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Synthesis, Cross-Linking, and Properties of Benzocyclobutene-Terminated Bisphenol A Polycarbonates

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ABSTRACT: Benzocyclobutene-terminated Bisphenol A polycarbonates (BCB PC's) cross-link upon heating to form network polymers having excellent solvent and ignition resistance combined with good toughness over a wide range of cross-link densities. BCB PC's having a wide range of molecular weights were prepared by the interfacial phosgenation of Bisphenol A and 4-hydroxybenzocyclobutene. These telechelic PC's cross-link upon heating to temperatures above 200 °C to form completely insoluble networks. Cross-linking kinetics estimated by DSC and rheological measurements are consistent with a first-order BCB homopolymerization process. Many of the mechanical properties of cross-linked BCB PC's depend strongly on cross-link density. Particularly noteworthy is the high to moderate notched Izod impact strength of BCB PC's over a wide range of cross-link densities. Any degree of cross-link density imparts improved ignition resistance in these materials due to the absence of melt dripping. Cross-linked BCB PC's swell in good solvents for the un-cross-linked polymer in proportion to their cross-link density and do not suffer stress crack failure upon exposure to aggressive (to un-cross-linked PC) organic lipids such as acetone. At high cross-link densities BCB PC's have a relatively high fracture toughness and show improved surface hardness. Above their glass transition temperatures cross-linked BCB PC's show stable elastic moduli by dynamic mechanical analysis.

Introduction

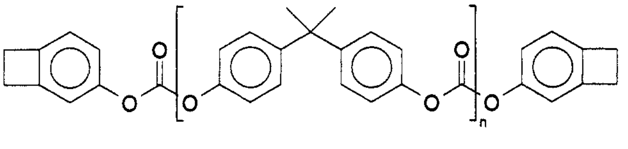
Bisphenol A polycarbonate (BA PC) is a linear engineering thermoplastic well-known for its remarkable balance of outstanding mechanical properties, good heat tolerance, and excellent optical clarity.[1] However, BA PC does suffer from relatively poor solvent resistance and low surface hardness. Modification of BA PC by cross-linking is one approach which could significantly improve upon these deficiencies.

While cross-linking of thermoplastic polymers has been achieved in various ways, a systematic study of the effect of cross-linking from low to high cross-link density on a broad range of physical and thermomechanical properties of the resulting materials has not been published. Cross-linking of high-performance amorphous thermoplastics by both pendant and end-group reactions has been shown to yield materials with improved solvent resistance. Examples of the many types of reactive end groups which have been employed to cross-link thermoplastics such as polyimides, poly(ether sulfones), poly(aryl ethers), and poly(aryl ether ketones) include acetylene,[2] maleimide,[3] nadimide,[4] and biphenylene.[5] This approach has been widely used in the preparation of modified high-performance thermoplastic composites,[6] although materials having only a relatively narrow range of cross-link densities have been reported. Many types of reactive oligomers have been prepared for use in high-performance composites, electronic materials, adhesives, and coatings,[7] but these materials have tended to be relatively low molecular weight species which cure to very high cross-link density networks.

A few BA PC's bearing cross-linkable groups have also been reported, the reactive moieties including maleimide,[8] which cross-links in the presence of radical initiators; methacrylate,[9] which photo-cross-links in the presence of photoinitiators; and pendant benzocyclobutene (BCB),[10] which cross-links upon heating above 200 °C. In none of these reports were the properties of the resulting cross-linked PC's described in detail.

Various types of thermosets based on BCB-functionalized compounds have been studied recently, and these materials have the advantage of cross-linking solely by exposure to high temperatures without the evolution of volatiles to form nonpolar hydrocarbon network junctions.[11] While most of the BCB-based materials prepared to date have been designed for highly cross-linked electronics or composites applications, BCB-terminated polyquinolines,[12] BCB pendant polyterephthalamides,[13,14] and BCB pendant poly(aryl ether ketones)[15] have also been recently prepared. However, structure–property relationships for these new thermosets are also yet to be reported.

In this study BA PC's bearing BCB terminal groups (BCB PC's, 1) were prepared with controlled molecular weights using varying amounts of 4-hydroxybenzocyclobutene (BCB-OH, 2) chain terminator and were subsequently cross-linked to give new thermoset polymers.[16] The linear BCB PC's were characterized by a variety of techniques, and the properties of BCB PC's having a wide range of cross-link densities were examined.



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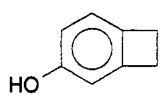

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Experimental Section

Chemicals. Bisphenol A (BA; Dow Chemical Co.; PARABIS), dichloromethane (Dow Chemical Co., technical grade), 50 wt % aqueous sodium hydroxide (caustic, Fisher Scientific), triethylamine (TEA; Aldrich Chemical Co.), phosgene (5-lb. cylinder from Matheson Gas Products), Bisphenol A polycarbonate (Dow Chemical Co.; CALIBRE 300-6 grade PC), and tetrahydrofuran

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(THF; Fisher Scientific) were used as received. Distilled or recrystallized 4-hydroxybenzocyclobutene was prepared as previously described.[17]

Analytical Methods. Liquid chromatography (LC) and gel permeation chromatography (GPC) analyses were done on a Hewlett-Packard Model 1090 system connected to a UV diode-array detector. Reversed-phase LC analysis was done using a Scientific Glass Engineering glass-lined column (150 × 4 mm) containing Spherisorb ODS2 (3 μm). GPC analyses were done using two DuPont ZORBAX PSM Bimodal-S columns (6.2 mm × 25 cm) with 1 mL/min of THF. A single broad molecular weight Bisphenol A polycarbonate standard (M_w = 30 000; dispersity = 2.50) was used for calibration.

