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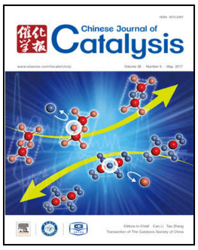

Article

Synthesis of isosorbide-based polycarbonates via melt polycondensation catalyzed by quaternary ammonium ionic liquids

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ABSTRACT

A series of quaternary ammonium ionic liquids (ILs) were synthesized and employed as catalysts for the production of poly(isosorbide carbonate) (PIC) from diphenyl carbonate and isosorbide via a melt polycondensation process. The relationship between the anions of the ILs and the catalytic activities was investigated, and the readily-prepared IL tetraethylammonium imidazolate (TEAI) was found to exhibit the highest catalytic activity. After optimizing the reaction conditions, a PIC with a weight-average molecular weight (M_w) of 25600 g/mol was obtained, in conjunction with an isosorbide conversion of 92%. As a means of modifying the molecular flexibility and thermal properties of the PIC, poly(aliphatic diol-co-isosorbide carbonate)s (PAIC)s were successfully synthesized, again using TEAI, and polymers with M_w values ranging from 29000 to 112000 g/mol were obtained. ^{13}C NMR analyses determined that the PAIC specimens had random microstructures, while differential scanning calorimetry demonstrated that each of the PAICs were amorphous and had glass transition temperatures ranging from 50 to 115 °C. Thermogravimetric analyses found $T_{d\text{-}5\%}$ values ranging from 316 to 332 °C for these polymers. Based on these data, it is evident that the incorporation of linear or cyclohexane-based diol repeating units changed the thermal properties of the PIC.

1. Introduction

Polycarbonate (PC) is an excellent engineering plastic widely used for various industrial applications owing to its unique properties, including high tensile strength, impact resistance, and good transparency [1,2]. Currently, one of the most important and widely commercialized PCs is bisphenol A PC (BPAPC) [3,4]. However, bisphenol A is a toxic, petroleum-derived chemical [5,6], and so much effort has been devoted to replacing this compound with bio-based monomers [7–9]. Isosorbide (1,4:3,6-dianhydro-D-sorbidol) is a well-known potential replacement and has the advantages of rigidity, chirality and low toxicity [10,11]. Moreover, it is the only carbohydrate-based bicyclic monomer currently commercially available [12] and so could represent an ideal renewable monomer for polymer synthesis [13]. To date, isosorbide has been widely used for the synthesis of polyesters [14–16], polyurethanes [17–19], poly(ester-co-carbonate)s [20,21] and PCs

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[22–26]. The large-scale production of poly(isosorbide carbonate) (PIC) via the melt polycondensation of isosorbide with dimethyl carbonate (DMC) or diphenyl carbonate (DPC) has also been investigated recently [5,27–29].

Isosorbide has some associated challenges such as its higher hydrophilic and lower acidity than that of bisphenol A, so the synthesis of PIC is complex [10]. The production of high molecular weight PIC requires suitable catalysts for the melt polycondensation process because of the severe reaction conditions. To date, basic catalysts have been found to be the most efficient for PIC synthesis [5,30,31]. Li et al. [29] synthesized a PIC by melt polycondensation of isosorbide with DMC, using lithium acetylacetonate as the catalyst. Shin et al. [5] reported that cesium carbonate exhibited superior catalytic activity during the synthesis of a PIC by melt polycondensation with DPC. Although inorganic bases have been used for this reaction [32,33], they tend to have several drawbacks, including unsatisfactory activities, difficult separations and branching. More recently, basic ionic liquids (ILs) have been shown to be promising substitutes for inorganic bases [34–39]. As an example, Park et al. [40] demonstrated the transesterification of ethylene carbonate with methanol catalyzed by 1-alkyl-3- methylimidazolium ILs.

In recent years, many researchers have paid much attention to the functionalized ILs by designing the structures of cations or anions according to practical requirements and special purposes [41–46]. In the present work, we designed and synthesized several basic ILs and investigated the effects of the anions on the catalytic activities of these compounds during the synthesis of a PIC via the melt polycondensation of DPC with isosorbide. The results demonstrate that the readily synthesized IL tetrabutylammonium imidazolate (TEAI) shows the highest activity, producing a PIC with a weight-average molecular weight (M_w) of 25600 g/mol in conjunction with an isosorbide conversion of 92%. In addition, the molecular flexibility and thermal properties of the PIC were modified by synthesizing poly(aliphatic diol carbonate)s (PAIC)s through combining isosorbide and various aliphatic diols (diethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and 1,4-cyclohexanedimethanol). The PIC and PAICs samples were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy, gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

2. Experimental

2.1. Materials and measurements

Isosorbide (98%) was purchased from Alfa Aesar, while 1,4-cyclohexanedimethanol (*cis*+*trans*, 99%), 1,5-pentanediol (97%), 1,6-hexanediol (98%), 1,3-propanediol (≥99.5%), imidazole (99%), 1,2,4-triazole (99%), sodium dicyanamide (96%), diethylene glycol (>99%), tetramethylammonium hydroxide solution (TMAH, 25% aqueous solution), tetraethylammonium hydroxide solution (TEAH, 25% aqueous solution), tetrapropylammonium hydroxide solution (TPAH, 1.0 mol/L aqueous solution) and diphenyl carbonate (99%) were purchased from Shanghai Aladdin Bio-chem Technology. The remaining reagents, 1,4-butanediol, silver nitrate, benzoic acid, tetrabutylammonium hydroxide solution (TBAH, 10% aqueous solution), acetic acid, lactic acid, isopropyl alcohol, dichloromethane, phosphorus oxide, sodium hydroxide and tetraethylammonium bromide, were purchased from Sinopharm Chemical Reagent.

