

## Improving the Mechanical Properties of Isosorbide Copolycarbonates by Varying the Ratio of Comonomers

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**ABSTRACT:** Polycarbonates were synthesized by transesterification polymerization of isosorbide, bisphenol A, and diphenyl carbonate in the presence of *n*-BuSn(=O)OH as the catalyst. The polymers were prepared by varying the ratio of the two monomers. The polymers exhibited good thermal stability, rigidity, and strength. The storage moduli for the polymers were 2.6 to 3.2 GPa at 25°C and increased with increasing isosorbide content. The dynamic mechanical analysis indicated that the storage moduli ( $E'$ ) of the polymers are constant to higher temperatures than that of bisphenol A polycarbonate. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** biomass; isosorbide; copolycarbonates; viscoelastic properties

Received 22 November 2010; accepted 29 March 2012; published online

**DOI:** 10.1002/app.37838

### INTRODUCTION

In recent years, there has been considerable interest in the synthesis and characterization of compounds containing 1,4 : 3,6-dianhydro-D-sorbitol (isosorbide).<sup>1–15</sup> Isosorbide is derived from glucose and is thus a functional group containing monomer based on natural resources. Obtained by dehydration of D-sorbitol, it is a well documented byproduct of the starch industry and is produced worldwide at a rate of 650,000 tons per annum.<sup>16,17</sup> Isosorbide is among the important products obtained from biomass, which constitutes a renewable resource for natural products that can be used as reliable starting materials in the production of environmentally benign petroleum derivatives. As the depletion of fossil resources has continued, much attention has been directed toward the effective utilization of plant-based biomass including wood, grasses, and agricultural crops and residues in polymer synthesis.<sup>18–20</sup> Among a wide variety of candidate compounds from biomass, 1,4 : 3,6-dianhydrohexitols, including isosorbide, are promising materials for polymer synthesis. In fact, isosorbide is thermally stable, of low cost, and available in large quantities, and may prove to be an interesting monomeric reagent for the synthesis of bio-based polymers such as polyesters,<sup>21–29</sup> polyamides,<sup>30</sup> polyurethanes,<sup>31–36</sup> and epoxy resin.<sup>37</sup>

Polycarbonate is another type of bio-based polymer that can be derived from isosorbide (Figure 1). The most common polycarbonate is bisphenol A-based polycarbonate (BPAPC), which

possesses superior characteristics including high transparency, impact resistance, high tensile strength, durability, and heat resistance. Because of these attributes, it is widely used as a material for electric and electronic, automotive, and optical components.<sup>38</sup>

The preparation of homo- and copolycarbonates via solution polymerization of isosorbide and phosgene have been reported.<sup>12,13</sup> The homopolycarbonate is obtained by solution polymerization of isosorbide and phosgene and has a glass transition temperature ( $T_g$ ) of 163 to 165°C. It has a rigid structure, however, and thus has a considerably high melt viscosity and accordingly is difficult to mold. If suitable copolymers can be successfully synthesized, this rigidity and associated problems may be addressed.

In this article, we synthesized new copolycarbonates from isosorbide and bisphenol A using bulk polycondensation and investigated their thermal and viscoelastic properties. The polycarbonate contains isosorbide moieties in the main chain. The polymers exhibited good thermal stability, rigidity, strength, and high  $T_g$  values.

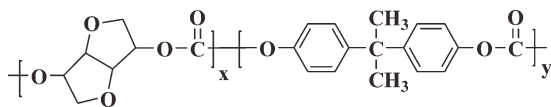
### EXPERIMENTAL

#### Materials

*n*-Butyltin oxidehydroxide (*n*-BuSn(=O)OH) (Strem Chemicals), isosorbide (Roquette), and 4,4'-isopropylidenediphenol (bisphenol A) (Wako Pure Chemical) were used as received.

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**Figure 1.** Isosorbide polycarbonate containing the bisphenol A moiety.