Differential scanning calorimetry (DSC) was performed using a TA Model 912 dual-sample differential scanning calorimeter connected to a TA 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. Kinetic parameters were calculated using the Borchardt–Daniels program. Char yield and decomposition temperature (T_d) were determined by thermogravimetric analysis using a TA Model 943 thermogravimetric analyzer connected to the above controller. Char yield is reported as the weight percentage of the residue remaining after heating the material up to 800 °C in air. T_d is the temperature at which 5% of sample is lost by heating under N_2 at 10 °C/min.

Complex viscosities were measured using a Rheometrics 605 mechanical spectrometer run in the cure mode and fitted with parallel 25-mm-diameter plates set at a 1-mm gap and oscillated at 1 Hz with 5–30% strain. Low-density BCB PC's were heated under nitrogen to about 200 °C and quenched to about 160 °C prior to starting the temperature ramp at 2 °C/min.

Tensile property data were generated using a MTS 50 kpsi servohydraulic test frame in accordance to ASTM D-638 using type V specimens (2.5-in. length, 0.0625-in. thickness) cut from plaques using a TensilKut router and an appropriately shaped stainless steel template. Measurements were conducted at room temperature and a constant displacement rate of 0.2 in./min. Local strain determinations were done using an attached microextensiometer, gauge = 0.12 in. and full scale = 0.0096 in. (8%). Flexural moduli were determined on $^1/_{16}$-in. bars in accordance to ASTM D-790. Notched Izod impact testing was done in accordance to ASTM D-246-72A on a TMI pendulum testing instrument. Fracture toughness was measured in accordance to ASTM E-399. These mechanical properties are reported as the average results from three samples.

Limiting oxygen index (LOI) and UL-94 tests were performed in accordance to ASTM A-2863-87 and D-4804-88, respectively, on $^1/_8$-in. bars. Scratch and pencil hardness tests were done in accordance to ASTM D-3363. Dynamic mechanical analysis (DMA) was performed on a Rheometrics 7700 dynamic spectrometer from −160 to about +360 °C (to sample failure) using an oscillatory frequency of 1 Hz and a strain of 0.05%.

Swelling of compression-molded films of 0.01–0.02-in. thickness which were immersed in dichloromethane was calculated from the increase in film surface area after equilibrium was achieved (up to 24-h exposure). Strips of 0.01-in.-thick films were clamped at a radius of 0.5 in. (strain − 1%) and immersed in acetone to measure comparative solvent resistance.

General Synthesis. Phosgenation reactions were conducted in a class A fume hood. MDA tape was applied to the apparatus at various locations to detect possible phosgene leaks. A 1-L resin kettle was fitted with a mechanical stirrer, a stirrer baffle, a thermometer, a pH electrode connected to a Fisher Model 805 pH meter/controller, a caustic inlet tube, a phosgene inlet–dip tube, and a gas outlet tube connected to a phosgene scrubber containing 50 wt % aqueous caustic and a small amount of triethylamine. Aqueous sodium hydroxide (50%) was added from a graduated addition funnel by a Masterflex pump connected to the pH controller through a relay switch. Phosgene was added from a 5-lb. cylinder through a gas flow meter. The mass of the phosgene added was determined from the cylinder weight loss using a Flex-weigh Corp. balance. The reactor and solvents were thoroughly purged with N_2 prior to phosgenation. The stirrer was set at 800–1000 rpm to give turbulent mixing throughout the vessel. The reactor was immersed in an ice bath to maintain its temperature below 30 °C. The relative amount of BCB in BCB PC's is designated by the mole ratio of BCB-OH and BA used in each preparation, termed herein as mole/mole or m/m.

0.03 m/m BCB PC. To the reactor as described above was added 68.5 g (0.3 mol) of BA, 1.08 g (0.009 mol) of BCB-OH, 360 mL of water, and 180 mL of dichloromethane. With stirring 30 mL (48 g, 0.6 mol) of 50% aqueous sodium hydroxide was added followed by 37 g (0.375 mol) of phosgene at about 1 g/min with addition of sodium hydroxide to maintain a pH of about 12.5. Then 390 mL of dichloromethane and 0.44 mL (0.30 g, 1 mol %) of triethylamine were added. The mixture was agitated for 20 min to produce the linear BCB PC. The pH of the mixture was reduced to about 7 with addition of 9 g of phosgene. The polymer solution was washed with 1 N HCl and with water, and the polymer was then isolated by addition of the solution to ~90 °C water with stirring.

The relative amounts of BA and BCB-OH were adjusted using the process to prepare 0.06–1.00 m/m BCB PC's. 0.60–1.00 m/m BCB PC's were isolated by addition of the polymer solution to boiling heptane followed by rotary evaporation of the solvent.

0.03 m/m BCB PC, Absent Bis(benzocyclobutenyl) Carbonate). To the reactor as described above was added 68.5 g (0.3 mol) of BA and 360 mL of water. With stirring 53 g (0.66 mol) of 50% aqueous sodium hydroxide was added followed by 38 g (0.39 mol) of phosgene at about 1 g/min. Then 160 mL of dichloromethane and 1.08 g (0.009 mol) of BCB-OH were added, and the mixture was stirred for 2 min. The pH of the mixture was increased to 12.5 with addition of 50% aqueous sodium hydroxide, and 275 mL of dichloromethane and 0.10 g of triethylamine were added. The mixture was agitated for 30 min with addition of 50% sodium hydroxide to maintain a pH of about 12.5. The pH of the mixture was then reduced to about 7 with addition of 19 g of phosgene to produce the BCB-terminated polycarbonate. The polymer solution was washed, and the polymer was isolated as described above.

Molding and Casting. 0.03–0.40 m/m BCB PC's dried at 100 °C under vacuum were compression molded into $^1/_8$- and $^1/_{16}$-in. plaques using a Tetrahedron MTP-14 compression molder. The temperature/pressure program used is described below:

temp (°C)	pressure (klb.)	rate* (°C/min)	time (min)
200	0.4	200	30
200	40	200	1
300	40	200	1
100	40	200	1

(*maximum rate settings on instrument)

The actual cooling rate was about 10 °C/min during the last step in the above program.

