBP BA PC's depends on the molecular weight of the linear precursor polymer and the degree of branching (X_{BCB}) as shown in Table 1. Interestingly, this relationship is not uniformly dependent on M_w; the branched PC's at each level of total coterminator show a distinct relationship for T_g vs M_w (Figure 5). However, the T_g vs $10^5/M_n$ data collapse to a single line (Figure 6), illustrating that these polymers follow the usual direct relationship between T_g and the number of chain ends.[11]

The physical properties of branched BCB-OH/PTBP BA PC's have not yet been studied, but it was noticed in the handling of thin, solvent cast films of these polymers that, irrespective of molecular weight, those materials made from 0.10 and 0.06 m/m total coterminators were relatively tough and flexible, while those from 0.20 m/m coterminators were brittle and friable. This trend roughly relates to branched polymer M_n, such that polymer toughness requires that M_n is greater than about twice the entanglement molecular weight of BA PC (M_e, which is ~2700 Da).[12]

The M_w by GPC-UV of each series of BCB-OH/PTBP BA PC's increases exponentially with X_{BCB} up to the gel point (Figure 7). The M_w values of the branched polymers depend more on X_{BCB} at its lower values because as branching increases with X_{BCB}, M_w approaches its pregel limit. The apparent decrease in M_w after the gel point reflects the values of the soluble fraction only, which are therefore not representative of the entire sample.

LC Analysis of BCB-OH/PTBP BA PC Hydrolysate. Understanding the degree of long chain branching in BCB-OH/PTBP BA PC's requires a knowledge of the types and distribution of BCB reaction products formed. In previous studies the products formed by the thermal cross-linking of BCB-OH terminated BA PC's were identified by hydrolysis of the resulting polymer networks and analysis by LC/mass spectroscopy.[13] These hydrolysates were comprised of BA and associated compounds and a complex mixture of BCB dimers, trimers, and tetramers (Figure 8). The average BCB functionality based on the relative amounts of these poly-BCB products was estimated to be about 2.6. The hydrolysate of a branched 0.03/0.03 m/m BCB-OH/PTBP BA PC shows, in addition to the expected PTBP, the presence of the same mixture of poly-BCB products, absent BCB tetramers (Figure 9). The average BCB functionality in these branched PC's is calculated from the approximate relative amounts of the poly-BCB products *n* (the response factors were assumed identical) and their functionality ϕ (Table 2). Since PTBP coelutes with one of BCB trimers (at ~29 min), the amount of this poly-BCB product is assumed to be the same as its later eluting isomers.[13] The calculated average BCB functionality ($f = \sum n_i\phi_i$) is 2.6. These results show that cross-linked and branched BCB PC's have both the same types and average distribution of poly-BCB products.

Theoretical Analysis of Gelling vs Branching. Knowledge of the distribution of the three types of linear BCB-OH/PTBP BA PC's, the average functionality of the reacted BCB groups, and the theory of multifunctional polymerizations can be combined to predict which of the polymer compositions will branch without gelation. Condensation polymers can be randomly branched without gelation by the addition of a >2 functional monomer (branching agent) and sufficient monofunctional chain terminator such that the weight-average

