

ORIGINAL ARTICLE

Preparation and mechanical properties of a copolycarbonate composed of bio-based isosorbide and bisphenol A

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A series of copolycarbonates were prepared by transesterification polymerization of isosorbide, bisphenol A and diphenylcarbonate using several catalysts. The copolymers with the highest molecular weights were obtained using *N,N*-dimethylaminopyridine as a catalyst. The storage moduli of the polymers ranged from 2.3 to 3.5 GPa at 25 °C, and the tensile moduli were 1.7–2.6 GPa, increasing with the isosorbide content. The storage and tensile moduli of the polymers indicated that they could exhibit better strength than bisphenol A-based polycarbonates. These properties endow the polymers with potential for use as high-performance materials.

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INTRODUCTION

Biomass is a renewable resource of natural products that can be used as starting materials for the synthesis of bio-based polymers. Bio-based polymers derived from natural products are one of the most promising materials. The development of bio-based polymers needs to be sustainable due to the limited fossil resources and the need to reduce carbon dioxide emissions.

In particular, 1,4:3,6-dianhydro-D-sorbitol (isosorbide) is an available material for organic synthesis. In recent years, the use of isosorbide for synthesis and characterization has been reported.^{1–15} Isosorbide is obtained by dehydration of D-sorbitol and produced worldwide at a rate of 650 000 tons per annum.^{16,17} Isosorbide is thermally stable, available in large quantities and useful for the synthesis of bio-based polymers, such as polyesters,^{18–28} polyamides²⁹ and polyurethanes.^{30–36}

A polycarbonate derived from petroleum is a bisphenol A-based polycarbonate (BPAPC). BPAPC possesses superior properties, such as high transparency, impact resistance, high tensile strength, durability and heat resistance.

The synthesis of homopolycarbonate from the solution polymerization of isosorbide and phosgene has been reported.¹³ Homopolycarbonates produced using only isosorbide have a rigid structure, which results in a high melt viscosity that makes the polymer difficult to mold. Therefore, the synthesis of suitable copolymers is expected to solve the rigidity problem.

Copolycarbonates of isosorbide were also produced by interfacial polycondensation of bisphenol A with isosorbide bischloroformate.^{13,37} Isosorbide-derived copolycarbonates polymerized by the bulk

polymerization of bisphenol A with isosorbide have not been previously reported.

We have nearly successfully synthesized bio-based copolycarbonates from isosorbide and bisphenol A using *n*-butyltin oxide (*n*-BuSn (=O)OH) (Figure 1).³⁸ However, the molecular weights of the obtained copolymers were not sufficient to allow us to measure the mechanical properties, such as the tensile properties.

In this study, we attempted to improve the preparation of copolycarbonates from isosorbide and bisphenol A using transesterification polymerization in the presence of various organic nitrogen-containing catalysts and investigate their thermal, viscoelastic and tensile properties. These materials are expected to be suitable for use as high-performance polymeric materials.

EXPERIMENTAL PROCEDURE

General

N,N-dimethylaminopyridine (DMAP, Wako Pure Chemical, Osaka, Japan), 4-aminopyridine, 2-dimethylaminopyridine (2-DMAP), 1,2,4-triazole, imidazole, 2-methylimidazole (Tokyo Chemical Industry, Tokyo, Japan), isosorbide (Roquette, Lestern, France) and 4,4'-isopropylidenediphenol (bisphenol A) (Acros, Geel, Belgium) were used as received. BPAPC (Iupilon S-2000UR, Mitsubishi Engineering Plastics, Tokyo, Japan) in the form of pellets was dried for 12 h prior to press molding. ¹H nuclear magnetic resonance (NMR) (500 MHz) spectroscopy was carried out using a JEOL LA-500 spectrometer with Fourier transform using CDCl₃ as the solvent and TMS as an internal standard. The Fourier Transform Infrared (FT-IR) spectra were recorded on a JASCO FT-IR-5M (Avatar 360, Thermo Spectra-Tech, Shelton, CT, USA) spectrophotometer at a resolution of 4 cm⁻¹ in absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden

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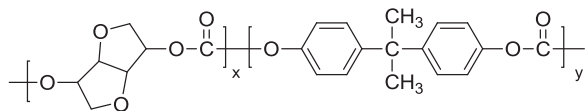


Figure 1 Isosorbide copolycarbonate.