0.60–1.00 m/mm BCB PC's dried at 100 °C under vacuum were melt casted into a preheated open-topped mold. The mold was fabricated from two 6 × 6 × $^1/_8$ in. aluminum plates and a three-sided $^1/_8$- or $^1/_{16}$-in. spacer. An aluminum sheet was placed on both plate surfaces and the C-clamped assembly was preheated to 215 °C in a vacuum oven. A 25% excess BCB PC sample was placed in a Petri dish and heated for 15–30 min at 215 °C to form a low-viscosity, clear fluid. The BCB PC melt was poured into the hot mold, and both were placed in a N_2 purged oven to heat at 215 °C for 30 min, then ramped at 1 °C/min to 300 °C, held at 300 °C for 1 min, and cooled slowly.

Compression-molded and melt-casted plaques were cut into appropriate test specimens using a Hermes safety saw and/or a Hermes Shear-Plastic cutter.

Results and Discussion

Linear BCB PC's (1) were prepared by the interfacial polycondensation of BA, phosgene, and BCB-OH (2) as chain terminator. These linear BCB PC's were analyzed by gel permeation chromatography (GPC), reversed-phase liquid chromatography (LC), and differential scanning calorimetry (DSC). Thermal cross-linking of linear BCB PC's was accomplished during compression molding or melt casting of test films and plaques. The resulting networks were characterized by several thermal, mechanical, and solvent exposure methods. Additionally, the

Table 1. BCB PC Properties vs Molecular Weight or Cross-Link Density

	mole/mole BCB-OH/BA									
property	1.00	0.80	0.60	0.40	0.30	0.20	0.10	0.06	0.03	PC
M_w(GPC)	1327	1451	2088	3105	4128	6057	11634	18190	31894	31112
M_n(GPC)	500	518	718	927	1408	2072	4518	6951	11803	11802
disp.(GPC)	2.65	2.80	2.91	3.35	2.93	2.92	2.58	2.62	2.70	2.64
M_n(LC)	957	1155	1046	1390						
theor av dp	2	2.3	2.7	3.5	4.3	6	11	27	32	32
LC calc av dp	2.5	2.9	3.1	4.1						
T_g (°C), precure	~130		125	125	130	135	139	150	150	
T_m (°C), precure		145	190	205						
ΔH (J/g)		241.6	174.0	89.2	79.3	52.1	26.7	19.6	5.8	
E_a (kJ/mol)	184	190	190	188	182	173	208	213	304	
reaction order	1.1	1.1	1.2	1.5	1.2	1.1	1.8	2.0	3.2	
$T_{1/2}$ @ 250 °C (min)	2.7	2.8	2.8	3.3	3.7	3.8	6.8	8.4	65.4	
T_g (°C), postcure	207	198	194	180	181	176	170	165	160	150
T_d (−5%) (°C)	415	436		447					469	475
% char yield	27								19	24
log η^* (minimum)		0.30		1.82	2.20	3.00	5.21	5.85	6.37	
ten mod (MPa)	2262	2255	2262	2221	2041	1966	2000	1931	1952	1862
yd stress (MPa)	85.5	82.0	79.3	71.0	66.2	62.1	62.1	61.4	59.3	58.6
yd elong (%)	14	13	13	16	16	16	16	15	16	15
bk stress (MPa)	85.5	81.4	75.2	61.4	55.2	49.7	48.3	53.8	55.2	62.1
bk elong (%)	14	14	16	24	23	31	38	40	111	200
flex mod (MPa)		2690		2641			2428			2662
notch Izod (J/m)		53	59	139	198	240	235	256	101 262[a]	801
film ductility	low	low	low	med	high	high	high	high	high	high
K_{1c} (MPa·m$^{0.5}$)	1.07	1.15	1.46	1.83	1.90					
LOI								42	42	27
UL-94 $^1/_8$ in.		V-0						V-0	V-0	V-2
scratch hardness	H	F	F	HB	HB	B	2B	2B	3B	3B
pencil hardness	H	H	F	F	F	F	HB	HB	HB	HB
% swell CH_2Cl_2	18	13	20	39	33	56	64	105	148	sol.
acetone break (s)							>10^7	>10^7	>10^7	1

[a] Product absent bis(benzocyclobutenyl) carbonate.

kinetics of BCB PC cross-linking was estimated by DSC, and isothermal and variable-temperature rheology evaluations were performed. The properties of linear and cross-linked BCB PC's as a function of cross-link density are shown in Table 1. For comparative purposes, the properties of an engineering grade BA PC are also shown.

The relative amount of BCB in BCB PC's is designated by the mole ratio of BCB-OH and BA used in each preparation, termed herein as mole/mole or m/m. The molecular weight of linear BCB PC's is inversely proportional to the BCB-OH/BA mole ratio.

Synthesis and Analysis of Linear BCB PC's. BCB PC's were prepared by the interfacial phosgenation of mixtures of BA and BCB-OH (Scheme 1). The 0.03 and 0.06 m/m BCB PC's have molecular weights within the range of those of engineering grades of commercially available BA PC's.[1] The greater m/m BCB PC's have molecular weights below the BA PC brittle point and are increasingly friable with decreasing molecular weight. (Since the GPC calculations are based on a single high molecular weight Ba PC standard, the results become less accurate with decreasing molecular weight.) A modification of the interfacial BCB PC process entails addition of BCB-OH after phosgenation of BA, thereby precluding formation of bis(benzocyclobenyl) carbonate (bis-BCB CO_3). A 0.03 m/m BCB PC was prepared using this modification to compare with the one containing the monocarbonate.

The modality of BCB PC's increases with decreasing molecular weight as shown in the GPC curves (Figure 1). The peak in these curves at 17.64 min corresponds to bis(benzocyclobutenyl) carbonate, the lowest molecular weight product obtainable by this polycondensation process. The higher molecular weight carbonate compounds are not resolved by the GPC column and conditions employed, although peaks corresponding to di-, tri-, and tetracarbonates appear to be partially resolved in the 1.00 m/m BCB PC chromatograph.