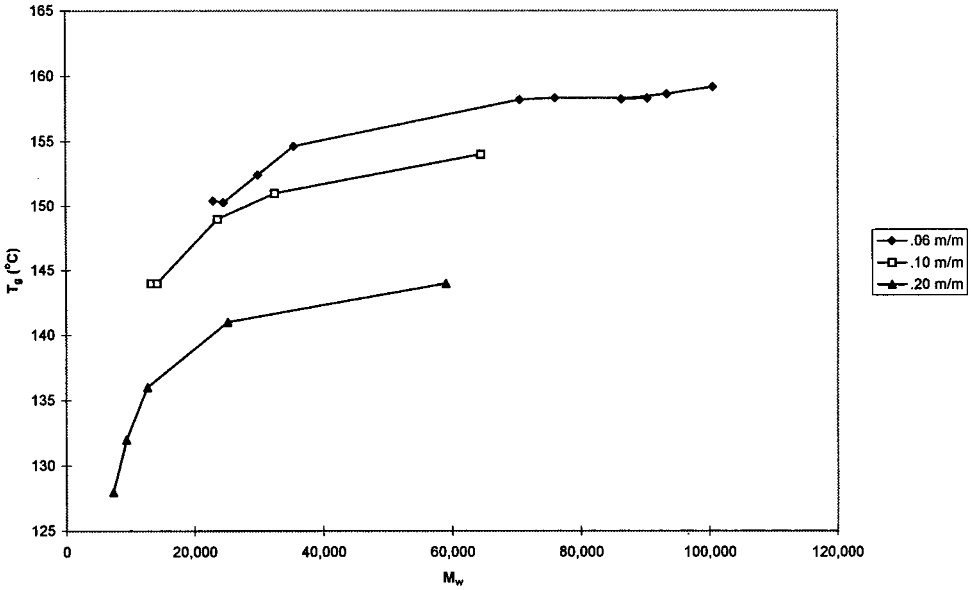


Figure 5. Branched BCB-OH/PTBP BA PC T_g vs M_w.

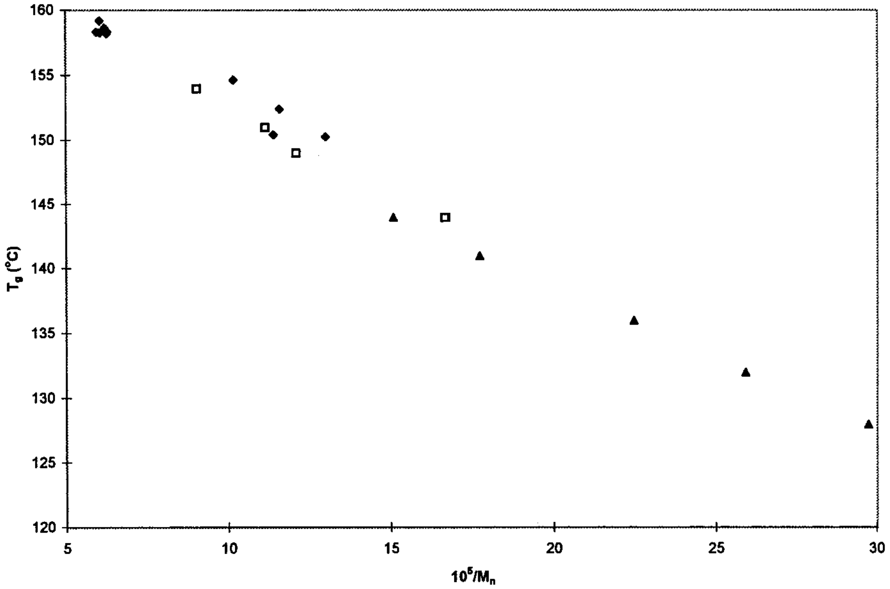


Figure 6. Branched BCB-OH/PTBP BA PC T_g vs $10^5/M_n$.

monomer functionality is 2.0 or less.[5] For branching of BCB-OH/PTBP BA PC's, the "monomers" are the precursor linear PC's, and their relative amounts (number or weight) m are calculated by a simple normal distribution based on the mole fractions of the two monophenol terminators (since the two have equal reactivity) as shown in Table 3, where P-P is PTBP terminated PC, B-P is BCB-OH/PTBP coterminated PC, B-B is BCB-OH terminated PC, and F is the functionality of the reacted PC based on the average BCB functionality f. Since the PTBP terminal groups are unreactive, P-P is unaffected by BCB homopolymerization and its functionality term $\Phi - 1$ is zero, but its presence does affect the functionality of the mixture. The functionality Φ of the components bearing BCB groups is simply the product of the number of BCB's per molecule and f. Gelation of BCB-OH/PTBP BA PC's thus only occurs when the total polymer functionality F is ≥ 2.0 (eq 1).

$$F = \sum m_i(\Phi_i - 1) \qquad (1)$$

A plot of F vs X_{BCB} at various values of f shows that gelation is predicted for $X_{\mathrm{BCB}} = 0.55$ and $f = 2.6$ (Figure 10), consistent with the gel and hydrolysate analyses described above, while greater values of f predict gelation at lower X_{BCB}, and vice versa.