Bisphenol A polycarbonate (PC, Iupilon S-2000UR, Mitsubishi Engineering Plastic) in the form of pellets was dried for 12 h before molding.

#### Characterization

$^1\text{H-NMR}$  (500 MHz) spectroscopy was carried out using a JEOL LA-500 spectrometer with Fourier transform capability using  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. FTIR spectra were recorded on a JASCO FT-IR-5M (Avatar 360, Thermo Spectra-Tech) spectrophotometer with a resolution of  $4\text{ cm}^{-1}$  in absorbance mode. An attenuated total reflection (ATR) accessory with thermal control and a diamond crystal (Golden Gate heated single-reflection diamond ATR) was used to determine the FTIR spectra.

Differential scanning calorimetry (DSC) was conducted using a TA Instruments DSC Q1000 thermal analyzer with  $\text{N}_2$  purging (50 mL/min) at a rate of  $10^\circ\text{C}/\text{min}$ . Samples of about 5 mg were tested in duplicate on closed aluminum pans. Thermogravimetric analysis (TGA) was performed using a Rigaku Thermoplus TG8120 with a heating rate of  $10^\circ\text{C}/\text{min}$  under air flow (500 mL/min). Samples of about 5 mg were tested on opened aluminum pans. Figure 2 shows a thermogravimetric curve of polymer 3, for an example. A weight loss of polymer 3 started from about  $300^\circ\text{C}$ , and a weight loss of this polymer became 5% at  $313^\circ\text{C}$ . The temperature of 5% weight loss was defined as  $T_d$ , the heat resistance properties of the copolycarbonates were evaluated with  $T_d$ .

Molecular weights were determined against a polystyrene standard using gel permeation chromatography (GPC) on a K805L, Showadenko k. k. column (Shodex GPC-101, Showatsusho., Ltd) with  $\text{CHCl}_3$  at a flow rate of 1.0 mL/min and the column oven at  $40^\circ\text{C}$ . Dynamic viscoelastic measurements were conducted using an IT-Keisokuseigy automatic dynamic viscoelastometer model DVA-220 at a heating rate of  $4^\circ\text{C}/\text{min}$ . The viscoelastic properties of the copolycarbonates were investigated by dynamic mechanical analysis (DMA). A copolycarbonate was molded at  $250^\circ\text{C}$  and press-melted to a thickness of 0.5 mm. Thereafter, a test piece of  $5.0 \times 30 \times 0.5\text{ mm}^3$  was cut off. The size of the test piece was accurately measured, and then the storage modulus of the copolycarbonate was determined on a viscoelasticity spectrometer at a frequency of 10 Hz, a temperature range of  $-100$  to  $250^\circ\text{C}$  and a temperature increase rate of  $4^\circ\text{C}/\text{min}$ .

#### Transesterification Polymerization Procedures

Polymers 1–7. A generalized polymerization procedure is described in case of polymer 1. In a round-bottom flask equipped with a decompressor, isosorbide (1.46 g, 10.0 mmol), bisphenol A (0.114 g, 0.5 mmol), diphenylcarbonate (2.29 g, 10.7 mmol), and  $n\text{-BuSn(=O)OH}$  (2.0 mg) as the catalyst were added under  $\text{N}_2$  atmosphere. The temperature inside the reaction flask was increased to  $160^\circ\text{C}$  and then maintained for 5

min. The temperature inside the reaction flask was then further increased to  $187^\circ\text{C}$ , resulting in phenol generation. The reaction mixture was then depressurized to 0.1 Torr to distill off phenol, and this condition was continued for 1 h. Next, the temperature inside the flask was increased to  $200^\circ\text{C}$  and the feed of  $\text{N}_2$  stopped. Subsequently, the flask was maintained for 20 min at this temperature. Thereafter, the temperature inside the flask was gradually increased to  $230^\circ\text{C}$ . Other polymers (2–7) were prepared by varying the ratio of the bisphenol A.