Table 1 Molecular weight of polymer 5 prepared using various nitrogen-containing organic catalysts

Polymer	x/y^a	Catalyst	Molecular weight		
			$M_n (\times 10^4)$	$M_w (\times 10^4)$	M_w/M_n
Polymer 5	80/20	DMAP	3.9	8.2	2.1
		1,2,4-Triazole	3.7	8.9	2.4
		Imidazole	3.6	7.8	2.1
		2-Methylimidazole	2.9	6.9	2.4
		4-Aminopyridine	3.3	8.1	2.4
		2-DMAP	2.3	5.2	2.4

Abbreviations: DMAP, *N,N*-dimethylaminopyridine; 2-DMAP, 2-dimethylaminopyridine.
^aThe feed ratio of [isosorbide]/[bisphenol A].

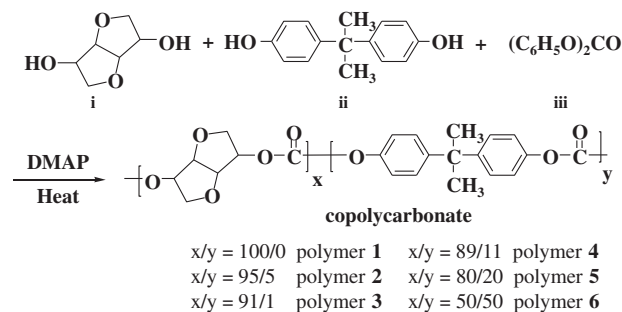
Gate heated single-reflection diamond ATR) was used to determine the FT-IR spectra.

Differential scanning calorimetry (DSC) was conducted using a TA Instruments (New Castle, DE, USA) DSC Q1000 thermal analyzer with N_2 purging (50 ml min^{-1}) at a rate of $10^\circ\text{C min}^{-1}$. Approximately 5.0 mg samples were tested in duplicate on closed aluminum pans. Thermogravimetric analysis was performed using a Rigaku Thermoplus TG8120 (Tokyo, Japan) with a heating rate of $20^\circ\text{C min}^{-1}$ under a nitrogen flow (200 ml min^{-1}). The molecular weights were determined against a polystyrene standard using gel permeation chromatography on a K805L Showa Denko K.K. column (Shodex GPC-101, Showa Tsusho, Ltd., Saitama, Japan) using CHCl_3 at a flow rate of 1.0 ml min^{-1} and a column oven temperature of 40°C . The viscoelastic properties of the copolycarbonates were investigated by dynamic mechanical analysis using a viscoelasticity spectrometer (IT-Keisokuseigy automatic dynamic viscoelastometer model DVA-220). The copolycarbonates were molded at 250°C and press-melted to a thickness of 0.5 mm. A test piece of $5.0 \text{ mm} \times 30 \text{ mm} \times 0.5 \text{ mm}$ was cut off and accurately measured, the storage modulus was measured at a frequency of 10 Hz in a temperature range of -100 to 250°C , and the temperature was increased at a rate of 4°C min^{-1} .

Tensile tests were performed at 23°C at a constant speed of 10 mm min^{-1} on an Instron 5566 universal testing machine (Ithaca, NY, USA) equipped with a 20 N load cell using rectangular specimens (that is, 100 mm long, 10 mm wide and 0.5 mm thick). The results are reported as an average of three measurements with an error range of within 5%.

Transesterification polymerization procedure

A generalized polymerization procedure is described below. In a round-bottom flask equipped with a decompressor, isosorbide (2.92 g, 20.0 mmol), bisphenol A (0.228 g, 1.0 mmol), diphenylcarbonate (4.60 g, 21.5 mmol) and the DMAP (1.4 mg) catalyst were added under a N_2 atmosphere. The temperature inside the reaction flask was increased to 160°C , which was maintained for 5 min. Then the temperature was increased to 187°C , which resulted in the generation of phenol. The reaction mixture was depressurized to 0.1 Torr for 1 h to distill off the phenol. Next the temperature inside the flask was then increased to 200°C , and the N_2 feed was terminated. The flask was maintained in this state for 20 min, and then the temperature was gradually increased to 230°C . Transesterification polymerization was carried out while the temperature was maintained between 250 and 270°C for 2 h, producing the copolycarbonate. After completion of the reaction, the contents of the flask were cooled to room temperature. The crude copolycarbonate was dissolved in chloroform, and this solution was added to methanol to precipitate the copolycarbonate. The refined copolycarbonate was dried at 120°C for 24 h *in vacuo*.