These relationships can also be used to estimate the minimum degree of branching in these polymers. A BCB functionality f value of 2.6 means that, on average, 60% of the poly-BCB products are trimers and 40% are dimers. Of course, only those chains having a BCB trimer are branched, so the minimum number fraction of branched chains N_b is the product of the percent BCB trimer and the fraction of the linear polymer mixture that contains BCB end groups (eq 2).

$$N_b = 0.6(m_{\mathrm{B-B}} + m_{\mathrm{B-P}}) \qquad (2)$$

For example, a branched equimolar BCB-OH/PTBP BA PC ($X_{\mathrm{BCB}} = 0.50$) has a N_b value of 0.45. Note that N_b represents the minimum number fraction of branched

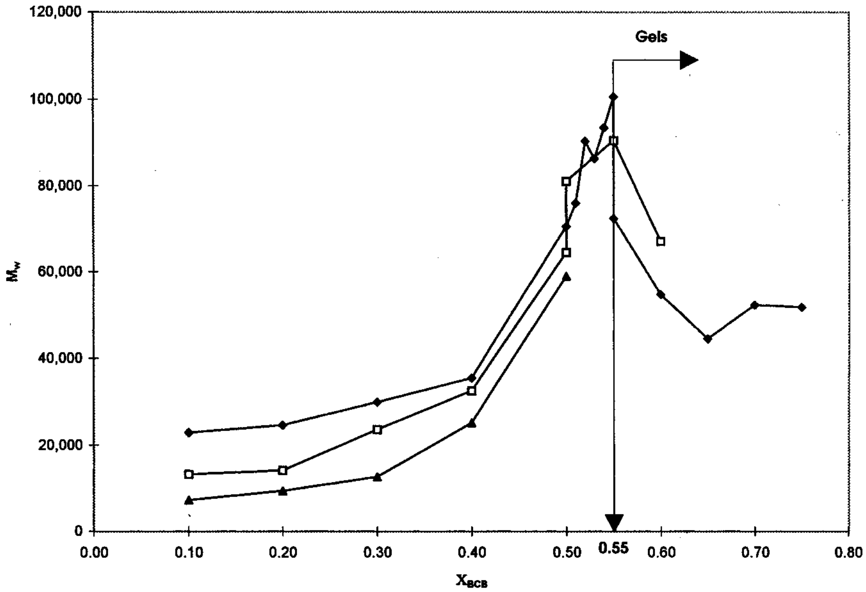


Figure 7. M_w vs X_{BCB} for BCB-OH/PTBP BA PC.

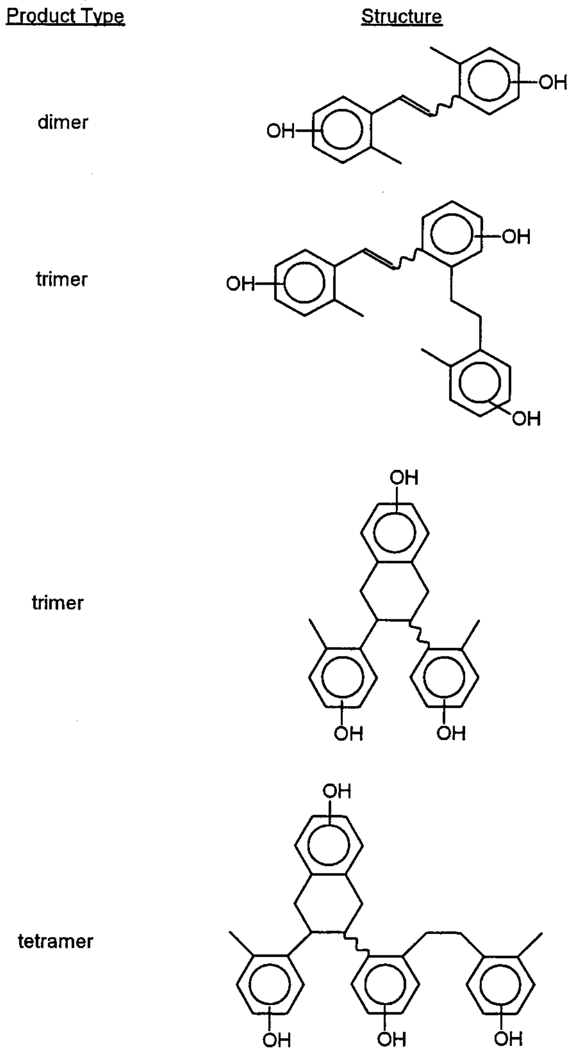


Figure 8. Structures of BCB reaction products from cross-linked BCB PC hydrolysate.

chains since branched molecules can contain both BCB trimers and dimers.

