

Synthesis and properties of 2,2'-dibromobisphenol A polycarbonate

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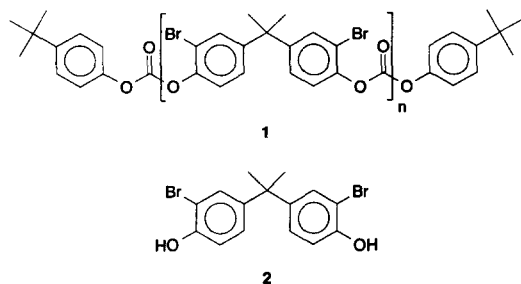
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The synthesis and properties of 2,2'-dibromobisphenol A polycarbonate (2,2'-DBBA PC) were studied. The monomer, 2,2'-DBBA, was selectively prepared by the direct bromination of bisphenol A in dichloromethane with an inert gas purge. High molecular weight 2,2'-DBBA PC was prepared by interfacial phosgenation of the monomer followed by coupling of the resulting oligomers catalysed by 4-*N,N*-dimethylaminopyridine. The thermal, tensile, flexural and impact properties of 2,2'-DBBA PC were determined and compared to those of bisphenol A PC, and 1:1 bisphenol A-tetrabromobisphenol A copolycarbonate.)

(Keywords: 2,2'-dibromobisphenol A; polycarbonate; bromination)

INTRODUCTION

Bisphenol A polycarbonate (BA PC) is an engineering thermoplastic well known for its outstanding combination of toughness, optical clarity and heat resistance^{1,2}. PCs based on many types of diphenols have been prepared and evaluated, among them many types of halogenated PCs have been studied. For example, tetrabromobisphenol A (TBBA) PC and BA-TBBA copolycarbonates (coPCs) can be used to improve the ignition resistance of BA PC¹. An improved synthesis^{3,4} of BA-TBBA coPCs produces copolymers having better solution washability and thermal stability^{5,6} due to their greater end group selectivity. These halogenated PCs have higher heat resistance yet similar puncture impact strength compared to BA PC⁷. 2,2'-Dibromobisphenol A (DBBA) PC (**1**) is an unreported member of the family of halogenated PCs which is expected to have both similar and dissimilar properties of TBBA-based PCs. In this study the synthesis of 2,2'-DBBA (**2**) and its PC were investigated and selected properties of the homopolycarbonate were evaluated.



EXPERIMENTAL

General. Bromination and phosgenation reactions were carried out in a Class A fume hood. Rubber gloves were

worn at all times when handling bromine. Reaction vessels were made as air-tight as possible. MDA tape (MDA Scientific) was attached to the phosgenation reactor at various locations to detect phosgene leaks.

Chemicals. Bisphenol A (BA, PARABISTM grade, Dow Chemical), methanol (Fisher Scientific, l.c. grade), bromine (Br₂, Aldrich Chemical Co.), dichloromethane (Dow Chemical, technical grade), anhydrous ethyl ether (EM Science), toluene (Fisher Scientific, reagent grade), carbon tetrachloride (CCl₄, EM Science), Norit-A decolorizing carbon (Eastman Kodak), *p*-*t*-butylphenol (PTBP, Schenectady Chemical), 50 wt% aqueous sodium hydroxide (NaOH, Fisher Scientific), *N,N*-dimethylaminopyridine (DMAP, Aldrich Chemical Co.), tetrahydrofuran (THF, Fisher Scientific) and phosgene (2.3 kg cylinder from Matheson Gas Products) were used as received.

Analytical. Reversed phase liquid chromatography (l.c.) and gel permeation chromatography (g.p.c.) were done on a Hewlett-Packard (HP) model 1090 system connected to a u.v. diode-array detector. L.c. analyses were done using a Scientific Glass Engineering glass-lined column (150 × 4 mm) containing Spherisorb ODS2 (3 μm). Analysis of 2,2'-DBBA was performed with detection at 288 nm and mobile phase flow rate of 0.5 ml min⁻¹ with a linear THF/water gradient programme of 40%. THF at 0 min and 100% THF at 20 min. The retention times of specific compounds are as follows: BA, 5.55 min; monobromobisphenol A (MBBA), 6.26 min; 2,2'-DBBA, 6.90 min; tribromobisphenol A (TriBBA), 7.91 min; TBBA, 8.89 min. Relative amounts are reported as percentage area. Prior to analysing samples, a few drops of acetone were added to react with any residual Br₂.

G.p.c. analyses employed two DuPont ZORBAX PSM Bimodal-S columns (6.2 mm × 25 cm) with 1 ml min⁻¹ THF eluant. G.p.c. calculations were performed using

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a single broad molecular weight BA PC standard ($M_w = 30\,000\text{ g mol}^{-1}$; polydispersity = 2.50). Fourier transform infra-red (FTi.r.) spectra were recorded on a Digilab FX 60 FTIR spectrophotometer from dichloromethane solution cast films on a salt plate. Spectra were collected from 680 to 4000 cm^{-1} . Residual bromomethane (CH_3Br) was detected by adding a few drops of an aqueous silver nitrate solution to a sample; a precipitate indicated the presence of CH_3Br .