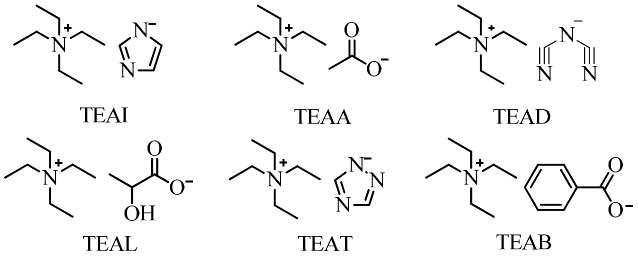
^{1}H NMR spectra were recorded in deuterated water (D_2O) or deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal reference, using a Bruker Avance III-600 spectrometer. GPC was employed to estimate the M_w and polydispersity (PDI = M_w/number-average molecular weight (M_n)), using an Agilent PL-GPC 50 system at 30 °C, with chloroform as the eluent (1.0 mL/min) and generating a calibration curve with polystyrene standards. The glass transition temperature (T_g) of each polymer was determined by DSC using a DSC 1 instrument (Mettler Toledo) at a heating rate of 10 °C/min with a nitrogen gas purge (50 mL/min). TGA data were acquired with a NETZSCH STA449F3 thermogravimetric analyzer under a nitrogen flow rate of 20 mL/min, heating samples (2.0–3.0 mg) from 50 to 600 °C at a rate of 10 °C/min. Fourier transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet 380 spectrophotometer.

2.2. Synthesis of the quaternary ammonium IL catalysts

The structures of the quaternary ammonium IL catalysts synthesized in this study are shown in Scheme 1, and the methods used to obtain these compounds are described below.

Tetraethylammonium imidazolate (TEAI) was prepared using a modification of a reported procedure [47]. Imidazole (0.68 g, 0.01 mol) was added to a solution of NaOH (0.40 g, 0.01 mol) in isopropyl alcohol (20 mL) followed by refluxing for 30 min. Tetraethylammonium bromide (3.09 g, 0.01 mol) was then added at room temperature and the resulting mixture was refluxed for a further 6 h. The solid portion of the reaction mixture was removed by filtration, the solvent was evaporated under vacuum, and the residue (TEAI) was dried at 60 °C under vacuum over 2 d. Yield: 1.87 g (95%); ^{1}H NMR (600 MHz, D_2O, 298 K): 7.62 (s, 1H), 7.00 (d, 2H), 3.08–3.11 (q, 8H), 1.10–1.13 (m, 12H).

The synthetic method for tetraethylammonium 1,2,4-triazolate (TEAT) was the same as that used to obtain TEAI, except that 1,2,4-triazole (0.69 g, 0.01 mol) was added to the NaOH solution. Yield: 1.90 g (96%); ^{1}H NMR (600 MHz, D_2O, 298 K): 8.02 (s, 2H), 3.10–3.14 (q, 8H), 1.12–1.15 (m, 12H).



Scheme 1. Structures of the quaternary ammonium ionic liquids synthesized in this work.

Tetraethylammonium dicyanamide (TEAD) was synthesized according to reference [48]. A slight excess of freshly prepared silver dicyanamide (1.90 g, 0.011 mol, obtained by mixing aqueous solutions of sodium dicyanamide and silver nitrate, removing the resulting white solid by filtration and then washing with water) was added to an aqueous solution of tetraethylammonium benzoate (TEAB, 3.09 g, 0.01 mol), after which the mixture was heated to 30–40 °C and stirred for approximately 1 h. The solid precipitate (AgI and excess $AgN(CN)_2$) was filtered off and the water was removed by rotary evaporation. The resulting material was dissolved in dichloromethane to precipitate a small quantity of silver dicyanamide, which was filtered off, following which the filtrate was evaporated to dryness. The TEAD was then dried under vacuum over 2 d. Yield: 1.90 g (97%); ^1H NMR (600 MHz, D_2O, 298 K): 3.25–3.28 (q, 8H), 1.26–1.29 (m, 12H).

Tetraethylammonium lactate (TEAL) was synthesized by the acid-base neutralization method. Lactic acid (0.90 g, 0.01 mol) was added dropwise to a 100 mL single-necked flask containing TEAH (1.47 g, 0.01 mol), after which the mixture was stirred for approximately 5 h at room temperature. Following this, water was removed by rotary evaporation and the sample was dried under vacuum for 2 d. Yield: 2.10 g (96%); ^1H NMR (600 MHz, 298 K): 3.96–3.99 (q, 1H), 3.13–3.17 (q, 8H), 1.21–1.22 (d, 3H), 1.14–1.17 (m, 12H).

Tetraethylammonium acetate (TEAA) was obtained using the same method employed to synthesize TEAL, except that acetic acid (0.60 g, 0.01 mol) was added. Yield: 1.80 g (95%); ^1H NMR (600 MHz, D_2O, 298 K): 3.13–3.17 (q, 8H), 1.80 (s, 3H), 1.14–1.17 (m, 12H).

The synthetic method for tetraethylammonium benzoate (TEAB) was the same as that for TEAL, except that benzoic acid (1.22 g, 0.01 mol) was added. Yield: 2.41 g (96%); ^1H NMR (600 MHz, D_2O, 298 K): 7.79 (d, 2H), 7.47 (m, 1H), 7.40 (d, 2H), 3.09–3.13 (q, 8H), 1.12–1.15 (m, 12H).

2.3. Synthesis of homopolycarbonates

Isosorbide-based homopolycarbonates were synthesized by a one-pot melt polycondensation method, including transesterification and polycondensation (Scheme 2). A typical polymerization procedure (sample PIC-1) was performed as follows. Under a nitrogen atmosphere, isosorbide (4.38 g, 0.03 mol) and DPC (6.43 g, 0.03 mol) were transferred into a 250 mL three-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, reflux condenser, thermometer and feeding funnel. During the transesterification stage, the reaction mixture was heated to 98 °C, after which the catalyst TMAH (0.014 g, 1.50×10^{-5} mol) was injected into the flask and the mixture stirred continuously for 5 h. The temperature was then gradually increased to 180 °C, while the pressure was gradually reduced to 10 kPa and maintained at this level for 10 min to completely remove the phenol byproduct as well as any unreacted DPC. In the polycondensation stage, a high vacuum (10 Pa) was applied and the temperature was gradually increased to 240 °C and maintained at that level for 5 h. The resulting polymer was dissolved in a minimal amount of chloroform and then precipitated by addition to methanol. The PC was recovered by filtration and dried at 80 °C under vacuum overnight. The PIC samples obtained by the melt polycondensation of isosorbide and DPC using the various catalysts are referred to herein as PIC-1 to PIC-10 as shown in Table 1. PIC-1, ^1H NMR (600 MHz, $CDCl_3$, 298 K): 3.89–4.06 (m, 4H), 4.50–4.54 (m, 1H), 4.87 (t, 1H), 5.06–5.09 (m, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$, 298 K): 70.6, 73.1, 76.9, 81.0, 81.6, 85.8, 153.3, 153.6, 154.0.