Melt Shear Sensitivity. The effect of long chain branching on the melt rheology of BA PC's was briefly examined by dynamic mechanical analysis (DMA) using a parallel plate fixture. The complex viscosities η^* of 3 MFR linear BA PC, a randomly branched BA PC having approximately the same molecular weight, and branched 0.03/0.03 and 0.05/0.05 BCB-OH/PTBP BA PC's were measured at 280 °C as a function of low to medium

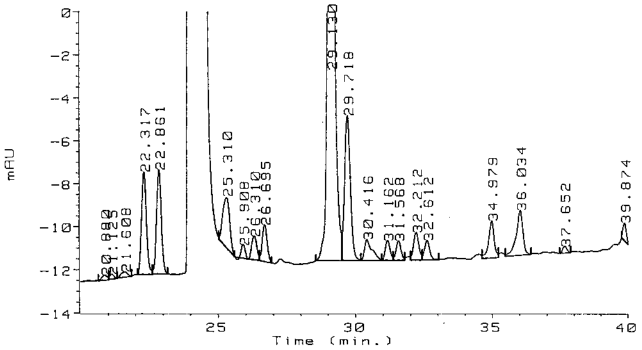


Figure 9. LC of branched 0.03/0.03 m/m BCB-OH/PTBP BA PC hydrolysate.

Table 2. Poly-BCB Product Distribution and Average Functionality in Branched 0.03/0.03 m/m BCB-OH/PTBP BA PC

peak RT	area	area, %	type	ϕ_i	$n_i\phi_i$
22.317	59.62	20.79	dimer	2	0.42
22.861	59.24	20.66	dimer	2	0.41
25.310	42.09	14.68	trimer	3	0.44
25.908	4.97	1.73	trimer	3	0.05
26.310	13.36	4.66	trimer	3	0.14
26.695	20.55	7.17	trimer	3	0.21
~29.000	12.00	4.18	trimer	3	0.13
30.416	19.74	6.88	trimer	3	0.21
31.162	12.04	4.20	trimer	3	0.13
31.568	11.92	4.16	trimer	3	0.12
32.212	19.56	6.82	trimer	3	0.20
32.612	11.69	4.08	trimer	3	0.12
					f = 2.59

Table 3. Distributions and Functionality of BCB-OH/PTBP BA PC's

polymer type	m	Φ
P-P	$(1 - X_{BCB})^2$	1
B-P	$2X_{BCB}(1 - X_{BCB})$	f
B-B	$(X_{BCB})^2$	$2f$

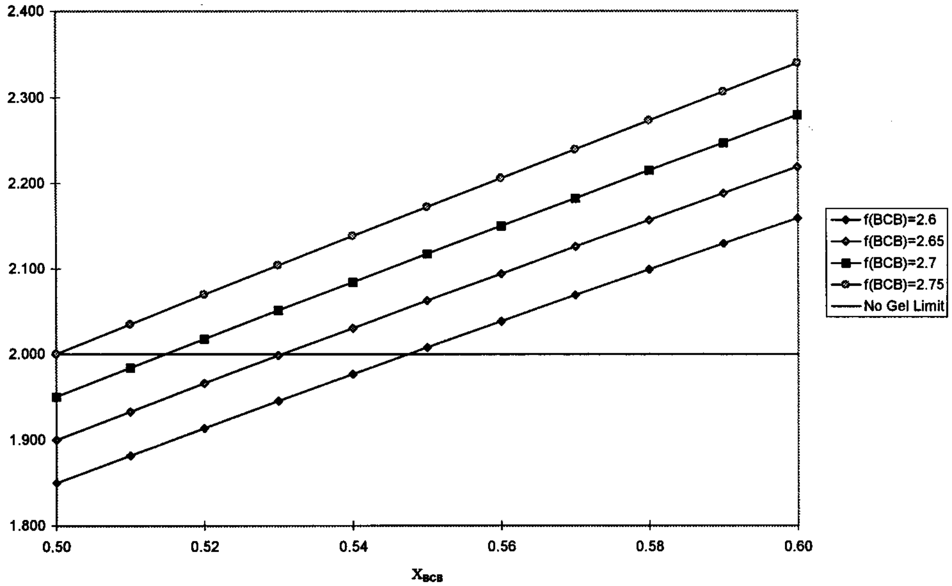


Figure 10. BCB-OH/PTBP BA PC functionality vs BCB mole fraction.