The transesterification polymerization was carried out while the temperature was maintained between 250 and  $270^\circ\text{C}$  for 2 h to yield the copolycarbonate. After completion of the reaction, the contents of flask were cooled to room temperature. The obtained crude copolycarbonate was dissolved in chloroform and then precipitated by adding this solution to methanol. The refined copolycarbonate was dried at  $110^\circ\text{C}$  for 12 h *in vacuo*.

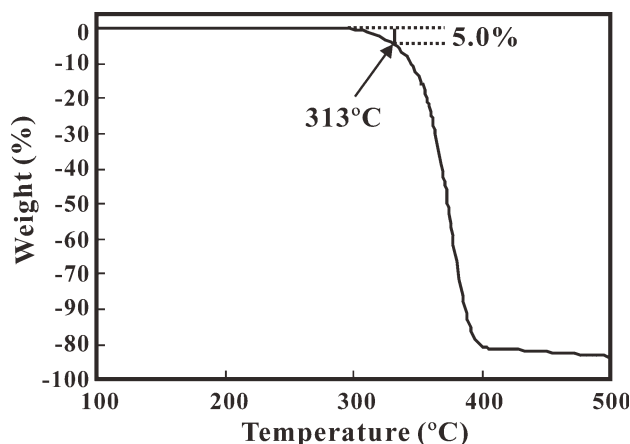
The proton NMR and IR data of polymers 1–7 are listed in Table I

## RESULTS AND DISCUSSION

### Polymer Preparation

Generally, all copolycarbonates 1–7 were synthesized from isosorbide, bisphenol A, diphenylcarbonate, and  $n\text{-BuSn(=O)OH}$  as the catalyst via a transesterification procedure (Figure 3). All of the transesterification reactions proceeded successfully; random copolycarbonates were obtained in good to quantitative yields.<sup>12</sup>

Structural characterization of the polymers was carried out using FTIR and  $^1\text{H-NMR}$  spectroscopy. The FTIR spectra of polymers 1–7 exhibited characteristic absorption bands at  $1747\text{--}1753\text{ cm}^{-1}$  ( $\text{C=O}$  stretching of carbonyl bond) and  $1202\text{--}1244\text{ cm}^{-1}$  ( $\text{C-O-C}$  stretching of ether bond). The polymers were soluble in organic solvents including  $\text{CHCl}_3$ ,  $N,N$ -dimethylacetamide (DMAc), DME, DMSO, and  $N$ -methylpyrrolidone (NMP). The FTIR and  $^1\text{H-NMR}$  spectra were interpreted to be similar to each other and were consistent with the structure. No particular side reactions were found to have taken place. The  $^1\text{H-NMR}$  spectra did not reveal clearly detectable end group signals.