Reversed-phase liquid chromatography of BCB PC's shows the presence of both linear and cyclic oligocarbonates, the amount and distribution of which depends on the polymer molecular weight (Figure 2). (In these chromatographs, only the oligomer regions are shown; the polymer peaks were removed for clarity.) In 0.03 m/m BCB PC (Figure 2a) the predominant low molecular weight species are cyclic oligomers, but in all lower molecular weight BCB PC's the linear BCB-capped oligomers are predominant. The 0.40 m/m and higher BCB PC's (Figure 2c) contain essentially no high molecular weight polymer; thus, from the molecular weights and relative amounts of each oligomer the molecular weight averages of these materials can be calculated (M_n(LC) in Table 1). In these calculations data from the first 13, clearly resolved linear BCB-capped oligomers were used in addition to that of bis-BCB carbonate and BCB-BA monocarbonate and the response factors of each component were assumed to be identical. The M_n's calculated from the LC data are considerably greater than those determined by GPC, which is not unexpected due to the GPC calibration employed, and more accurately reflect the contribution of the BCB end group to molecular weight as the BCB m/m increases.

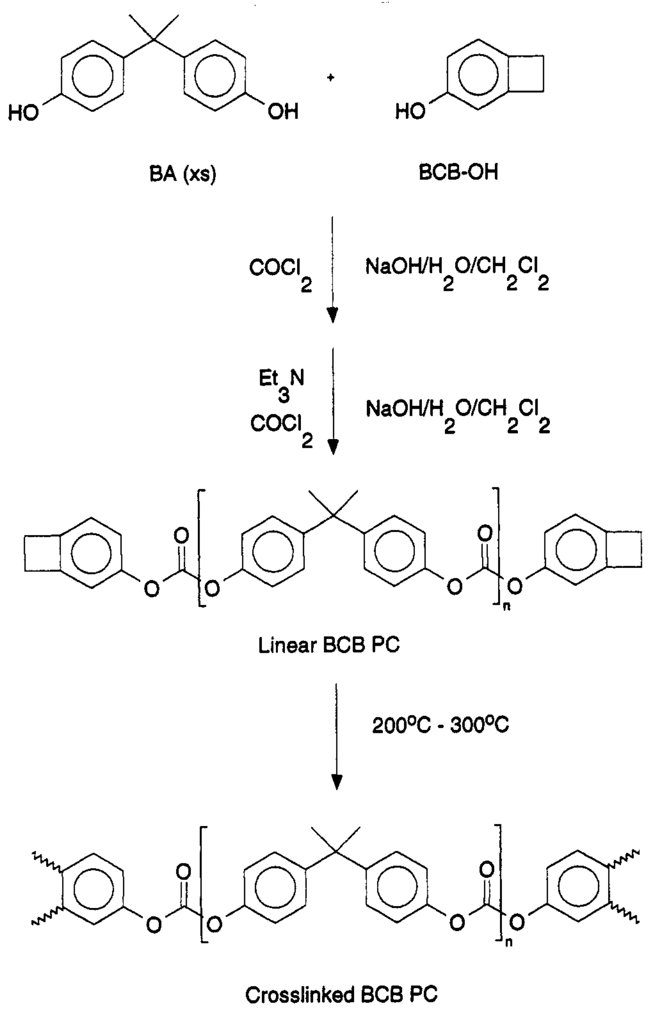
The degree of polymerization (n) of each BCB PC can be calculated from the BCB/BA molar ratio using eqs 1 and 2,[18] where r is the mole ratio of reactive groups

$$n = (1 + r)/(1 + r - 2pr) \qquad (1)$$

$$r = X_a/(X_a + 2X_t) \qquad (2)$$

(monomer/terminator), p is the extent of reaction (taken

Scheme 1. Synthesis and Cross-Linking of BCB PC's



as 0.999), X_a is the mole fraction of difunctional monomer (BA), and X_t is that of the terminator (BCB-OH). These calculated n values, ranging from 32 to 2, agree reasonably well with both those calculated by dividing M_n by the repeat unit molecular weight and with those calculated from the LC analysis. Noteworthy is the less than a fraction of a monomer unit change in the degree of polymerization per decimal increase in mole/mole terminator in the 0.30 and greater m/m BCB PC's.

Thermal Analysis of Linear and Cross-Linked BCB PC's. Analysis of linear BCB PC's by differential scanning calorimetry (DSC) shows in the first scan a glass transition (T_g) and/or a diffuse melting point (T_m), followed by an exotherm ranging from about 225 to 325 °C due to BCB ring opening and polymerization.[11] The higher molecular weight BCB PC's (0.03–0.30 m/m) have T_g's which decreased with decreasing molecular weight in the range from about 155 to 110 °C. The lower molecular weight BCB PC's have broad T_m's ranging from about 175–210 °C for the 0.40 m/m material to about 125–175 °C for the 1.00 m/m sample. The ΔH of the BCB reaction integrated from the exotherm peak is proportional to the BCB content in the polymer.

The kinetic parameters of the BCB exothermic polymerization were estimated by DSC using the method of Borchardt and Daniels.[19] While this method is quite approximate, the kinetic parameters obtained are useful for comparative purposes. The activation energy (E_a), reaction order, and 250 °C half-life ($T_{1/2}$) decrease with increasing BCB/BA mole ratio up to about 0.20 m/m BCB, upon which these values remain approximately constant.