Melting point and glass transition temperature (T_g) data were obtained by differential scanning calorimetry (d.s.c.) using a DuPont 2100 thermal analyzer and a heating rate of 20°C min^{-1} . T_g s are reported as the inflection point of the heat flow curve.

Mass spectral analysis was done using a Finnigan 4500 mass spectrometer fitted with a thermal desorption probe. The sample was deposited in a capillary quartz cup, inserted into the probe, and then heated from 30 to 400°C to obtain electron impact spectra on the vapour.

The distortion temperature under load (DTUL) was determined in accordance with ASTM D-648-72 on a Tinius Olsen heat distortion tester.

Dynamic mechanical analysis (d.m.a.) was performed on a Rheometrics 7700 dynamic spectrometer from -160 to ~200°C (to sample failure) using an oscillatory frequency of 1 Hz and a strain of 0.05%.

Tensile property data were generated using a MTS 50 kpsi (345 MPa) servo-hydraulic test frame in accordance to ASTM D-638 using type V specimens (6.4 cm length, 0.16 cm thickness). Measurements were conducted at room temperature and a constant displacement rate of 0.5 cm min^{-1} . Local strain determinations were done using an attached micro-extensometer, gauge = 0.3 cm and full scale = 0.02 cm (8%). Flexural moduli were recorded on an Instron model 1130 test frame according to ASTM D-790.

Notched Izod impact testing was done in accordance to ASTM D-256-72A on a TMI pendulum testing instrument.

Compression moulding. Samples were moulded in a 7.6 cm \times 6.4 cm \times 0.16 cm or \times 0.32 cm mould at 307°C using a Tetrahedron MTP-14 compression moulder. Specimens were cut to the appropriate dimensions for testing.

2,2'-Dibromobisphenol A. Bromination of bisphenol A in dichloromethane. A 100 ml three-necked round bottom flask was fitted with a reflux condenser and a N_2 sparge tube. The flask was charged with 5.71 g BA (0.025 mol), 50 ml dichloromethane, and a stir bar. A brisk N_2 purge was employed during bromination; the effluent was passed through a trap containing a 4 wt% aqueous caustic solution. A syringe pump was used to add Br_2 (10% v/v in CCl_4) at an average rate of 7×10^{-4} mol min^{-1} . Samples were taken at various intervals to monitor the reaction. The reaction temperature was controlled by dichloromethane reflux. The final product was composed of (by l.c. analysis): BA, 0.4%; MBBA, 0.3%; 2,2'-DBBA, 97.2%; TriBBA, not detectable; TBBA, not detectable.

This procedure was repeated in a 1 l resin kettle fitted with a mechanical stirrer, a stirrer baffle, a reflux condenser connected to a trap containing a 25 wt% aqueous caustic solution, a N_2 inlet-dip tube (4 mm i.d.),

a 250 ml graduated addition funnel, and thermometer. The reactor was charged with 75.0 g BA (0.328 mol) and 500 ml dichloromethane. Then 34 ml Br_2 (0.659 mol, 34% v/v in CCl_4) was added at a rate of 1.48×10^{-2} mol min^{-1} . The reaction mixture was stirred at 1250 rev min^{-1} with a brisk N_2 purge applied during Br_2 addition. The reactor solution was sampled after adding all of Br_2 ; l.c. analysis indicated 92.5% 2,2'-DBBA. Another 0.5 ml of Br_2 was added to give: BA, 2.0%; MBBA, 1.1%; 2,2'-DBBA, 95.2%; TriBBA, 1.2%; TBBA, 0.1%.

An equal volume of diethyl ether was added to the reactor and the organic solution was washed repeatedly with deionized water until the aqueous phase was neutral. Rotary evaporation of the organic phase gave a reddish-purple, gelatinous solid. The crude product (128.5 g) was dissolved in toluene (0.5 g 2,2'-DBBA ml^{-1} toluene), heated to boiling with 2 g Norit A decolorizing carbon, filtered, and allowed to cool slowly to room temperature. The resulting crystals were collected by vacuum filtration, washed twice with toluene, and dried at room temperature to give 55.3 g (43% yield) of 2,2'-DBBA having a melting point of 95.9°C. L.c. showed: BA, not detectable; MBBA, 0.8%; 2,2'-DBBA, 98.3%; TriBBA, 0.9%; TBBA, not detectable. Direct probe mass spectroscopy gave $m/e = 384$ parent ion.