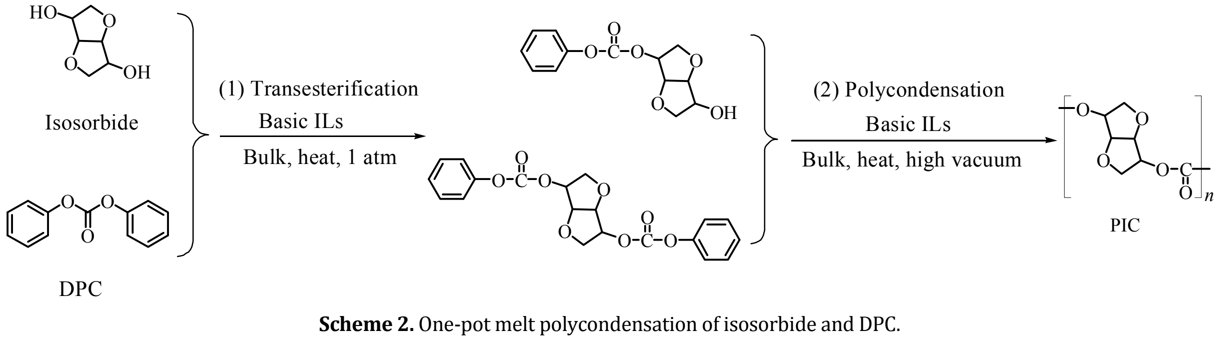
Table 1
Results obtained from the melt polycondensation of isosorbide and DPC using various catalysts.

Sample	Catalyst	Conversion of isosorbide (%)	M_w [a] (g/mol)	M_w/M_n
PIC-1	TMAH	94	17200	1.92
PIC-2	TEAH	95	21300	1.98
PIC-3	TPAH	92	22300	2.36
PIC-4	TBAH	96	19700	1.94
PIC-5	TEAI	93	23600	1.96
PIC-6	TEAD	74	17500	2.08
PIC-7	TEAT	92	19400	2.14
PIC-8	TEAB	81	21800	2.33
PIC-9	TEAL	77	15500	2.17
PIC-10	TEAA	77	19600	2.09

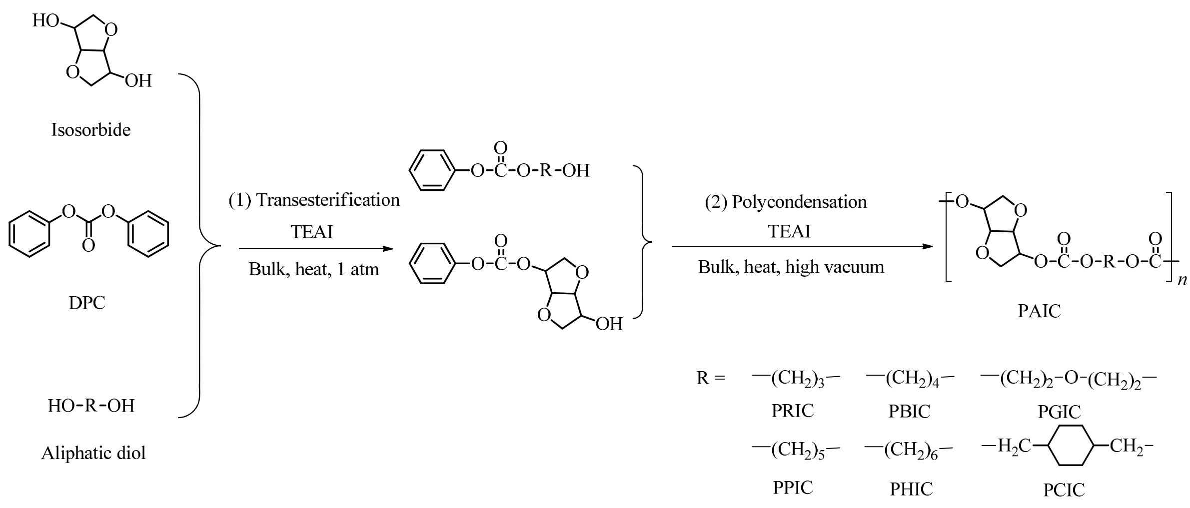
Reaction conditions: isosorbide (0.03 mol), DPC (0.03 mol), catalyst (1.50×10^{-5} mol), 98 °C, 5 h (first step), 230 °C, 5 h (second step).
[a] Determined by GPC in chloroform (1.0 mL/min) at 30 °C with polystyrene standards.

2.4. Synthesis of copolycarbonates

The copolycarbonates of isosorbide and various aliphatic diols were also synthesized using a one-pot melt polycondensation method (Scheme 3). A typical copolymerization proce-



Scheme 2. One-pot melt polycondensation of isosorbide and DPC.



Scheme 3. One-pot melt polycondensation of DPC with isosorbide and aliphatic diols.

dure (sample PCIC) was carried out as follows. In the transesterification stage, isosorbide (2.19 g, 0.015 mol), 1,4-cyclohexanedimethanol (2.16 g, 0.015 mol) and DPC (6.43 g, 0.03 mol) were transferred into a 250 mL three-necked round-bottom flask. The temperature was gradually increased to 98 °C and the catalyst TEAI (0.003 g, 1.5×10^{-5} mol) was injected into the flask followed by continuous stirring for 5 h. The remaining synthesis steps were the same as those applied in the synthesis of the homopolycarbonates. As a result, a PAIC incorporating 1,4-cyclohexanedimethanol was obtained, referred to herein as PCIC. PCIC, ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 0.99–1.08 (br, 2.6H), 1.37–1.50 (br, 2.6H), 1.50–1.72 (br, 3.9H), 1.77–1.91, (br, 3.9H), 3.88–4.13 (br, 9.2H), 4.52–4.60 (br, 1H), 4.88 (br, 1H), 5.06–5.12 (br, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 25.1, 28.6, 34.5, 37.1, 70.6, 71.1, 72.8, 73.3, 76.7, 77.2, 81.0, 81.2, 81.5, 85.9, 85.7, 154.0, 153.6, 153.3, 154.4, 154.7, 155.5.