Scheme 1 Synthesis of polycarbonates using DMAP as a catalyst.

Polymer 1. Yield: 99%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 3.90\text{--}5.11$ (m, 8H, isosorbide). FT-IR (ATR) 2970, 2878, 1746, 1242, 1093, 783 cm^{-1} .

Polymer 2. Yield: 99%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 1.62\text{--}1.66$ (m, 6H, CH_3), 3.89–5.11 (m, 160H, isosorbide), 7.07–7.23 (m, 8H, ArH). FT-IR (ATR) 2971, 2878, 1745, 1242, 1092, 783 cm^{-1} .

Polymer 3. Yield: 99%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 1.62\text{--}1.66$ (m, 6H, CH_3), 3.89–5.11 (m, 80H, isosorbide), 7.06–7.23 (m, 8H, ArH). FT-IR (ATR) 2970, 2878, 1748, 1243, 1093, 783 cm^{-1} .

Polymer 4. Yield: 99%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 1.62\text{--}1.66$ (m, 6H, CH_3), 3.90–5.11 (m, 64H, isosorbide), 7.08–7.23 (m, 8H, ArH). FT-IR (ATR) 2971, 2878, 1747, 1241, 1092, 783 cm^{-1} .

Polymer 5. Yield: 99%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 1.62\text{--}1.66$ (m, 6H, CH_3), 3.90–5.11 (m, 32H, isosorbide), 7.06–7.23 (m, 8H, ArH). FT-IR (ATR) 2971, 2878, 1748, 1239, 1085, 781 cm^{-1} .

Polymer 6. Yield: 98%, $^1\text{H NMR}$ (500 MHz, CDCl_3) $\delta = 1.62\text{--}1.66$ (m, 6H, CH_3), 3.90–5.11 (m, 8H, isosorbide), 7.06–7.23 (m, 8H, ArH). FT-IR (ATR) 2968, 2876, 1764, 1223, 1081, 831 cm^{-1} .

RESULTS AND DISCUSSION

Synthesis and characterization of polymers 1–6

Initially, various organic catalysts containing nitrogen were used for transesterification polymerization of isosorbide, bisphenol A and diphenyl carbonate. Among the catalysts examined, DMAP exhibited a favorable effect on the molecular weight of 5 ($x/y = 80/20$). The molecular weights of the polymers obtained using various catalysts are shown in Table 1. The melt transesterification of the polycarbonate by diphenyl carbonate and bisphenol A using DMAP as a catalyst has been previously reported.³⁹ When $n\text{-BuSn(=O)OH}$ was used as a reaction catalyst for polycarbonate in our study,³⁸ transesterification of isosorbide (secondary alcohol) and bisphenol A did not proceed smoothly compared with that with DMAP. Based on the results using the various catalysts, DMAP was selected because it resulted in high molecular weight (M_n) polymers (Table 1).

Polymers 1–6, which were synthesized in the presence of DMAP, were obtained in good quantitative yield. In Scheme 1, x/y represents the feed ratio of [isosorbide]/[bisphenol A].

The structural characterization of the polymers was carried out using FT-IR and $^1\text{H NMR}$ spectroscopy. The FT-IR spectra of 1–6 exhibited characteristic absorption bands at $1745\text{--}1764 \text{ cm}^{-1}$ (C=O stretching of the carbonyl bond) and $1202\text{--}1244 \text{ cm}^{-1}$ (C-O-C stretching of the ether bond). The polymers were soluble in organic solvents, such as CHCl_3 , *N,N*-dimethylacetamide (DMAC), dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and *N*-methylpyrrolidone (NMP). The integral intensity ratio of the aromatic peaks over the isosorbide peaks agreed very well with the x/y ratio, which indicated that both the isosorbide group and the

bisphenol A group were completely incorporated into the copolymers. The ^1H NMR spectra did not reveal clearly detectable end-group signals.