2,2'-Dibromobisphenol A. Bromination of bisphenol A in methanol. A 25 ml round bottom flask fitted with a reflux condenser was charged with 2.28 g BA (0.01 mol), 10 ml of methanol, and two to three boiling chips. The mixture was heated to reflux and 1 ml Br_2 (0.04 mol) was added dropwise from a syringe through the top of the condenser. A sample was taken after adding half of the Br_2 . After all of the Br_2 was added the condenser was replaced with a distillation head and the mixture was distilled until CH_3Br was not detected in the distillate by AgNO_3 . L.c. analysis gave: BA, 12.4%; MBBA, 1.8%; 2,2'-DBBA, 37.7%; TriBBA, 13.1%; TBBA, 16.0%.

The reaction was repeated at reduced temperature and concentration in a 100 ml three-necked round bottom flask fitted with a reflux condenser and a thermometer and charged with 2.28 g BA (0.01 mol), 50 ml methanol, and a stir bar. The flask was cooled to ~4°C and then 1 ml Br_2 (0.04 mol) was slowly added dropwise. L.c. analysis gave: BA, 0.3%; MBBA, 17.2%; 2,2'-DBBA, 60.6%; TriBBA, 8.3%; TBBA, 11.2%.

2,2'-Dibromobisphenol A PC. Synthesis of the homopolymer was carried out in a 1 l resin kettle 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 NaOH 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 2.3 kg cylinder through a gas flowmeter. The mass of the phosgene added was determined from the cylinder weight loss using a Flex-weight Corp. balance. The reactor and solvents were thoroughly purged with N_2 prior to phosgenation. The stirrer was set at 800–1000 rev min^{-1} to give turbulent mixing throughout the vessel. The reactor was immersed in an ice bath to maintain its temperature below 30°C.

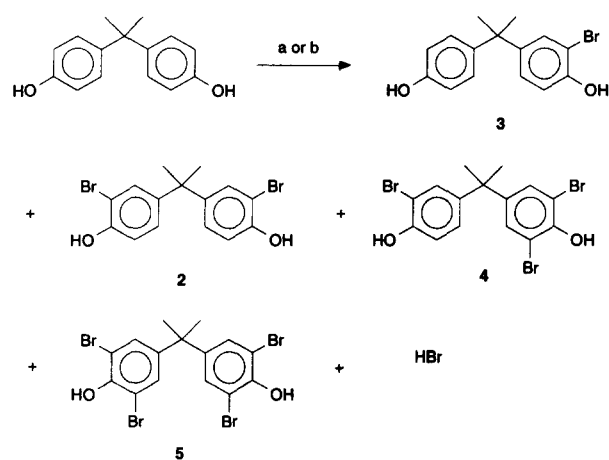
The reactor was charged with 51.10 g 2,2'-DBBA (0.132 mol), 0.39 g PTBP (0.0026 mol, 2 mol% of 2,2'-DBBA), 265 ml deionized water, and 101 ml dichloromethane. Then 21.17 g 50% NaOH (0.2646 mol) was added which gave an aqueous phase pH of 12.7. With rapid stirring 20 g phosgene (0.1984 mol) was added at $\sim 0.6 \text{ g min}^{-1}$ while a pH of 12.5 was maintained by addition of 50% NaOH. After phosgenation the phases separated slowly with the stirrer off. A sample of the aqueous phase tested negative for 2,2'-DBBA by acidification with 1 N HCl. Then 0.08 g DMAP (0.00066 mol) and 170 ml dichloromethane were added with increased agitation (to 1250 rev min^{-1}) to compensate for increasing viscosity. The pH of the mixture was maintained at 12.5, as indicated by pH paper, by addition of 6 ml 50% NaOH. After 15 min, homopolymer formation was complete; organic phase chloroformates were undetectable by MDA tape. The aqueous phase was neutralized to pH 7.5 with phosgene and the organic solution degassed ($-\text{CO}_2$). The reactor contents were transferred to a separatory funnel in which the organic phase was separated and washed once with dilute (1 N HCl) and then repeatedly with deionized water until neutral to pH paper. G.p.c. analysis gave: $M_w = 43\,677$; $M_n = 14\,971$; polydispersity = 2.92. D.s.c. showed a T_g of 159°C . FTi.r. (film) showed the carbonate absorption band at 1785 cm^{-1} .

RESULTS AND DISCUSSION

Synthesis of 2,2'-DBBA

The bromination of BA proved to a convenient method to obtain 2,2'-DBBA. Halogenation of BA by usual methods produces mixtures of 2-mono-, 2,2'-di-, 2,2',6-tri- and 2,2',6,6'-tetrahalogenated products⁸. A BA halogenation method which employs purging of the reaction mixture with an inert gas to remove hydrogen

halide claimed to yield highly pure 2,2'-dihalogenated diphenols⁹. Chlorination of BA with nitrogen purging reportedly gave 98% selectivity to the 2,2'-isomer, but bromination of BA was not specifically studied. Indeed, 2,2'-DBBA can be selectively prepared by bromination of BA suspended in dichloromethane with N_2 purging (Scheme 1). Hydrogen bromide, a by-product of the electrophilic aromatic substitution reaction, is known to catalyse bisphenol rearrangements to form highly coloured side products. With efficient removal of HBr by the N_2 purge, the reaction mixture became pale red in colour rather than a dark purple colour formed during other methods. 2,2'-DBBA was produced in 95–97% selectivity at 98% BA conversion upon addition of two equivalents of bromine. Reversed phase l.c. shows the crude DBBA contains only traces of BA, 2-bromobis-