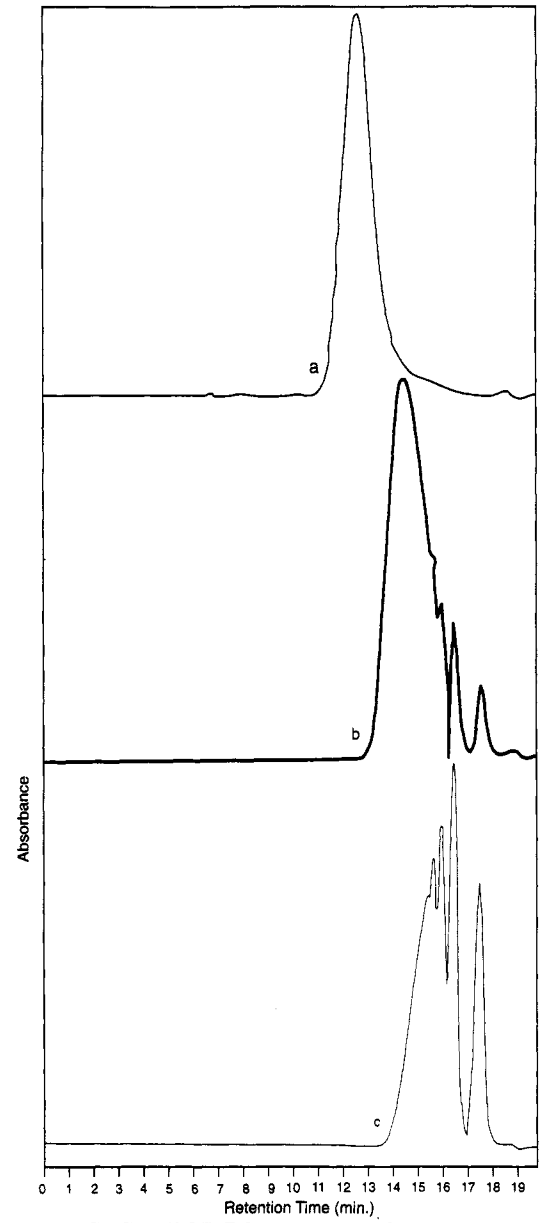


Figure 1. GPC of BCB PC's: (a) 0.03, (b) 0.30, (c) 1.00 m/m.

A first-order reaction is expected for BCB homopolymerization.[11] This trend in apparent reaction order suggests that the viscosity of the higher molecular weight linear BCB PC's plays a significant role in the overall cross-linking kinetics under the static DSC conditions.

The cross-linked BCB PC's are entirely amorphous and as shown in the second scan of the DSC analysis have T_g's from 160 to 207 °C. The T_g of 0.40 m/m cross-linked BCB PC is about 5–10 °C lower than expected and may be due to the somewhat broader polydispersity of this sample compared to the other BCB PC's in this series.

The thermal stability of BCB PC's is reduced from BA PC proportionally with BCB/BA mole ratio, as measured by thermal gravimetric analysis (TGA), with the 1.00 m/m material having a decomposition temperature (T_d) about 60 °C less than linear BA PC. The thermooxidative stability of BCB PC's is also apparently lower than BA PC as evidenced by the dark coloration of samples exposed to air at high temperatures. The char yield yield of BCB PC's is about the same as BA PC and is largely unaffected by cross-link density over the range examined.

Compression Molding and Melt Casting of BCB PC's. As shown by the DSC kinetic analysis, BCB PC's cross-link very rapidly at 300 °C, the standard melt

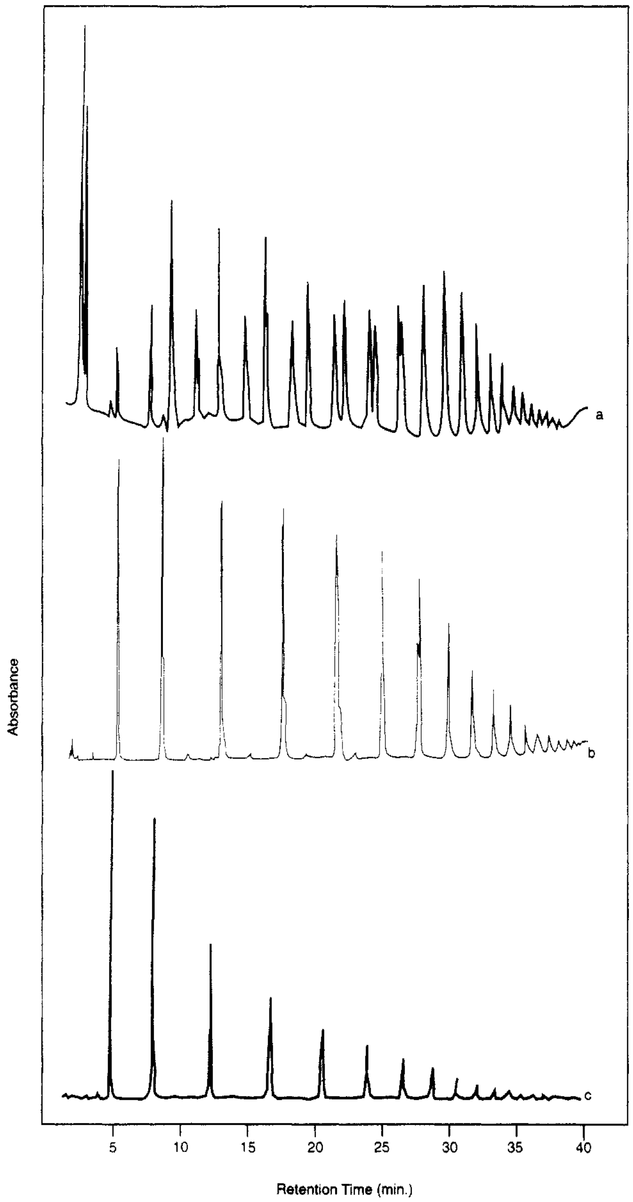


Figure 2. BCB PC oligomers by reversed-phase liquid chromatography: (a) 0.03, (b) 0.30, (c) 1.00 m/m.

processing temperature used for high molecular weight BA PC. Compression molding of low bulk density, higher molecular weight (0.03–0.40 m/m) linear BCB PC's at this temperature produced highly stressed cross-linked plaques. Under these conditions the plaques did not fully fill $^1/_8$- or $^1/_{16}$-in. molds and remained about 10% thicker than the mold thickness. Voiding along the edges of these plaques was observed upon their removal from the mold. Relaxation of the molded-in stresses in these samples with exposure to temperatures above T_g or to good BA PC solvents was evidenced by sample dimensional changes.