The molecular weights and polydispersities of the polymers were investigated using gel permeation chromatography calibrated with polystyrene standards using CHCl_3 as a solvent. The results are summarized in Table 2. The number average molecular weights (M_n) ranged from 3.7×10^4 to 6.7×10^4 , and the weight average molecular weights (M_w) ranged from 7.9×10^4 to 13.4×10^4 , giving a M_w/M_n ratio of between 2.0 and 2.1. The molecular weights of the polymers were dependent on the bisphenol A content. The molecular weights of the polymers may be due to the lower reactivity of bisphenol A compared with isosorbide.

Thermal stability

Thermal characterization of the polymers was carried out by DSC and thermogravimetric analysis, and the results are shown in Table 2. No endothermic or exothermic peaks were recorded during the first or second heating runs in the DSC experiments, which indicated that all of the polymers were of a completely amorphous nature. The T_g values of the polymers were determined by DSC based on the onset temperature of the first inflection point recorded during the second heating (Table 2). As the isosorbide content increased, the T_g values of 1–6 increased gradually. For BPAPC, a T_g of 146°C was observed by DSC. Based on the 5% weight loss decomposition temperature (T_d), the polymers were stable up to approximately 320°C , except for 1 (isosorbide homopolycarbonate). The T_d values of the copolycarbonates were dependent on the bisphenol A content. Therefore, the T_d

values increased as the bisphenol A content increased, which was due to the thermal stability of bisphenol A (the T_d value of BPAPC was found by thermogravimetric analysis to be 413°C).

The polymers synthesized in this study using DMAP as a catalyst yield uncolored transparent sheets after press molding.

Transparent and flexible molded sheets were obtained for all polymers (1–6) by press molding. The sheets of 2–6 were stiff but flexible enough to bend completely without any problems.

Dynamic mechanical analysis results

Dynamic mechanical analysis was carried out for 1–6. Figure 2 shows the temperature dependence of the storage modulus (E'), loss modulus (E'') and $\tan \delta$ for 2. In a temperature range from 140 to 160°C , E' began to decrease substantially owing to the onset of softening near the glass transition. The polymers exhibited a single glass transition with their T_g values shifting to higher temperatures as the isosorbide content increased. The other copolycarbonates exhibited behaviors similar to 2 with their E' values remaining constant up to

Table 2 Molecular weights and physical properties of polycarbonates synthesized using DMAP as a catalyst

Polymer	x/y	Molecular weight			T_g^a ($^\circ\text{C}$)	T_d^b ($^\circ\text{C}$)
		M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n		
Polymer 1	100/0	6.7	13.4	2.0	174	283
Polymer 2	95/5	6.5	13.3	2.1	173	319
Polymer 3	91/9	4.5	9.5	2.1	170	321
Polymer 4	89/11	4.0	8.4	2.1	169	323
Polymer 5	80/20	3.9	8.2	2.1	165	330
Polymer 6	50/50	3.7	7.9	2.1	153	348

Abbreviation: DMAP, *N,N*-dimethylaminopyridine.

^aDetermined by differential scanning calorimetry ($10^\circ\text{C min}^{-1}$).

^bMeasured by thermogravimetric analysis, 5% weight loss decomposition temperature.

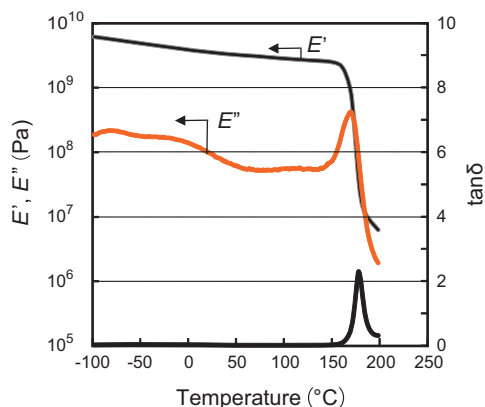


Figure 2 Temperature dependence of E' , E'' and $\tan \delta$ for polymer 2.