**Figure 2.** The thermogravimetric curve of polymer 3.

Table I. List of the Proton NMR Signal and the IR Absorption Peak in Wavenumber

Polymer	NMR signal (chemical shift, ppm)			ArH	IR absorption peak (cm <sup>-1</sup> )
	CH <sub>3</sub>	Isosorbide	ArH		
Polymer 1	1.62-1.66 (m, 6H)	3.89-5.11 (m, 160H)	7.07-7.23 (m, 8H)	2971( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1745( $\nu_{\text{C=O}}$ ), 1242( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 783( $\nu_{\text{C-H}}$ )	
Polymer 2	1.62-1.66 (m, 6H)	3.89-5.11 (m, 80H)	7.06-7.23 (m, 8H)	2970( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1748( $\nu_{\text{C=O}}$ ), 1243( $\nu_{\text{C-O}}$ ), 1093( $\nu_{\text{C-O}}$ ), 1093( $\nu_{\text{C-O}}$ ), 783( $\nu_{\text{C-H}}$ )	
Polymer 3	1.62-1.66 (m, 6H)	3.90-5.11 (m, 64H)	7.08-7.23 (m, 8H)	2971( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1747( $\nu_{\text{C=O}}$ ), 1241( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 783( $\nu_{\text{C-H}}$ )	
Polymer 4	1.62-1.66 (m, 6H)	3.89-5.11 (m, 48H)	7.08-7.23 (m, 8H)	2970( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1747( $\nu_{\text{C=O}}$ ), 1243( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 1092( $\nu_{\text{C-O}}$ ), 781( $\nu_{\text{C-H}}$ )	
Polymer 5	1.62-1.66 (m, 6H)	3.90-5.11 (m, 32H)	7.06-7.23 (m, 8H)	2971( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1748( $\nu_{\text{C=O}}$ ), 1239( $\nu_{\text{C-O}}$ ), 1085( $\nu_{\text{C-O}}$ ), 1085( $\nu_{\text{C-O}}$ ), 781( $\nu_{\text{C-H}}$ )	
Polymer 6	1.62-1.66 (m, 6H)	3.90-5.11 (m, 24H)	7.06-7.23 (m, 8H)	2968( $\nu_{\text{asC-H}}$ ), 2876( $\nu_{\text{sC-H}}$ ), 1750( $\nu_{\text{C=O}}$ ), 1239( $\nu_{\text{C-O}}$ ), 1084( $\nu_{\text{C-O}}$ ), 1084( $\nu_{\text{C-O}}$ ), 780( $\nu_{\text{C-H}}$ )	
Polymer 7	1.62-1.66 (m, 6H)	3.90-5.11 (m, 16H)	7.08-7.23 (m, 8H)	2971( $\nu_{\text{asC-H}}$ ), 2878( $\nu_{\text{sC-H}}$ ), 1753( $\nu_{\text{C=O}}$ ), 1236( $\nu_{\text{C-O}}$ ), 1081( $\nu_{\text{C-O}}$ ), 1081( $\nu_{\text{C-O}}$ ), 780( $\nu_{\text{C-H}}$ )	

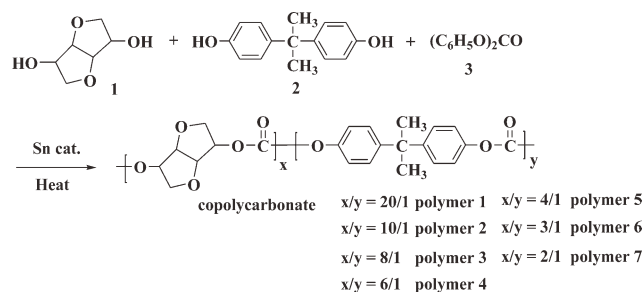


Figure 3. Synthesis of polycarbonates using a Sn catalyst.

The molecular weights and polydispersities of the polymers were investigated using GPC calibrated with polystyrene standards with  $\text{CHCl}_3$  as the solvent. The results are summarized in Table II. The number average weights ( $M_n$ ) ranged from  $1.3 \times 10^4$  to  $3.3 \times 10^4$ , and the weight average weights ( $M_w$ ) ranged from  $3.1 \times 10^4$  to  $9.3 \times 10^4$ , giving  $M_w/M_n$  ratios between 2.4 and 2.9. As can be seen from these results, the molecular weights of the polymers were dependent on the content of bisphenol A. As the ratio of bisphenol A content increased, the molecular weights of the polymers decreased. We think this decrease is attributed to the reactivity of isosorbide and bisphenol A.

### Thermal Properties

Thermal characterization of the polymers was carried out by DSC and TGA, and the results are listed in Table II. No phase transitions were recorded during the first and second heating in the DSC experiments. The absence of melting endotherm confirmed the amorphous nature of the polymers. The glass transition temperatures ( $T_g$ ) of the polymers were also determined by DSC based on the onset temperature of the first inflection point recorded during the second heating (Table II). The  $T_g$  was dependent on the content of isosorbide. As the ratio of isosorbide content increased, the  $T_g$  of polymers 1–7 increased gradually. In the case of BPAPC, the  $T_g$  was determined to be  $146^\circ\text{C}$  by DSC.