To produce fully formed, stress-free molded test films and plaques, the higher molecular weight BCB PC's were compression-molded using a two-stage procedure. Densification and mold filling were accomplished at 200 °C, followed by cross-linking by heating to 300 °C. A small, yet measurable amount of cross-linking did occur at 200 °C (as shown by a slight increase in molecular weight), but this did not contribute significant amounts of molded-in stress. The lower molecular weight (0.60–1.00 m/m) linear BCB PC's do not have sufficient melt viscosities to form void-free plaques by compression molding. These samples were molded using a melt-casting technique (see the Experimental Section). Both $^1/_8$- and $^1/_{16}$-in. plaques were prepared by this method.

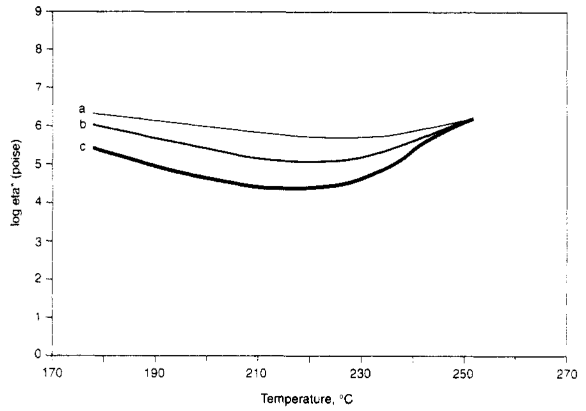


Figure 3. Dynamic mechanical analysis of linear BCB PC's, temperature sweep: (a) 0.03, (b) 0.06, (c) 0.10 m/m.

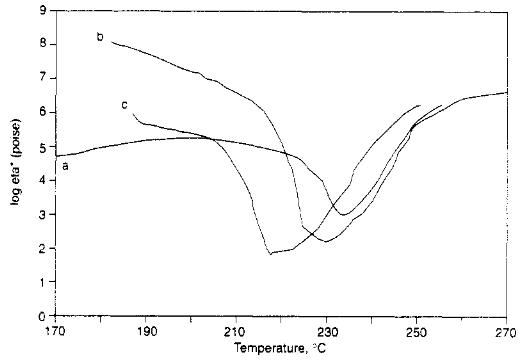


Figure 4. Dynamic mechanical analysis of linear BCB PC's, temperature sweep: (a) 0.20, (b) 0.30, (c) 0.40 m/m.

Rheology of Cross-Linking BCB PC's. The melt rheology of BCB PC's during cross-linking at constant shear and variable temperature or time was measured to assess their melt processability and to further study the BCB cross-linking kinetics. Temperature sweep studies show the complex viscosities of linear BCB PC's decreasing with increasing temperature in a manner identical to BA PC of the same molecular weights up to about 200 °C, at which BCB polymerization causes a rapid viscosity increase (Figures 3 and 4). The minimum complex melt viscosity (log η^*) for each BCB PC is listed in Table 1. The initial viscosities of the three highest molecular weight BCB PC's also decrease proportionally with molecular weight (Figure 3), whereas those of the lower molecular weight samples do not. These lower molecular weight (higher BCB/BA mole ratio) samples are semisolids well below their melting points (~220 °C) at the start of the measurements and thus have higher viscosities than the higher molecular weight materials (Figure 4). The viscosity minima observed in the 0.20–0.40 m/m BCB PC curves correspond to the melting temperatures of these materials. Both the viscosity minima and the temperature at that point are inversely dependent on the BCB mole ratio in this range of compositions.

Isothermal rheology experiments were performed on 0.03, 0.06, and 0.10 m/m BDB PC's. Each polymer shows an increase in complex viscosity at 200 °C, but complete cure was not achieved within 3 h (Figure 5). At 225 °C the viscosity increase is much more rapid, with complete cure rached within 2 h (Figure 6). This result is consistent with the approximate 1 h 225 °C half-life calculated by the DSC kinetic analysis.

Mechanical Properties of Cross-Linked BCB PC's. The tensile properties of cross-linked BCB PC's reveal a

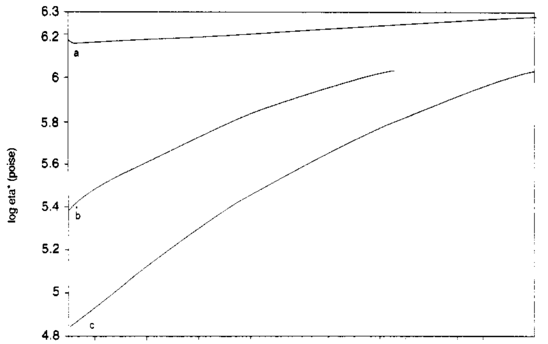


Figure 5. Dynamic mechanical analysis of linear BCB PC's, isothermal at 200 °C: (a) 0.03, (b) 0.06, (c) 0.10 m/m.

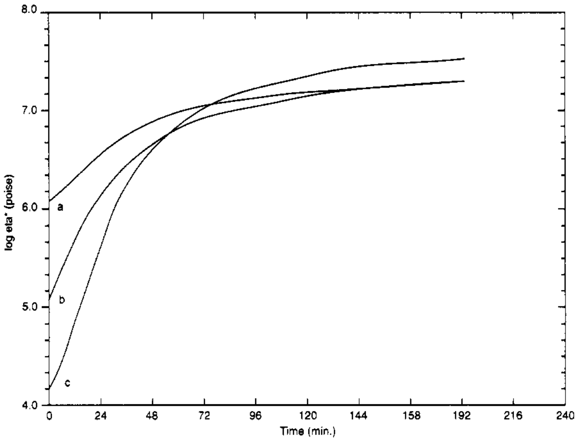


Figure 6. Dynamic mechanical analysis of linear BCB PC's, isothermal at 225 °C: (a) 0.03, (b) 0.06, (c) 0.10 m/m.