Table 3 Glass transition temperature (T_g) and storage moduli (E') of 1–6 and BPAPC

Polymer	T_g^a ($^\circ\text{C}$)	E' (GPa) at 25°C
Polymer 1	180	3.5
Polymer 2	179	3.5
Polymer 3	178	3.4
Polymer 4	178	3.3
Polymer 5	176	2.9
Polymer 6	168	2.3
BPAPC	158	2.3

Abbreviation: BPAPC, bisphenol A-based polycarbonate.

^aDetermined by dynamic mechanical analysis.

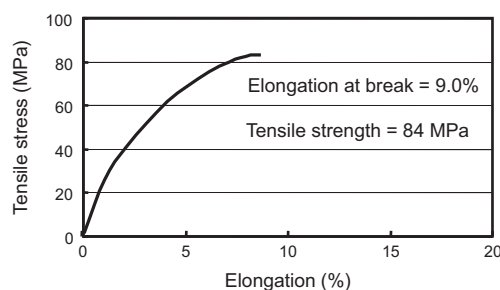


Figure 3 Stress–strain diagram of polymer 2.

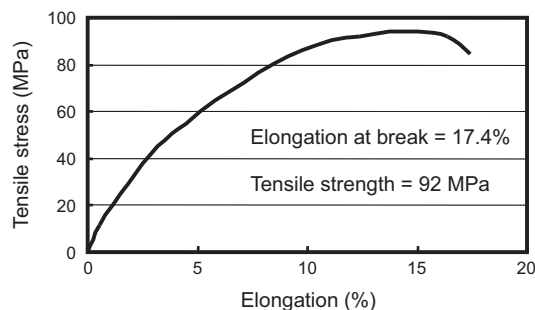
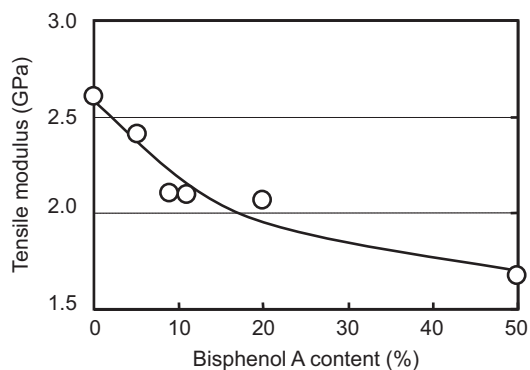


Figure 4 Stress–strain diagram of polymer 1.

Table 4 Tensile properties of 1–6 and BPAPC

Polymer	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at break (%)
Polymer 1	2.6	84	9.0
Polymer 2	2.4	92	17.4
Polymer 3	2.1	82	14.8
Polymer 4	2.1	81	14.2
Polymer 5	2.1	74	12.9
Polymer 6	1.7	61	12.2
BPAPC	1.6	60	>80

Abbreviation: BPAPC, bisphenol A-based polycarbonate.

**Figure 5** Correlation between bisphenol A content and the tensile modulus for 1–6 and BPAPC.

approximately 150 °C and then starting to decrease. The values obtained for E' are summarized in Table 3; these values tended to increase as the isosorbide content of the polymers increased. The obtained values (2.3–3.5 GPa at 25 °C) were higher than that of BPAPC (2.3 GPa).