Scheme 1 Synthesis of 2,2'-DBBA: (a) $\text{CH}_2\text{Cl}_2/\text{N}_2$; (b) CH_3OH , 65°C or 0°C

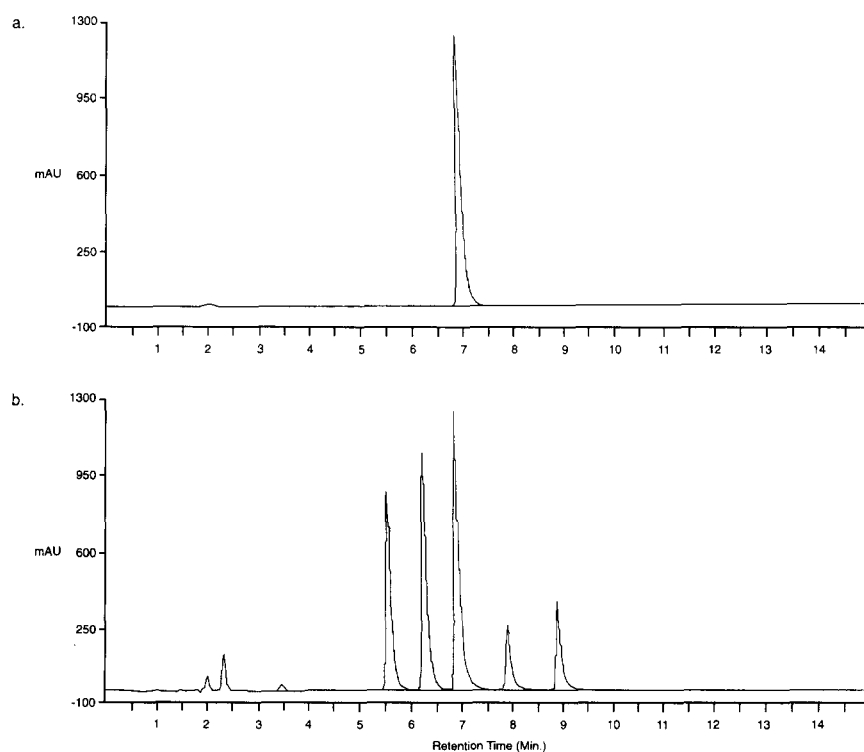


Figure 1 L.C. of BA + Br_2 reaction products: (a) $\text{CH}_2\text{Cl}_2/\text{N}_2$; (b) CH_3OH , 65°C or 0°C

phenol A (MBBA, **3**), 2,2',6-tribromobisphenol A (TriBBA, **4**) and TBBA (**5**) (Figure 1a).

During isolation and purification of the crude DBBA more rearrangement side products formed as evidenced by the appearance of a dark purple colour. A considerable amount of HBr remained in the crude product solution prior to work-up which probably led to the side reactions. Complete HBr removal prior to product isolation should

prevent this occurrence. The product recrystallized from toluene was obtained in 43% yield and 98% purity.

In contrast, bromination of BA in methanol at or below room temperature produced the entire family of brominated products in a very dark reaction solution (Scheme 1). The retention times of these bisphenols in the l.c. analysis increases with the number of bromine substituents (Figure 1b). The u.v. absorption maxima also

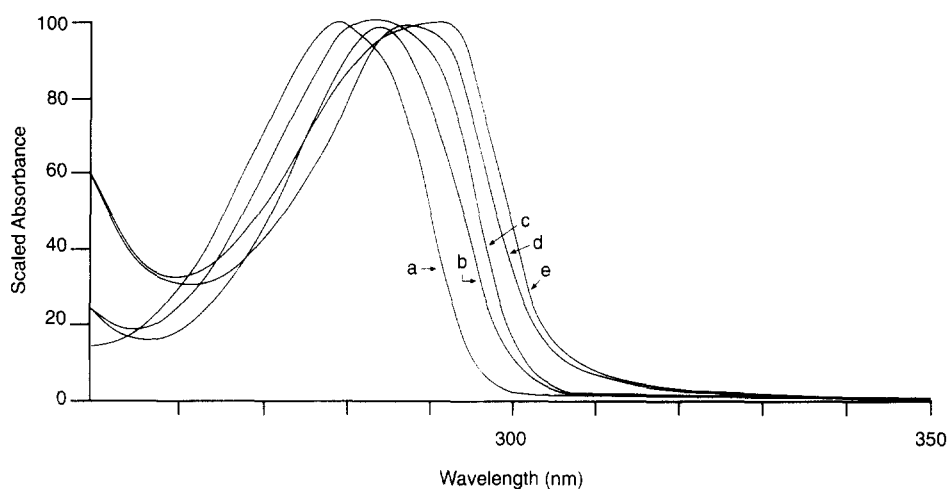


Figure 2 U.v. spectra of BA + Br₂ reaction products: (a) BA; (b) MBBA; (c) DBBA; (d) TriBBA; (e) TBBA