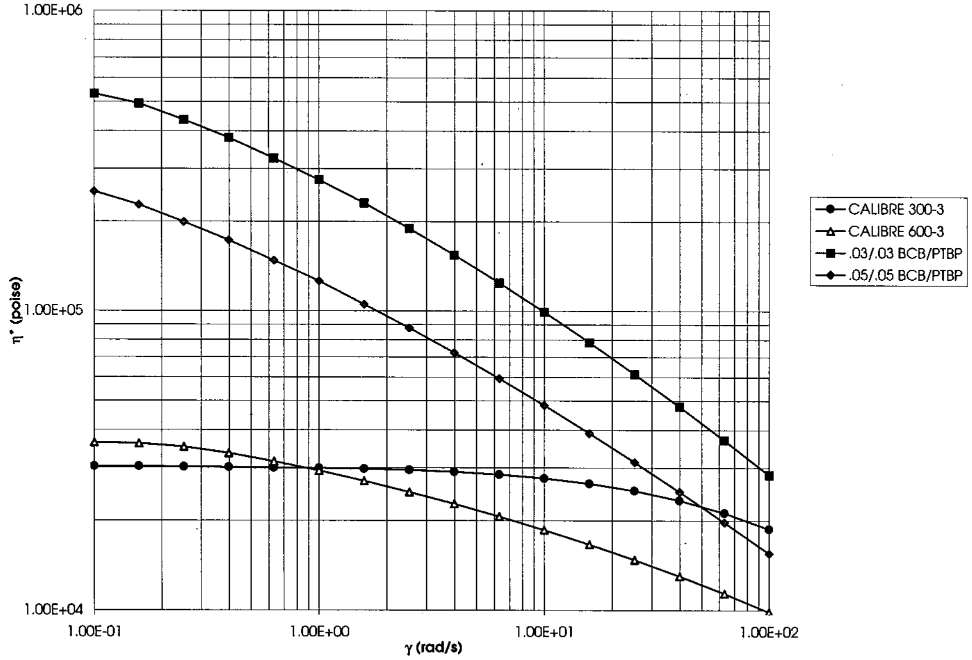


Figure 11. Parallel plate complex viscosity vs shear rate for branched BCB-OH/PTBP BA PC's, randomly branched BA PC, and linear 3 MFR BA PC at 280 °C.

shear rates γ (Figure 11). Linear BA PC's display relatively low degrees of shear rate sensitivity; η^* of 3 MFR BA PC is essentially constant at shear rates from 0.1 to 10 rad/s and then decreases only slightly at 100 rad/s. The randomly branched BA PC (CALIBRE 603-3 resin), which can have a maximum N_b value of 0.25,[5] is significantly more shear sensitive than its linear analogue, making it more suitable for certain types of melt processing techniques such as blow molding and profile sheet extrusion.[4] The long chain branched BCB-OH/PTBP BA PC's show much greater shear sensitivities than the conventional BA PC's. The η^*'s of these materials are very high at low γ's but decrease nearly linearly to values at 100 rad/s, approaching those of the conventional BA PC's. The low shear η^*'s should depend on M_w, so the high values observed are not unexpected. The branched 0.03/0.03 m/m polymer has a higher η^* than the 0.05/0.05 m/m sample, a result which is apparently due to a complex balance of molecular weight, polydispersity, and T_g effects. Very high shear sensitivities are observed for both long chain branched PC's, both of which have nearly twice the degree of branching as the randomly branched BA PC. The relative shear sensitivities of polymers can be expressed as the ratio R^* of η^*'s at arbitrary γ's, here taken as 1 and 100 rad/s (eq 3). R^* of both of the long chain branched BCB-OH/PTBP BA PC's is about 5 times greater than that of the randomly branched BA PC (Table 4).

$$R^* = \eta^*(1 \text{ rad/s})/\eta^*(100 \text{ rad/s}) \qquad (3)$$

Conclusions

Long chain branched BA PC's were prepared by use of a combination of thermally reactive BCB-OH and nonreactive PTBP chain terminators. These two mono-