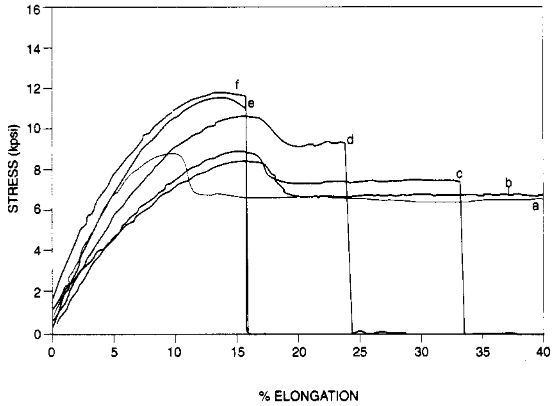


Figure 7. Stress-elongation curves of cross-linked BCB PC's: (a) linear BA PC, (b) 0.03 m/m, (c) 0.20 m/m, (d) 0.40 m/m, (e) 0.60 m/m, (f) 0.80 m/m.

remarkable degree of ductility over a wide range of cross-link densities, absent in abnormal morphology. Slight increases in modulus and yield and break stresses are observed with increasing cross-link density, with concurrent large drops in ultimate elongation. Tensile moduli of 1930–2260 MPa were found for each material tested. Cross-linked BCB PC's having up to and including 0.40 m/m BCB showed a slight decrease in the slope of the post yield stress drop (PSYD) before reaching the yielding plateau, as compared to BA PC (Figure 7). The 0.60 m/m BCB PC showed only a slight PSYD before failure, and the higher cross-link density samples yielded without a PSYD. Viewing yielding as a relaxation phenomena in which the flow of polymer chains relieves the applied stress, cross-linking is expected to retard polymer chain flow and thus decrease the relaxation rate. The tensile modulus is not much affected by cross-linking as this is a glassy state property.[20] Ultimate elongation of BCB PC's decreases with increasing cross-link density, a typical behavior attributed to the decreasing number of available polymer chain conformational states and the stress-concentrating effect of cross-link junctions.[20]

The BCB PC flexural modulus, also a glassy state property, is invariant with cross-link density and, within experimental error, is the same as that of BA PC. Toughness evaluations on films and plaques of cross-linked BCB PC's found that these materials are reasonably tough over a wide range of cross-link densities. The ductility of 0.01-in. cross-linked BCB PC films was examined by bending a strip of film over itself and slowly decreasing the radius (and thus increasing the stress) of the looped portion. The ductility of films which creased without breaking was denoted "high", and that of those which broke was termed "low". Cross-linked BCB PC's having from 0.03 to 0.30 m/m terminator formed creasable films. The ductility of the cross-linked 0.40 m/m BCB PC film was termed "medium" since it broke under a relatively high stress. The 1.00 mm BCB PC film was very brittle and in fact was difficult to manipulate without cracking.

Notched Izod impact testing of $^1/_8$-in. bars of cross-linked BCB PC's followed the above trend, except for the 0.03 m/m BCB PC which showed a very low impact strength. This anomaly proved to be due to the formation of phase-separated domains, observed by optical microscopy of the fracture surface, which act as flaws and thus reduce impact strength.[21] FTIR examination suggested that the composition of these occlusions is a poly-BCB material. Apparently in the 0.03 m/m BCB PC at least a portion of its bis-BCB CO_3 fraction cross-links to form phase-separated domains of high cross-link density material to produce an abnormal morphology. An analogous BCB PC prepared by a process which precludes formation of bis-BCB CO_3 showed a higher notched Izod impact strength consistent with the higher cross-link density materials. This 0.03 m/m BCB PC and those made with 0.06–0.30 m/m BCB-OH have very high impact strengths for cross-linked glassy polymers. The decrease in impact strength seen in the 0.40 m/m BCB PC sample correlates with the decrease in film toughness. This network cross-link density, which corresponds to an average degree of polymerization before cross-linking of about 3.5, appears to be at the transition point in the network fracture mechanism from a semi-tough to a brittle failure. This critical minimum molecular weight between cross-links, which corrected for BCB functionality[22] of about 2.6 gives a value of 9.1, is in the range of the 6–9 repeat unit segments required for cooperative chain motion and energy dissipation in BA PC.[23]

The more highly cross-linked BCB PC's show low Izod impact strengths typical of high cross-link density thermosets. Fracture toughness (K_{1c}) is a more meaningful measure of the toughness of these types of materials, and that of cross-linked BCB PC's is relatively high, ranging from 1.90 to 1.07 MPa·m$^{0.5}$, and is very sensitive to relatively small differences in cross-link density.

Ignition Resistance. The flammability behavior of BCB PC's is markedly different than BA PC. The limiting oxygen index (LOI) of cross-linked *and* linear 0.03 m/m BCB PC was found to be 42 and 40, respectively, compared to 27 for BA PC. Apparently a substantial amount of cross-linking of the linear BCB PC is achieved with heating by the flame during this test. This LOI increases manifests in an improved UL-94 rating for a $^1/_8$-in. bar from V-2 to V-0, largely due to a lack of dripping in the BCB PC samples. This result is consistent with the effects of

Table 2. Swelling of Cross-Linked BCB PC's in Organic Liquids

liquid	δ^a	0.10 m/m	0.06 m/m	0.03 m/m	BA PC
CH_2Cl_2	19.8	64	105	148	soluble
THF	18.6	48	95	137	soluble
toluene	18.2	50	69	49	crystallized
acetone	20.3	26	38	37	crystallized

[a] $(MPa)^{0.5}$, from ref 26.