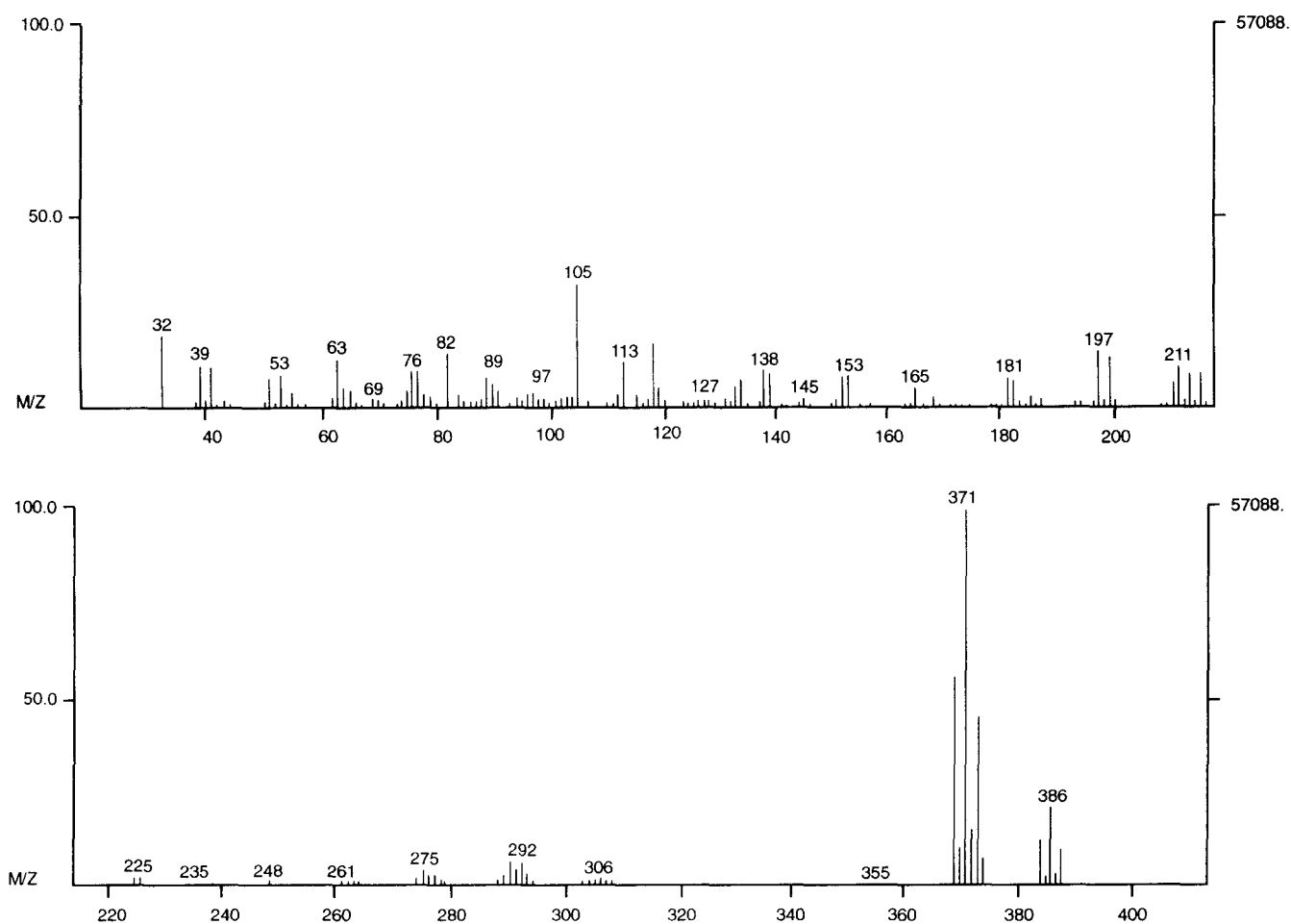


Figure 3 Mass spectrum of 2,2'-DBBA

shifts to higher wavelengths with increasing bromine substitution (*Figure 2*). Although the HBr by-product was removed from the mixture by reaction with methanol to form bromomethane, the rate of polybromination and of the rearrangement reactions appear to be much faster in this more polar solvent.