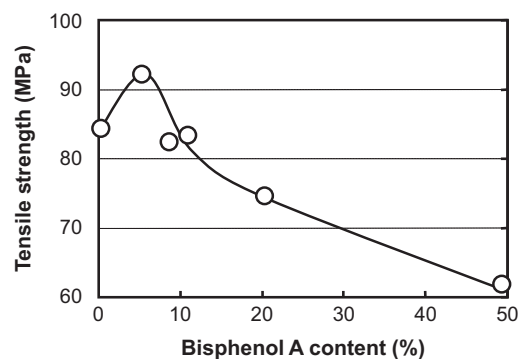
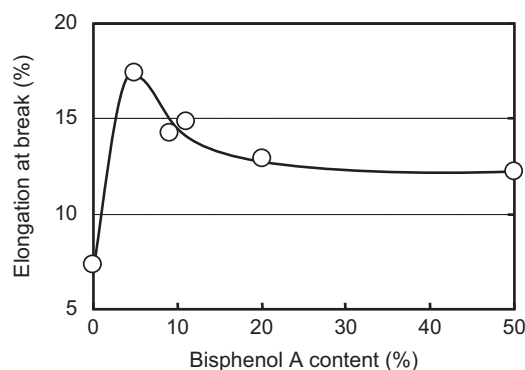
The temperature of the $\tan \delta$ peak was also dependent on the isosorbide content of the polymers, increasing as the isosorbide content increased (Table 3). Our results indicated that the E' values of the copolycarbonates tended to increase with T_g , which is consistent with the increase in the storage modulus as the isosorbide content increased (Figure 3).

These viscoelastic analyses revealed that an increase in T_g could be achieved by increasing the isosorbide content of the copolycarbonates. For 2, T_g was increased by approximately 20 °C compared with BPAPC, indicating the beneficial effect of the introduction of isosorbide. As described above, the T_g and rigidity of 2 were higher than those of BPAPC although the T_d value did not follow this trend.

Tensile properties

The tensile tests were performed at 23 °C at a constant speed of 10 mm min⁻¹ on an Instron universal testing machine equipped with a 20 N load cell. Figure 4 shows the stress–strain curve obtained for 2. Polymers 1 and 3–6 exhibited similar behaviors. The tensile strength and elongation at break were determined based on the curves, and the results are shown in Table 4. 1 ($x/y = 100/0$, homopolymer) exhibited linear elastic behavior with a tensile strength of 84 MPa and an elongation at break of 9.0%. The homopolymer could not be elongated past the yield point in the tensile test (Figure 3).

However, the introduction of the bisphenol A group resulted in a substantial change in the tensile strength. Figure 5 shows the correlation between the bisphenol A content and the tensile modulus

**Figure 6** Correlation between bisphenol A content and tensile strength for 1–6.**Figure 7** Correlation between bisphenol A content and elongation at break for 1–6.

for 1–6 and BPAPC. In contrast to the homopolymer, 2 exhibited signs of yielding, which led us to suggest that the elongation at break was dependent on the bisphenol A and isosorbide content. In addition, the relationship between tensile strength and elongation at break for 1–6 (Figures 6 and 7) was correlated with the bisphenol A content. The polymer sheet that exhibited the best results for the tensile properties was 2. Significant increases were observed in the tensile strength (92 MPa) of 2, which was approximately 53% greater than that of BPAPC (Table 4). Based on the results in Table 4, the tensile modulus of 2 was approximately 50% greater than that of BPAPC. All of the polymers exhibited better tensile strength than BPAPC, and the improved tensile properties of the polymers were due to the isosorbide to bisphenol A ratio. Based on a comparison of the results obtained for 2–6, the introduction of a small amount of bisphenol A into the copolycarbonates resulted in an increase in the tensile strength.

CONCLUSION

We prepared copolycarbonates containing isosorbide moieties in the main chain by transesterification polymerization of isosorbide, bisphenol A and diphenylcarbonate. The copolymers with the highest molecular weights were obtained when DMAP was used as a catalyst. Transparent, flexible sheets were easily obtained by press molding. The polymers exhibited good thermal stability, rigidity and strength and were soluble in organic solvents, such as CHCl₃, DMF, DMAc, NMP and DMSO. In addition, the polymers possessed high T_g values (153–174 °C). Polymer 2 ($x/y = 95/5$) exhibited a greater storage modulus than BPAPC. These results indicate that a larger isosorbide content

results in greater rigidity in the copolycarbonates. Polymer **2** exhibited the best results in terms of mechanical properties. In contrast to homopolymer **1** ($x/y=100/0$), **2** exhibited signs of yielding, and the elongation at break was correlated with the bisphenol A content. These enhanced mechanical properties at large deformations at room temperature were evidence of an increase in the tensile strength and strain at break compared with **1**. The tensile modulus of **2** was approximately 50% greater than that of BPAPC. These properties endow the copolycarbonates with the potential for use as high-performance polymeric materials.

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