The TGA thermograms of the polymers are also summarized in Table II. The polymers were stable up to about  $310$  to  $334^\circ\text{C}$  in air. These copolycarbonates showed decomposition temperatures [5% weight loss, ( $T_d$ )] that were dependent on the content of bisphenol A. As the ratio of bisphenol A content increased, the  $T_d$  of polymers 1–7 also increased. This increase is attributed to the thermal stability of bisphenol A; the  $T_d$  of BPAPC was determined to be  $413^\circ\text{C}$  by TGA.

### Dynamic Mechanical Analysis

Transparent and flexible molded sheets were prepared from all of the polymers 1–7 by press molding. As can be seen in Figure 4, the sheet prepared from polymer 1 had rigidity, strength, and flexibility and was completely bendable.

DMA was carried out for polymers 1–7. The DMA results confirmed that the properties of the copolycarbonates are significantly affected. Figure 5 shows the temperature dependence of the storage modulus ( $E'$ ), loss modulus ( $E''$ ) and  $\tan \delta$  for polymer 1. In the temperature range from  $140$  to  $160^\circ\text{C}$ , the  $E'$  starts to decline due to the onset of softening near the glass

**Table II.** Molecular Weight and Physical Properties of Polycarbonates ( $x/y$  = Isosorbide/Bisphenol A)

Polymer	$x/y$	Molecular weight			$T_g^a$ (°C)	$T_d^b$ (°C)	$E'$ (GPa)	$T_g^c$ (°C)	$T_g^d$ (°C)
		$M_n$	$M_w$	$M_w/M_n$					
Polymer 1	20/1	33,000	85,000	2.6	173	3.2	173	181	
Polymer 2	10/1	32,000	93,000	2.9	170	3.1	170	178	
Polymer 3	8/1	23,000	67,000	2.9	169	3.0	169	178	
Polymer 4	6/1	19,000	49,000	2.6	165	2.9	168	176	
Polymer 5	4/1	17,000	48,000	2.8	164	2.9	168	176	
Polymer 6	3/1	13,000	38,000	2.9	163	2.8	166	174	
Polymer 7	2/1	13,000	31,000	2.4	154	2.6	160	167	

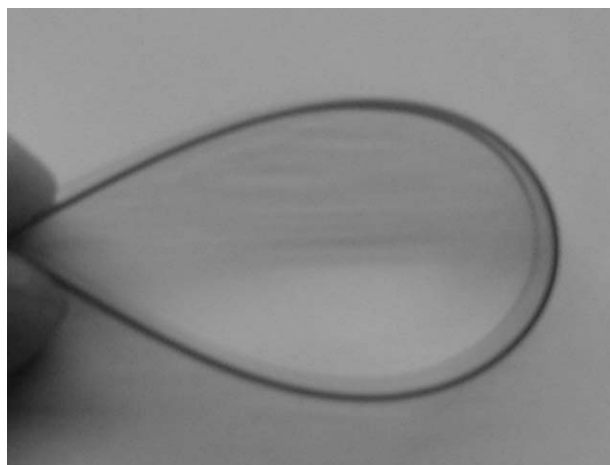
<sup>a</sup>Determined by DSC (10°C/min), <sup>b</sup>Measured by TGA (10°C/min), <sup>c</sup>Determined by  $E'$ , <sup>d</sup>Determined by  $\tan \delta$ .

transition. The polymers showed a single glass transition, the temperature of which shifted to higher values with increasing isosorbide content.