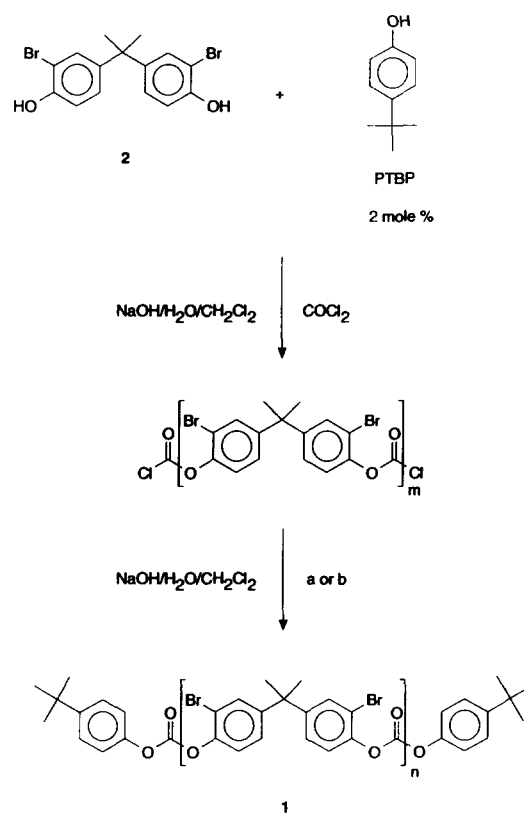
The regiochemistry of 2,2'-DBBA produced by N_2 purged bromination was confirmed by mass spectrometry (m.s.). A molecular ion of 384 amu with a two bromine atom isotope pattern was observed (*Figure 3*). Fragmentation ions at $m/e=275$ and 197 are attributed to monobrominated radicals, the first arising from two methyl radical losses from the molecular ion, and the second from the monobromovinylphenol radical. Also no fragmentation ions corresponding to dibrominated or non-brominated radicals are observed. These m.s. data prove the presence of one bromine atom per phenyl ring as expected for 2,2'-DBBA.

Purified 2,2'-DBBA showed a sharp melting point at 96°C and a u.v. maximum at $\sim 275\text{ nm}$ in THF (*Figure 2*). The $\text{p}K_a$ of 2,2'-DBBA is about the same as BA (9.8 and 11.0 for the first and second $\text{p}K_a$ s, respectively) as shown by the pH of an aqueous solution of 2,2'-DBBA disodium salt (pH = 12.5).

Synthesis of 2,2'-dibromobisphenol A polycarbonate

2,2'-DBBA PC was prepared by interfacial polycondensation of 2,2'-DBBA and phosgene with 2 mol% *p*-*t*-butylphenol chain terminator. The polymerization was conducted in two stages: phosgenation of 2,2'-DBBA disodium salt to form organic soluble chloroformates; and subsequent tertiary amine catalysed coupling to produce the polymer (*Scheme 2*). Phosgenation of 2,2'-DBBA at pH 12.5 to complete conversion of the

aqueous phase monomer gave low molecular weight bischloroformates. Methanol capped oligomers showed $M_w=3471$ and $M_n=1892$, corresponding to an average degree of polymerization of ~ 7 , and proving that a small extent of coupling occurred during phosgenation.



Scheme 2 Synthesis of 2,2'-DBBA PC: (a) Et_3N ; (b) DMAP

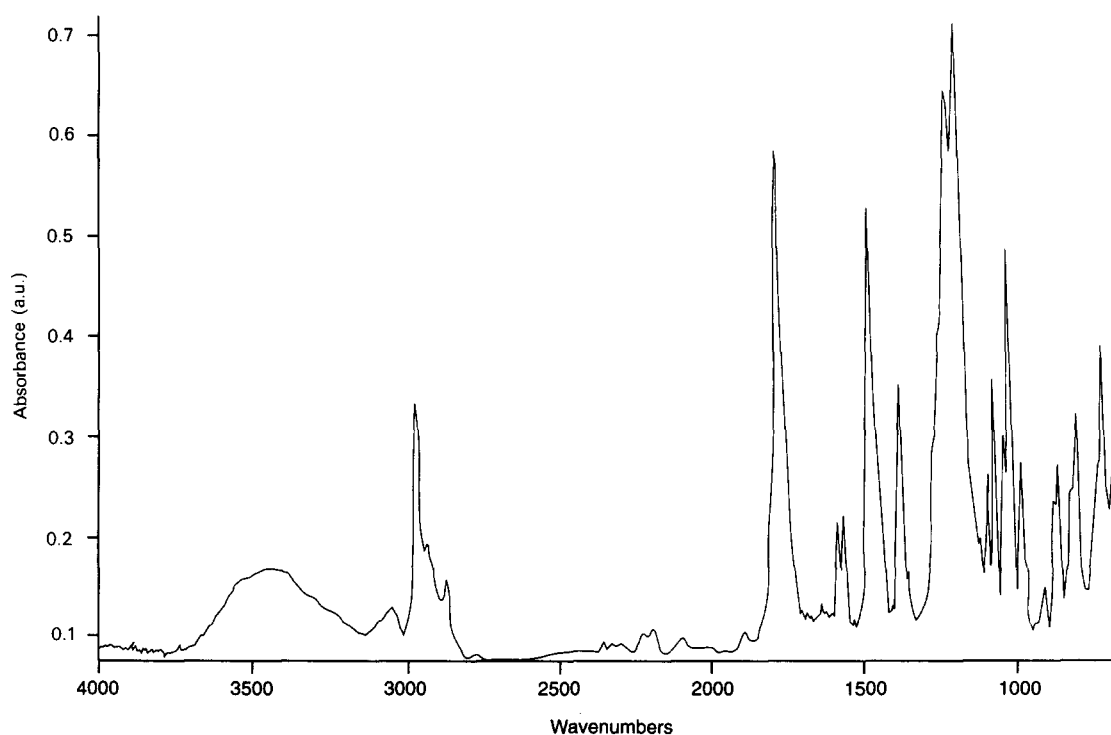
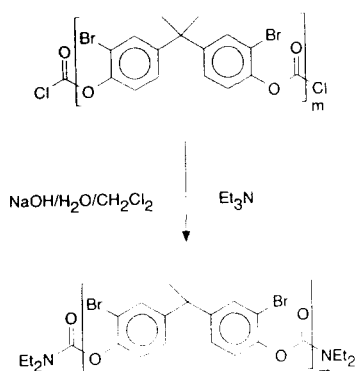