The synthetic method for PRIC was the same as that for PCIC, except that 1,3-propanediol (1.14 g, 0.015 mol) was added. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 2.01–2.13 (br, 0.4H), 3.86–4.08 (br, 4H), 4.11–4.29 (br, 0.8H), 4.52–4.58 (br, 1H), 4.89 (t, 1H), 5.06–5.13 (br, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 28.0, 64.3, 64.8, 70.6, 73.0, 73.1, 77.0, 77.2, 80.0, 81.2, 81.5, 85.7, 85.8, 153.9, 153.5, 153.0, 154.1, 154.4, 155.1.

The synthetic method for PBIC was the same as that for PCIC, except that 1,4-butanediol (1.35 g, 0.015 mol) was added. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 1.70–1.91 (br, 3.2H), 3.91–4.10 (br, 4H), 4.12–4.28 (br, 3.2H), 4.50–4.61 (br, 1H), 4.85 (t, 1H), 5.03–5.13 (br, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 25.0, 67.3, 67.8, 70.6, 73.1, 73.3, 77.0, 77.2, 81.0, 81.2, 81.6, 85.8, 86.0, 153.9, 153.6, 153.0, 154.2, 154.6, 155.2.

The synthetic method for PPIC was the same as that for PCIC, except that 1,5-pentanediol (1.56 g, 0.015 mol) was added. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 1.40–1.50 (br, 1H), 1.61–1.74 (br, 2H), 3.82–4.10 (br, 4H), 4.10–4.20 (br, 2H), 4.46–4.56 (br, 1H), 4.86 (t, 1H), 5.01–5.12 (br, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 22.0, 28.4, 67.7, 68.2, 70.6, 73.1, 73.3, 76.7, 77.3, 81.0, 81.2, 81.7, 85.8, 86.0, 153.9, 153.6, 153.0, 154.3, 154.6, 155.3.

The synthetic method for PHIC was the same as that for PCIC, except that 1,6-hexanediol (1.77 g, 0.015 mol) was added. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 1.31–1.47 (br, 1.6H), 1.60–1.72 (br, 1.6H), 3.82–4.08 (br, 4H), 4.08–4.17 (br, 1.6H), 4.47–4.56 (br, 1H), 4.86 (t, 1H), 5.01–5.11 (br, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 25.3, 28.5, 67.8, 68.4, 70.6, 73.1, 73.3, 76.6, 77.3, 81.2, 81.6, 81.7, 85.8, 86.0, 153.9, 153.6, 153.0, 154.3, 154.6, 155.3.

The synthetic method for PGIC was the same as that for PCIC, except that diethylene glycol (1.59 g, 0.015 mol) was added. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K): 3.64–3.76 (br, 4.4H), 3.92–4.08 (br, 4H), 4.21–4.34 (br, 4.4H), 4.46–4.55 (br, 1H), 4.85 (t, 1H), 5.00-5.11 (br, 2H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, 298 K): 66.8, 67.1, 67.2, 67.4, 70.5, 73.0, 73.2, 76.1, 77.3, 80.9, 81.1, 81.4, 85.8, 85.9, 154.2, 153.6, 153.0, 154.2, 154.5, 155.1.

3. Results and discussion

3.1. Synthesis and characterization of catalysts

Six quaternary ammonium IL catalysts were synthesized and the structures of these compounds were determined by ^{1}H NMR. The resulting spectra agreed with the anticipated chemical structures and with data from a prior study. The thermal stability of each of the synthesized ILs was also tested using TGA (Fig. 1), and each of these compounds exhibited excellent thermal stability.

3.2. Effect of catalysts

As noted, the polymerization of isosorbide and DPC was performed in the presence of a series of ILs based on quaternary ammonium cations combined with Im$^-$ (imidazolate), Tr$^-$ (1,2,4-triazolate), OH^-, OAc^-, $PhCOO^-$, $N(CN)_2^-$ or $CH_3CHOHCOO^-$ anions (Table 1). The effects of these cations and anions on the catalytic activity were investigated by comparing the M_w values of the resulting PIC. In the case of the ammonium-based ILs, the catalytic activity of the anions decreased in the order: Im$^-$ > OH^- > Tr$^-$ > $PhCOO^-$ > $N(CN)_2^-$, OAc^-,

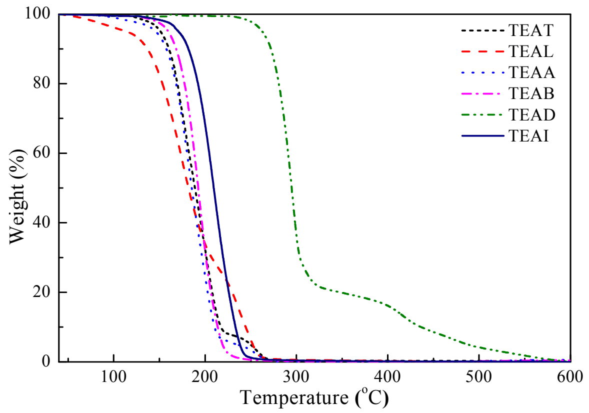


Fig. 1. TGA traces of the quaternary ammonium ILs.