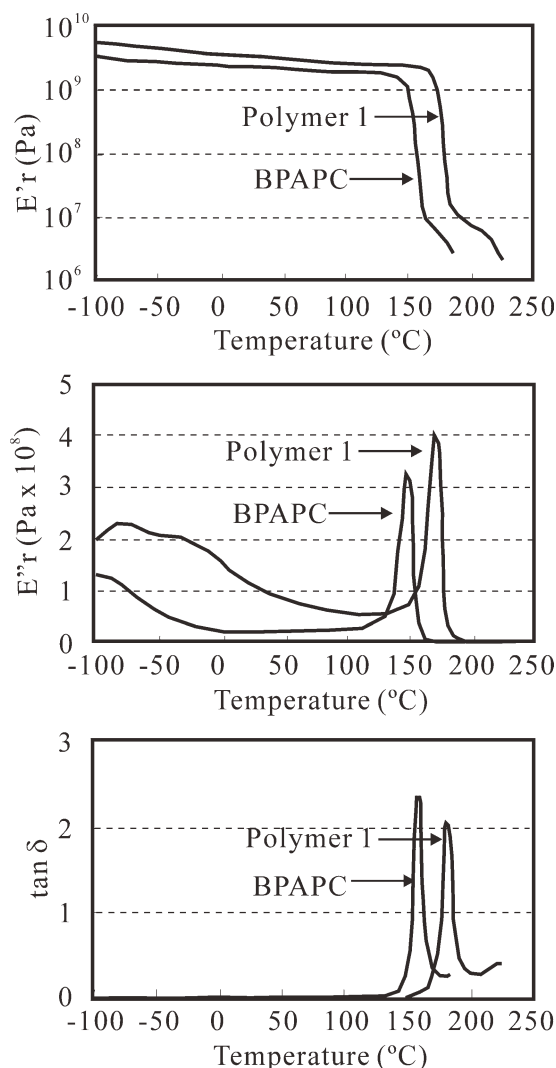
Copolycarbonates 2–7 showed similar behavior (see Supporting Information Figure S1–S6 for other samples). The  $E'$  of polymers 2–7 remained constant up to about 150°C and then started to decrease gradually.

Notably, polymer 1 showed a higher  $T_g$  value than that of polymer 7. This difference was attributed to the increased chain rigidity caused by the isosorbide rings along the backbone of polymer 1. The storage modulus values are summarized in Table II; the values obtained for polymers 1–7 were 2.6 to 3.2 GPa at 25°C. The  $E'$  of BPAPC was found to be 2.3 GPa under the same conditions.

Further, the  $\tan \delta$  peak is dependent on the content of isosorbide. As the ratio of isosorbide content increased, the  $\tan \delta$  peak increased. This result is consistent with the fact that increasing the ratio of isosorbide content increases the strength of the copolycarbonates while decreasing their flexibility. On the basis of a comparison of the results obtained for polymers 1–7, it was concluded that the introduction of bisphenol A groups into the copolycarbonates resulted in an increase in thermal stability.

**Figure 4.** The transparent and flexible molded sheet of polymer 1.

These viscoelastic analyses thus revealed that an increase in  $T_g$  was achieved. In the case of polymer 1, the increase was ca. 10°C over that for polymer 7, indicating the beneficial effect afforded by the introduction of isosorbide groups. As has been

**Figure 5.** Temperature dependence of  $E'$ ,  $E''$ , and  $\tan \delta$  for BPAPC and polymer 1.

described above, polymer **1** possessed a  $T_g$ , rigidity and strength that were higher than those of BPAPC. Only the  $T_d$  of BPAPC was higher than that for polymer **1**

## CONCLUSIONS

We synthesized new copolycarbonates containing isosorbide moieties in the main chain. The polycarbonates were synthesized by transesterification polymerization of isosorbide, bisphenol A, and diphenylcarbonate in the presence of *n*-BuSn(=O)OH as the catalyst. Transparent flexible sheets were easily obtained by press molding. The polymers exhibited good thermal stability, rigidity and strength and had high  $T_g$  values (153–173°C). The storage moduli for the polymers were 2.6 to 3.2 GPa at 25°C and increased with increasing isosorbide content. This result indicates that incorporating higher isosorbide content increases the strength of copolycarbonates. These properties make the new polymers attractive as potential high-performance polymeric materials. Currently, we are working on an improved transesterification polymerization process for isosorbide and other diols.

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