Figure 4 FTIR spectrum of 2,2'-DBBA PC

The use of an activated pyridine coupling catalyst, DMAP, gave 2,2'-DBBA PC with the expected molecular weight ($M_w = 43\,677$ and $M_n = 14\,971$) based on the terminator level. The more commonly used tertiary amine coupling catalyst triethylamine (TEA) formed a much lower molecular weight polymer ($M_w = 29\,256$ and $M_n = 7842$) having a high concentration of polymer bound nitrogen (72 ppm compared to 5 ppm in the polymer produced using DMAP). The results using TEA



Scheme 3 Reaction of Et₃N with 2,2'-DBBA oligochloroformates

are explained by the occurrence of a chloroformate-TEA side reaction which forms carbamate-terminated polymer chains (Scheme 3) as has been observed in the synthesis of other PCs¹⁰.

The carbonate absorption band in the i.r. spectrum of 2,2'-DBBA PC appears at 1785 cm^{-1} (Figure 4), which is midway between that of BA PC and TBBA PC and the same frequency found for 1:1 BA-TBBA coPC⁴.

Properties of 2,2'-dibromobisphenol A polycarbonate

The physical and thermomechanical properties of 2,2'-DBBA PC evaluated in this study are shown in Table 1. The corresponding properties of BA PC and 1:1 BA-TBBA coPC (which has the same total bromine content) are also shown for comparison. The 2,2' placement of the bromine groups on the polymer chain does little to increase the T_g . In fact, analogous substitution of methyl or chlorine groups results in PCs having lower T_g s than BA PC¹. The DTUL and flexural modulus of 2,2'-DBBA PC are also largely unchanged compared to BA PC. The notched Izod impact strength of 2,2'-DBBA PC is very low and the material fails in a brittle fracture. The tensile modulus and yield stress of 2,2'-DBBA PC are unexpectedly high, and again brittle failure was observed (Figure 5). The unusually high