$CH_3CHOHCOO^-$. These results imply that the basicity of the anion (with the exception of Im^-, Table 2) is an important factor in determining the catalytic activity of the IL. However, although Im^- is a weaker base than OH^-, the catalytic activity of its IL was greater (Table 1 and Table 2). The weakly nucleophilic anions, including $N(CN)_2^-$, OAc^- and $CH_3CHOHCOO^-$, also resulted in lower activities for this melt polycondensation reaction (PIC-6, 9 and 10, Table 1). In the case of the OH^- anion, the $(Et)_4N^+$ cation produced a higher catalytic activity than the other cations (Table 1, PIC-1–4). Among these catalysts, TEAI, TEAH and TPAH showed the highest catalytic activities. Similar isosorbide conversions were achieved using all three of these catalysts, but the PIC-3 had a higher PDI. As well, even though the PDI values of the PIC-2 and PIC-5 were almost the same, the M_w of the PIC-5 was higher, and so we selected TEAI as the best catalyst. The data in Table 1 also demonstrate that the isosorbide conversion ranged from 74% to 96%, which can be attributed to the evaporation of some of the isosorbide during the reaction process, in keeping with previous reports in the literature [49]. Therefore, we propose that the catalytic activity depends on both the basicity of the catalyst and the coordinating strength of the anion in the IL [50].

3.3. Effects of other reaction parameters

As can be seen from Fig. 2(a), the catalyst-to-isosorbide ratio had a pronounced effect on the reaction as it was varied from 1 × 10^{-4} to 1 × 10^{-3}. The M_w values increased significantly, from 14800 to 23600 g/mol, as n(catalyst):n(isosorbide) was increased from 1 × 10^{-4} to 5 × 10^{-4}, and then declined over the range of 5 × 10^{-4} to 1 × 10^{-3}. The conversion values also rose significantly, from 84% to 93%, as the n(catalyst):n(isosorbide) ratio was increased from 1 × 10^{-4} to 5 × 10^{-4}, although there were no further obvious variations in the 5 × 10^{-4} to 1 × 10^{-3} range. A low n(catalyst):n(isosorbide), such as 1 × 10^{-4}, resulted in difficulty in obtaining the desired polymerization activity, such that the M_w and isosorbide conversion were lower. However, ratios above 1 × 10^{-3} gave a brownish PIC. These results demonstrated that the optimum catalyst amount for the PIC synthesis was 5 × 10^{-4}.

Table 2
pH values of the catalysts.

Catalyst	pH [a]	Catalyst	pH [a]
TMAH	13.01	TEAD	7.39
TEAH	13.00	TEAT	10.48
TPAH	12.99	TEAB	7.98
TBAH	12.90	TEAL	7.54
TEAI	12.31	TEAA	6.62

[a] Determined by pH meter at 25 °C at a catalyst concentration of 0.1 mol/L.

The effects of polycondensation time on the M_w and isosorbide conversion were investigated at 230 °C and a catalyst-to-isosorbide ratio of 5 × 10^{-4} (Fig. 2(b)). The M_w values increased significantly as the polycondensation time was prolonged from 3 to 5 h, and then decreased over the range of 5 to 7 h. The change in the isosorbide conversion was not significant between 3 and 7 h owing to the excellent thermal stability of the PIC. However, overly long time spans can lead to degradation of the PIC at high temperatures, such that a brownish product was obtained following 7 h. These data indicate that the ideal polycondensation time for the PIC was 5 h.

The dependence of M_w and isosorbide conversion on the polycondensation temperature were also investigated, at a catalyst-to-isosorbide ratio of 5 × 10^{-4} over 5 h (Fig. 2(c)). The M_w values were found to increase gradually as the temperature was raised from 210 to 240 °C, followed by a decline between 240 and 250 °C. The change in the isosorbide conversion was insignificant from 210 to 250 °C, again owing to the superior thermal stability of the PIC. Because the product is more viscous at low temperatures, elevated temperatures are necessary for the polycondensation, although they can promote unde-

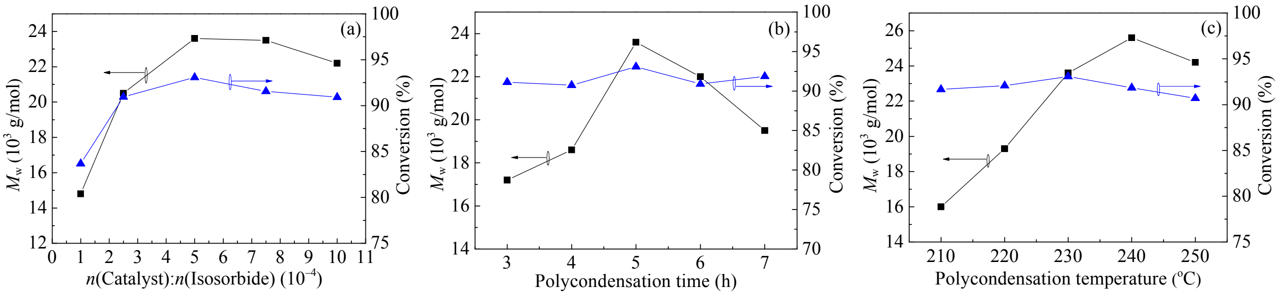


Fig. 2. Effect of the catalyst-to-isosorbide ratio (a), polycondensation time (b) and polycondensation temperature (c) on M_w and isosorbide conversion.

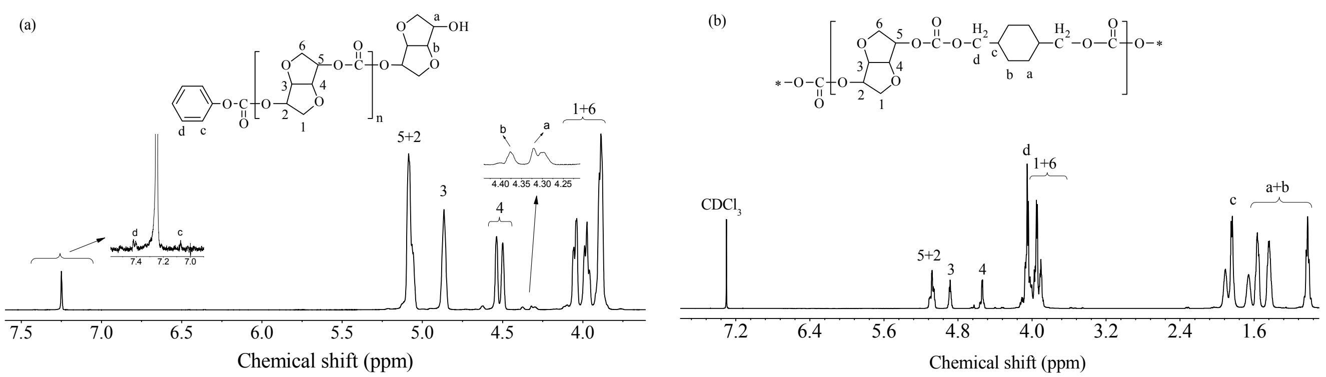


Fig. 3. ^{1}H NMR spectra of PIC-1 (a) and PCIC (b).

sired side reactions, resulting in a brown color and crosslinking. The results show that the optimum polycondensation temperature for the PIC was 240 °C.