Table 4. R^* of Linear, Branched, and Long Chain Branched BA PC's

BA PC	η^* (1 rad/s)	η^* (100 rad/s)	R^*
3 MFR	2.99×10^4	1.88×10^4	1.6
randomly branched	2.94×10^4	9.87×10^3	3.0
0.03/0.03 BCB-OH/PTBP	5.33×10^5	2.84×10^4	18.7
0.05/0.05 BCB-OH/PTBP	2.52×10^5	1.55×10^4	16.3

phenols react under interfacial conditions at similar rates to provide a statistical distribution of coterminated PC's having molecular weights controlled by the total amount of coterminators. Heating these materials to 300 °C causes branching and/or cross-linking depending on the value of X_{BCB}, thereby separating the polycondensation and branching processes and allowing greater degrees of branching than possible by random branching during polycondensation. At $X_{BCB} < 0.55$ the BCB-OH/PTBP BA PC's branch without cross-linking. The poly-BCB products formed upon the thermal branching of these PC's are the same as those observed in cross-linked BCB terminated BA PC's. The nongel value of X_{BCB} is that expected for a thermally reacted BCB functionality of 2.6, which is the same as that estimated for cross-linked BCB PC's. Based on the statistical distribution of the chain ends and the functionality of the poly-BCB products, BCB-OH/PTBP BA PC's having X_{BCB} values of 0.50 have a minimum of 0.45 number fraction branched chains.

The M_w and polydispersity of branched BCB-OH/PTBP BA PC's depend on their initial molecular weight and increase with X_{BCB}. The M_w's for each composition converge to large values (~100 000 Da) near the gel point, after which the M_w's of the soluble fractions decrease. The T_g's of these polymers scale inversely with M_n rather than M_w. Film toughness also trends with M_n. Films of branched BCB-OH/PTBP BA PC's having $M_n > \sim 2M_e$ are relatively tough and flexible, while those having lower M_n's, regardless of M_w, are relatively brittle.

The melt viscosities of branched BCB-OH/PTBP PC's are very high at low shear rates, as expected from their high M_w's, but decrease dramatically with increasing shear rates to values approaching those of conventional linear and randomly branched PC's. Such high zero-shear viscosity, which is indicative of high melt strength, and large shear sensitivity suggests that these new materials could display significant improvements in melt processing by techniques such as blow molding, thermoforming, injection molding, and extrusion.

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References and Notes

(1) Marks, M. J.; Sekinger, J. K. *Macromolecules* **1994**, *27*, 4106.
(2) Marks, M. J.; Scott, D. C.; Guilbeaux, B. R.; Bales, S. E. *J. Polym. Sci. Part A, Polym. Chem.* **1997**, *35*, 385.
(3) Marks, M. J.; Scott, D. C.; Guilbeaux, B. R. *J. Appl., Polym. Chem.*, accepted for publication.
(4) Pakull, R.; Grigo, U.; Freitag, D. Polycarbonates. In *RAPRA Review Reports*; Pergamon: New York, 1991; Vol. 42.
(5) Roovers, J. Branched polymers. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley: New York, 1985; Vol. 2, p 478.
(6) Wong, P. K. U.S. Patent 4,708,990, 11-24-87.
(7) Delassus, S. L.; Howell, B. A.; Cummings, C. J.; Dais, V. A.; Nelson, R. M.; Priddy, D. B. *Macromolecules* **1994**, *27*, 1307.
(8) Marks, M. J.; Schrock, A. K.; Newman, T. H. U.S. Patent 5,171,824, 12-15-92.
(9) Bailly, C.; Daoust, D.; Legras, R.; Mercier, J.; de Valck, M. *Polymer* **1986**, *27*, 779.
(10) Brunelle, D. J.; Shannon, T. G. *Macromolecules* **1991**, *24*, 3035.
(11) Nielsen, L. E. *Mechanical Properties of Polymers;* Dekker: New York, 1974; Vol. 1, p 22.
(12) Estimated by the method described in: Bicerano, J. *Prediction of Polymer Properties*; Dekker: New York, 1993.
(13) Marks, M. J.; Erskine, J. S.; McCrery, D. A. *Macromolecules* **1994**, *27*, 4114.

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