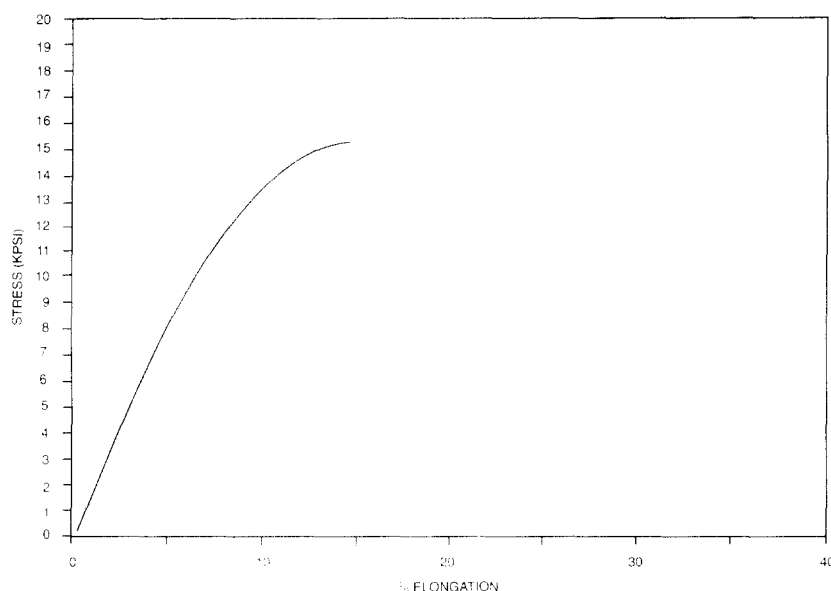


Figure 5 Stress-elongation curve of 2,2'-DBBA PC

Table 1 Properties of 2,2'-DBBA PC, BA PC and 1:1 BA-TBBA CoPC

Properties	2,2'-DBBA PC	BAPC	1:1 BA-TBBA CoPC
T_g (°C)	159	155	210
DTUL at 0.91 MPa (°C)	139	131	188
Tensile modulus (MPa)	3448	2034	2628
Tensile strength (MPa)			
Yield	105	65	88
Ultimate	105	52	86
Elongation at yield (%)	14.8	13.7	15.1
Elongation at break (%)	15	142	16
Flexural modulus (MPa)	2193	2200	3276
Notched Izod impact (J m^{-1})	53	849	80

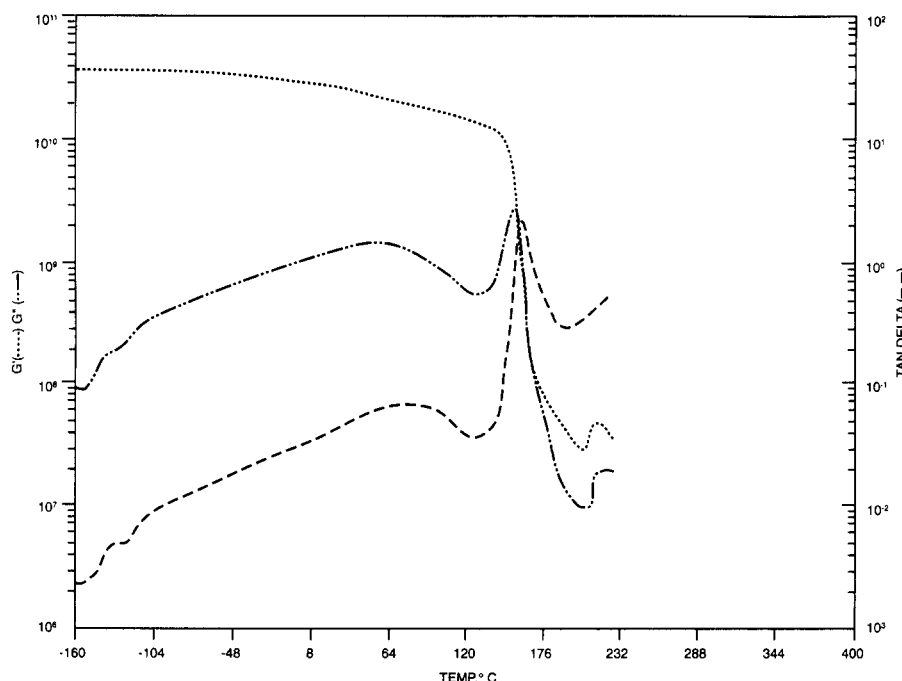


Figure 6 Dynamic mechanical analysis of 2,2'-DBBA PC

tensile modulus and yield stress results were obtained reproducibly, and are consistent with the high glassy modulus (G') observed by d.m.a. (see below). Further investigations on the mechanical properties of this polymer are in progress.

D.m.a. of 2,2'-DBBA PC shows a diffuse secondary (γ) transition at $\sim 80^\circ\text{C}$ followed by a glass (α) transition at 160°C (Figure 6). A d.m.a. study of TBBA PC concluded that its modulus-temperature response is similar to BA PC but each transition is shifted to $\sim 100^\circ\text{C}$ higher temperatures¹¹. These polymers show γ transitions at $\sim -90^\circ\text{C}$ and 90°C , and glass transitions at 155°C and 265°C , respectively. These lower temperature transitions are attributed to individual group motions, such as carbonate, isopropylidene, and phenyl, and are thought to be coupled to the larger scale motions associated with the glass transition¹². It is therefore interesting to note the apparent decoupling of these two transitions in 2,2'-DBBA PC.

CONCLUSIONS

2,2'-DBBA was prepared in high selectivity by direct bromination of BA with the use of an inert gas purge. The purge gas removes hydrogen bromide from the reaction medium and thus decreases the degree of acid catalysed bisphenol rearrangement side reactions. High molecular weight 2,2'-DBBA PC was prepared by interfacial phosgenation and DMAP coupling. The use of TEA coupling catalyst produced a polymer having relatively high bound nitrogen, presumably due to carbamate termination similar to that found in the synthesis of other halogenated PCs.

2,2'-DBBA PC has only marginally increased T_g , DTUL and flexural modulus compared to BA PC. The

notched Izod impact strength of this polymer is very low, like other PCs having substantial bromine content. The tensile modulus of 2,2'-DBBA PC is surprisingly $\sim 70\%$ higher than BA PC, but the flexural moduli of the two polymers are approximately equal. D.m.a. shows a relatively high temperature γ transition which, unlike those reported for other PCs, is not coupled to a correspondingly high T_g .

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