3.4. Synthesis and structure characterization of PIC and PAICs

The chemical structures of the PIC-1 and PAICs specimens were determined by ^{1}H NMR spectroscopy, and the ^{1}H NMR spectra of the PIC-1 and PCIC are presented in Fig. 3. In Fig. 3(a), the two multiplet signals between 4.28 and 4.40 ppm are attributed to terminal isosorbide groups and the two singlets at 7.09 and 7.43 ppm are assigned to terminal phenyl carbonate groups. The PAICs compositions (Table 3) were determined based on the integration values for peaks resulting from the repeating units, and the calculated compositions were found to deviate from the feed ratios. It is therefore evident that the hydroxyl groups of the different monomers had varying levels of reactivity, with the diethylene glycol and 1,4-cyclohexanedimethanol being the most active.

The ^{13}C NMR spectrum of the PIC-1 is provided in Fig. 4. As isosorbide has two different hydroxyl groups (exo and endo), the spectrum displays three C =O signals with intensity ratios of 1:2:1, attributed to the endo-endo, endo-exo, exo-endo and exo-exo linked carbonate groups. This random sequence was consistent with the PIC structure reported by Chatti et al. [26].

The microstructures of the PAIC samples were determined by ^{13}C NMR spectroscopy, and the assignments of signals are summarized in Fig. 5. As shown in Fig. 5(a), all the peaks ascribed to the PCIC repeating units were well resolved, especially the carbonyl carbons that are sensitive to sequence effects at the dyad level. The six different carbonyl carbon signals are denoted herein as AA, AIs (or IsA) and IsIs respectively, as shown in Fig. 5(b). The dyad contents were calculated by integration of the peaks included in these signals. Based on these values, the number-average sequence length (L_n) and the degree of randomness (B) were calculated according to the following equations [51].

$$L_{nAC} = (f_{AC/IsC} + 2\,f_{AC/AC})\ /\ f_{AC/IsC} \tag{1}$$

$$L_{nIsC} = (f_{AC/IsC} + 2\,f_{IsC/IsC})\ /\ f_{AC/IsC} \tag{2}$$

$$B = 1\ /\ L_{nAC} + 1\ /\ L_{nIsC} \tag{3}$$

Here, $f_{AC/AC}$, $f_{AC/IsC}$ and $f_{IsC/IsC}$ represent the molar fractions of the dyads, calculated from the integral intensities of the carbonyl carbon signals from the AA, AIs (or IsA), and IsIs dyads, respectively, and L_{nAC} and L_{nIsC} are the number average sequence lengths of the aliphatic carbonate (AC) and isosorbide carbonate (IsC) units, respectively. The results are summarized in Table 4. As shown, all the B values of the PAICs were different from one another, demonstrating that isosorbide had different levels of reactivity with the various aliphatic diols. Thus, the AC and IsC units exhibited statistically random distribution in each of the PAICs.

3.5. Thermal properties

The thermal properties of the PIC and PAIC specimens were evaluated by DSC and TGA, with the results shown in Table 5.

Table 3
Results obtained from the copolycondensation of isosorbide and aliphatic diols.

Sample	Is/Diol [a]	Conversion [b] (%)	M_w [c] (g/mol)	M_w/M_n
PHIC	1/0.4	82	43700	2.60
PPIC	1/0.5	88	40400	2.32
PBIC	1/0.8	87	70500	3.07
PCIC	1/1.3	83	95300	2.87
PGIC	1/1.1	89	112000	3.17
PRIC	1/0.2	75	29000	3.47

[a] Molar composition determined by ^{1}H NMR spectroscopy.
[b] Conversion of isosorbide and aliphatic diols to copolycarbonates.
[c] Determined by GPC in chloroform (1.0 mL/min) at 30 °C, with polystyrene standards.

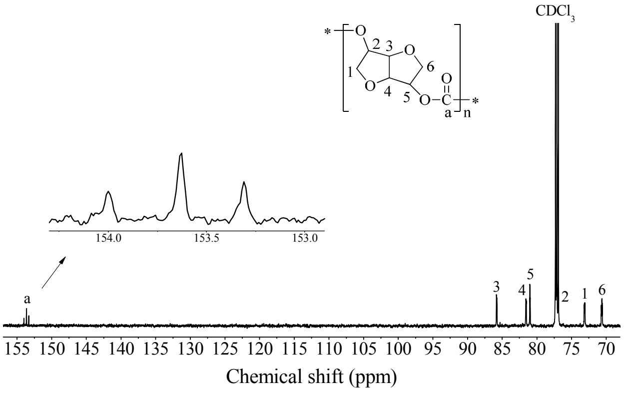


Fig. 4. ^{13}C NMR spectrum of PIC-1.