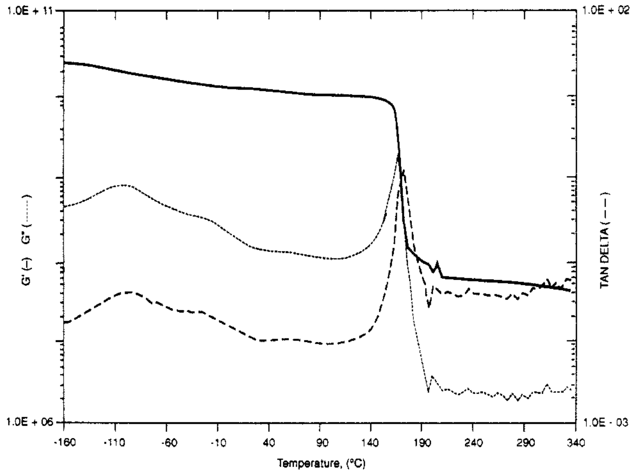


Figure 8. Dynamic mechanical analysis of cross-linked 0.03 m/m BCB PC.

radiation cross-linking on the ignition resistance of polyethylene.[24]

Solvent Resistance. Cross-linked BCB PC's swell upon prolonged exposure to various organic liquids with no measurable soluble fraction. Low concentrations of BA cyclic oligocarbonates can be detected by LC analysis of the liquid phase after such an exposure. Good solvents for BA PC such as dichloromethane and tetrahydrofuran swell cross-linked BCB PC's. As shown for dichloromethane exposure, the degree of BCB PC swelling is inversely proportional to cross-link density (Table 1). In general, the degree of swelling depends both on cross-link density and the liquid solubility parameter, δ (Table 2). These types of measurements can be used to calculate the cross-link density of these thermosets.[25] Also of note is the resistance of cross-linked BCB PC's to crystallization upon exposure to certain organic liquids. The environmental stress failure resistance of cross-linked BCB PC's was estimated by a loop immersion technique. Looped samples of BCB PC's under about 1% strain in continuous contact with acetone, which is very aggressive toward BA PC, have remained intact over several months. While good solvents for BA PC swell these looped materials, other organics show little or no effect.

Surface Hardness. The hardness of highly cross-linked BCB PC's is improved over BA PC as measured by scratch and pencil hardness. A significant increase in surface hardness is first observed in the 0.20 and 0.30 m/m BCB PC's and at the highest cross-link densities is better than that of poly(methyl methacrylate).

Dynamic Mechanical Analysis. Dynamic mechanical analysis (DMA) of cross-linked BCB PC's shows glassy behavior similar to BA PC but above T_g displays an elastic plateau as expected for network polymers (Figure 8). The low-temperature γ transition in cross-linked BCB PC's is somewhat broader than that seen in linear BA PC. The modulus above T_g is dependent on m/m BCB and can be used in calculations of cross-link density. This elastic modulus remains fairly constant to about 350 °C, above which the samples begin to decompose.

Conclusions

BCB-terminated BA PC's can be prepared by the interfacial phosgenation of BA in the presence of BCB-OH chain terminator. Linear BCB PC's having controlled molecular weights, from degrees of polymerization of ~32 to ~2, were prepared by varying the mole ratio of BCB-OH to BA.

Linear BCB PC's show by DSC analysis a T_g and/or a T_m, depending on its molecular weight, followed by a BCB homopolymerization exotherm. First-order BCB reaction kinetics are observed in the low molecular weight BCB PC's, but this reaction is slowed due to the higher melt viscosities of the higher molecular weight BCB PC's. Cross-linked BCB PC's are amorphous networks having T_g's from 160 to 210 °C depending on cross-link density, which in turn is determined by initial molecular weight. The thermal stability of cross-linked BCB PC's decreases from that of BA PC in proportion to BCB content, with as much as a 60 °C lower T_d observed in the most highly cross-linked sample.

The rheology of linear BCB PC's depends on its initial molecular weight. Higher molecular weight BCB PC's show viscosity–temperature behavior similar to BA PC until onset of the BCB reaction, after which the viscosity increases as the material cross-links. Low molecular weight linear BCB PC's show very low melt viscosities at temperatures above their melting point. The minimum melt viscosities occur in the range from 200 to 220 °C and are proportional to the BCB PC initial molecular weight. Isothermal rheology measurements support the kinetic parameters estimated by DSC.

Cross-linked BCB PC's show a remarkable degree of strength and toughness over a wide range of cross-link densities. Each composition examined in this study, spanning a degree of polymerization from 32 to 2, showed yielding before failure under tension. Notched Izod impact strengths of ~200–260 J/m were observed in samples having ~0.30 m/m BCB/BA or less. The estimated cross-link density at which the impact strength decreases is about the same as that proposed for the minimum sequence length of BA PC involved in cooperative chain motion and energy dissipation. The presence of inhomogeneities in BCB PC's, as in many plastics, greatly reduces its impact strength. The fracture toughness of high cross-link density BCB PC's is relatively high and is strongly depend on the cross-link density of the material.

The ignition resistance of both linear and cross-linked BCB PC's is substantially greater than BA PC as measured by LOI and UL-94 testing. Cross-linking, whether prior to or concomitant with burning, prevents the polymer for dripping after ignition and may also retard volatile fuel release. This phenomenon does not lead to higher char residues after complete sample oxidation.

Cross-linked BCB PC's are completely insoluble in good solvents for linear BA PC and also resist crystallization. These thermosets swell in good solvents for BA PC in proportion to their cross-link density and the solvent–BA PC interaction parameter. Strained films of these networks do not fail upon prolonged exposure to aggressive solvents such as acetone, which cause rupture of BA PC within seconds. Above T_g, cross-linked BCB PC's have stable elastic moduli up to their decomposition temperatures as shown by DMA.

Details on the chemistry of BCB PC cross-linking will be presented in a forthcoming paper.

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