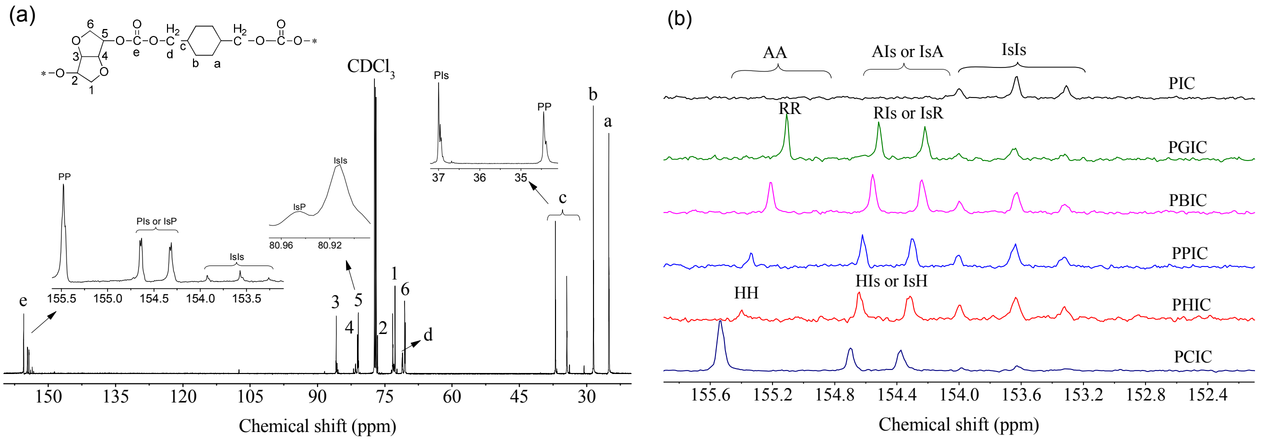


Fig. 5. (a) ^{13}C NMR spectrum of PCIC and (b) expanded spectra of the PAICs in the carbonyl carbon region.

All samples were found to be in an amorphous state. Fig. 6(a) presents the DSC traces of these samples. The PIC displayed a remarkably high T_g of 162 °C. This sample was amorphous as a result of the unsymmetrical carbonate linkages between repeat units, while its high T_g was due to the rigid structure of isosorbide. A single unique T_g was observed for each of the PAICs throughout the –100 to 200 °C range, and the T_g values ranged from 47 to 115 °C depending on the structure of the comonomer. The T_g of the linear diol PAICs were also observed to shift to lower temperatures with increasing methylene numbers in the linear aliphatic diol units. The PCIC displayed a higher T_g than the PAICs made with linear diols because of the rigid cyclohexane groups.

The TGA traces of PIC and PAICs are presented in Fig. 6(b). Each of these polymers displayed a single-step thermal decomposition process. Table 4 summarizes the T_d values of the samples at 5% weight loss ($T_{d\text{-}5\%}$) and maximum degradation rate ($T_{d\text{-max}}$). The PCIC, incorporating cyclohexane groups, displayed a higher $T_{d\text{-}5\%}$ and $T_{d\text{-max}}$ compared to the PIC-1, while both the PIC-1 and PCIC showed greater thermal stability than the PAICs incorporating linear diols. The thermal stability of each of the latter samples was improved with increases in the quantity of methylene groups in the linear aliphatic diol units.

3.6. *A discussion of the reaction mechanism*

Based on published reports and the results of this work, a probable catalytic cycle was proposed and is depicted in Scheme 4, using a homopolycarbonate as an example. Initially, isosorbide is transitioned to an alkoxide anion by the action of the feed catalyst (TEAI). Simultaneously, the DPC is polarized by the tetraethylammonium cation and thus undergoes reaction more readily (steps 1 and 2). Subsequently, the anions generated in the previous step attack the polarized DPC, while the phenol is removed under vacuum at a high temperature (step 3). An intermediate is produced and the polymer chain continues to grow until the PIC is obtained (step 4). The polycondensation mechanism affording the copolycarbonates is similar. However, because the hydroxyl groups of the various aliphatic diols have different reactivities, irregularly ordered PAIC chains are eventually formed. The validity of this mechanism was also assessed based on FT-IR data.

It is evident from the resulting IR spectra (Fig. 7(a) and (b)) that the characteristic sharp absorbance of the hydroxyl groups of the isosorbide shift from 3370 to 3415 cm^{-1} after the addition of the TEAI. This result suggests the formation of N–H bonds between the hydroxyl groups and the Im^{-}. In addition, the peak due to the C=O bond on the DPC (Fig. 7(c) and (d)) shifts only from 1775 to 1771 cm^{-1} upon adding the TEAI, suggesting that the $(Et)_4N^+$ cation has little effect on the C=O bond. However, it is important to note that the addition of the TEAI to the mixture of the DPC and isosorbide (Fig. 7(e)) does induce relatively large variations in the characteristic absorbances of the two raw materials. This result indicates that the isosorbide,

Table 4
The microstructural analyses of PAICs.

PAICs	Dyads [a] (mol %)			L_{nAC}	L_{nIsC}	B
	AA	AIs/IsA	IsIs			
PHIC	0.55	45.37	54.08	1.02	3.38	1.27
PPIC	8.20	51.52	40.28	1.32	2.56	1.15
PBIC	21.01	52.10	26.89	1.81	2.03	1.05
PCIC	51.28	42.56	6.15	3.41	1.29	1.07
PGIC	33.44	61.20	5.35	2.09	1.17	1.33
PRIC	4.76	23.60	71.65	1.40	7.07	0.85

[a] Experimental values obtained from ^{13}C NMR signals.

Table 5
Thermal properties of the PIC and PAICs.

Sample	T_g [a] (°C)	$T_{d\text{-}5\%}$ [b] (°C)	$T_{d\text{-max}}$ [b] (°C)
PIC	162	329	375
PCIC	115	332	373
PRIC	90	316	379
PGIC	80	328	374
PBIC	84	319	367
PPIC	50	322	369
PHIC	47	323	370

[a] Determined by DSC measurements at a heating rate of 10 °C/min (second heating).

[b] $T_{d\text{-}5\%}$ and $T_{d\text{-max}}$ determined by TGA under N_2 at a heating rate of 10 °C/min.

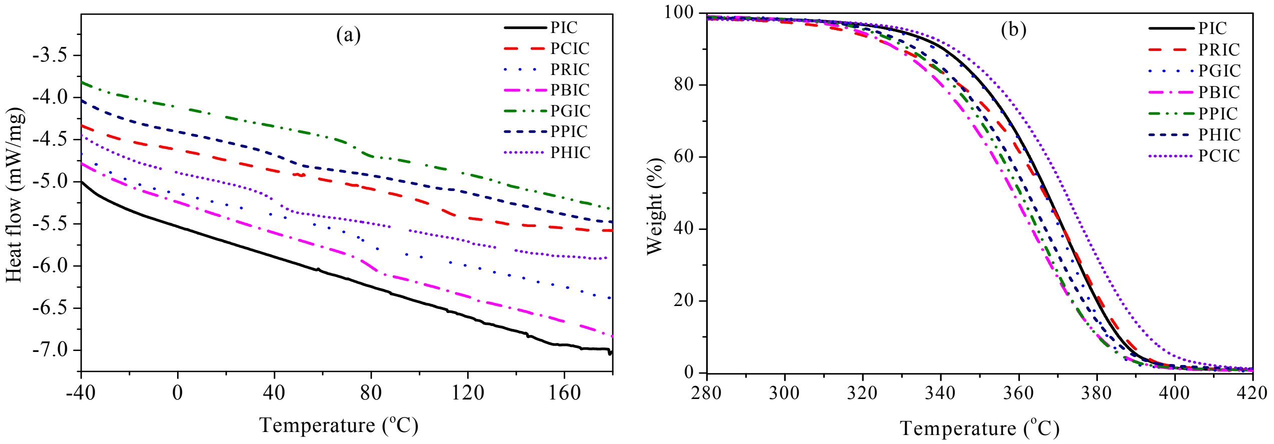
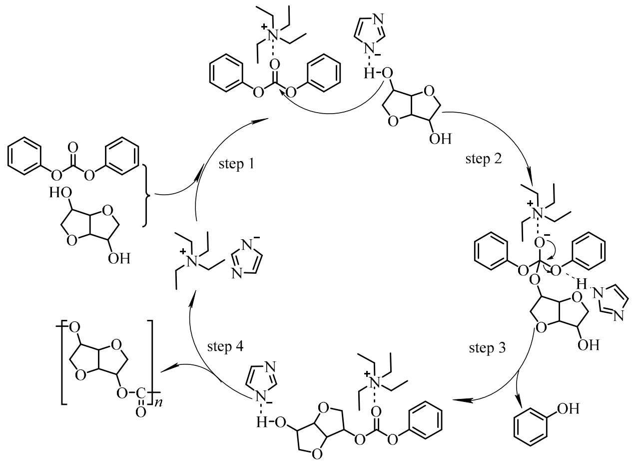


Fig. 6. DSC (a) and TGA (b) traces of the PIC and PAICs.



Scheme 4. Mechanism for the polymerization of PIC with TEAI as the catalyst.

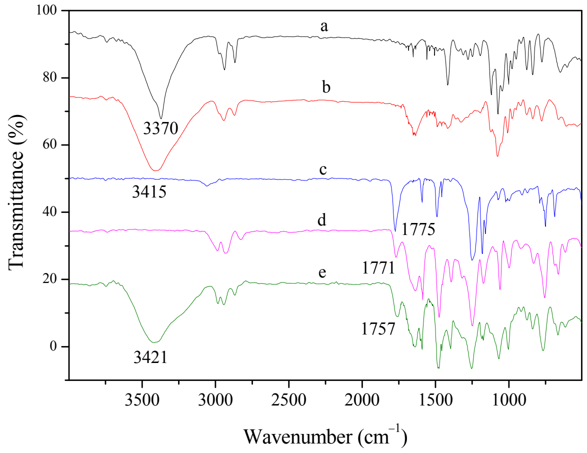


Fig. 7. IR spectra of isosorbide without TEAI (a), isosorbide with TEAI (b), DPC without TEAI (c), DPC with TEAI (d), and isosorbide and DPC with TEAI (e).

which transitions to an alkoxide anion, attacks the polarized DPC. Based on the experimental results and this proposed mechanism, we believe that ILs that have significant nucleophilic and electrophilic properties are more favorable to the polymerization. However, overly nucleophilic or electrophilic properties will lead to reciprocal annihilation. Therefore, an optimal range of such properties is required to achieve superior performance for the desired reaction.

4. Conclusions

A series of quaternary ammonium ILs were successfully synthesized using different methods. Both homopolycarbonates and copolycarbonates were then obtained by melt polycondensation catalyzed by these ILs. Among these catalysts, TEAI showed the best catalytic activity, producing a polymer with a M_w of 25600 g/mol and an isosorbide conversion of 92%. The best copolycarbonate performance was achieved in the case of PCIC, which had a M_w of 95300 and a diol conversion of 83%. The PAICs were found to have random microstructures, and their compositions showed significant variations from the theoretical values predicted from the feed ratios. The PCIC sample showed the highest T_g and exhibited better thermal stability than the polymers made using linear diols. The data presented herein demonstrate that copolycarbonates such as PCIC have the potential to function as high-performance polymeric materials.

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Graphical Abstract

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Synthesis of isosorbide-based polycarbonates via melt polycondensation catalyzed by quaternary ammonium ionic liquids

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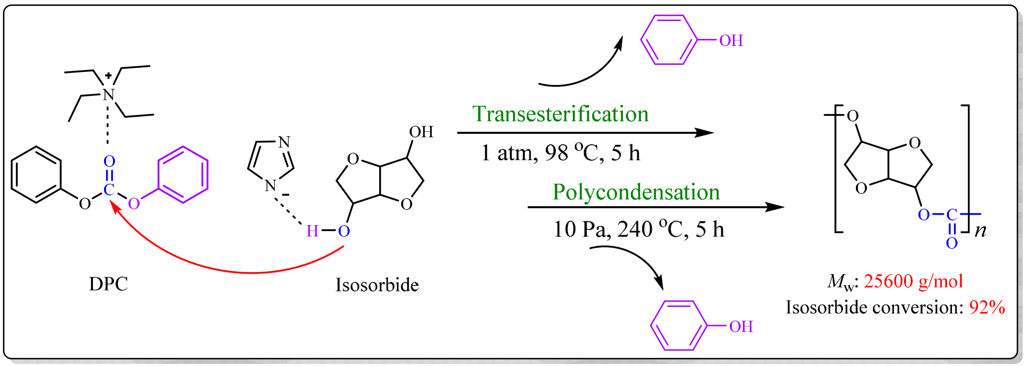

A series of quaternary ammonium ionic liquids were prepared and exhibited high catalytic activity for the synthesis of isosorbide-based polycarbonates via the melt polycondensation of diphenyl carbonate with isosorbide.

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