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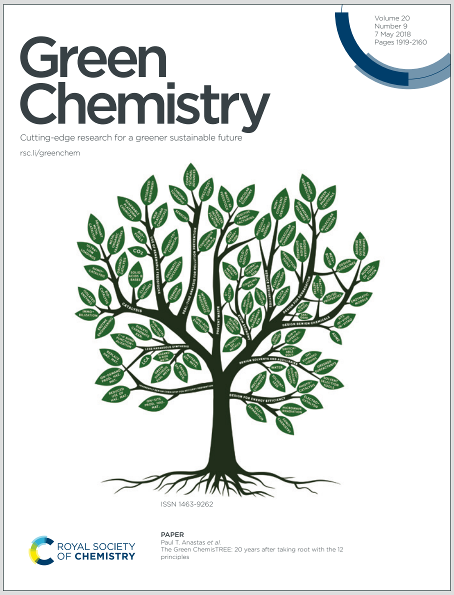

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ARTICLE

Synthesis of Bioderived Polycarbonates with Molecular Weight Adjustability Catalyzed by Phenolic-derived Ionic Liquids

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Synthesis of high-molecular-weight bioderived polycarbonates via green routes and regulation of molecular weight are of great significance but also enormous challenges. Herein, a green sequential approach toward the bio-derived polycarbonates with adjustable molecular weight from isosorbide and dimethyl carbonate (DMC) has been developed by employing ionic liquids (ILs) as a class of eco-friendly catalyst. The structures of IL catalysts are capable of being designed readily to control the molecular weight of isosorbide-derived polycarbonate (PIC), which is an attractive advantage of IL catalysts instead of the conventional metal-containing catalysts. In the presence of [Bmim][4-I-Phen] catalyst, PIC weight-average molecular weight (M_w) can reach to 50300 g/mol. By combination of the experimental results and DFT calculations, an IL's anion-cation synergistic catalytic polymerization mechanism has been proposed, which reveals that nucleophile electrophile dual activation by H-bonds and charge-charge interactions in catalyzing PIC formation. Further importance of this study is that we propose a guidance of developing IL catalysts for synthesizing higher molecular weight polycarbonates, thereby conveniently preparing a variety of polymers with tunable properties.

Introduction

Approach to polymeric materials from bio-derived monomers and green polymerization processes is currently recognized as an inevitable choice for sustainable development.[1, 2] Of polymeric materials, polycarbonate is extensively employed for various engineering fields because of its brilliant properties, such as high mechanical strength and excellent transparency.[3, 4] However, the traditional synthetic route for polycarbonate is interfacial or solution polycondensation of the highly toxic reagent phosgene and the petroleum-based monomer bisphenol-A (BPA) known for interfering with the body's endocrine system.[5-9] Hence, it is an insistent demand to develop green routes and alternative nontoxic bio-based monomers with equivalent properties for polycarbonate synthesis.

Isosorbide (1,4:3,6-dianhydro-D-sorbitol, IS), obtained from starch and cellulose, is considered as a promising biobased polymer building block attributing to its rigidity, chirality, and nontoxicity.[10, 11] Compared with the traditional BPA polycarbonate, isosorbide-derived polycarbonate (PIC) retains higher heat resistance and preferable UV resistance.[12-14] Furthermore, melt polymerization is a preferred approach circumventing toxic reagents and sophisticated technological processes.[15] However, previous studies were mainly focused on the melt polymerization of isosorbide with diphenyl carbonate (DPC) instead of with dimethyl carbonate (DMC).[14, 16-18] Compared with DPC pathway, the DMC route is more sustainable, which avoids the use of the toxic raw material phenol.[15] Moreover, DMC, a green biodegradable chemical, is derived from CO_2. And the DMC route can achieve at a relatively lower reaction temperature.[19] Therefore, the direct melt polymerization of isosorbide and DMC can simplify the reaction steps and reduce the cost and energy consumption. However, it is a challenging route to manufacture PIC via the DMC method.[20, 21] Because isosorbide is a dihydric alcohol with weak reactivity.[14] Additionally, DMC is difficult to act as a methoxycarbonylating agent for participating in a transesterification reaction in the presence of a basic catalyst at high temperatures.[20, 22] These reasons cause the enormous challenge in synthesizing PIC, particularly high-molecular-weight PIC.[11, 23] Considering the abovementioned factors, the bottleneck of developing this green route is the catalyst development. Consequently, only a few metal-containing catalysts (alkali metal acetylacetonate complexes) have been developed for the one-pot melt polymerization of isosorbide

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and DMC.[19, 24] In the presence of the lithium acetylacetone catalyst, the weight-average molecular weight (M_w) of the synthetic PIC can reach to 46500 g/mol under the optimum conditions.[19] However, it is generally known that metal-based catalysts may cause certain damages, for example, environmental concerns, and corrosions.[25, 26] Besides, the screening of the metal-containing catalysts for PIC synthesis without basis leaves PIC molecular weight being randomly varied. As a result, it is hopeless to expect that PIC molecular weight could be further enhanced via employing the abovementioned metal-containing catalysts.

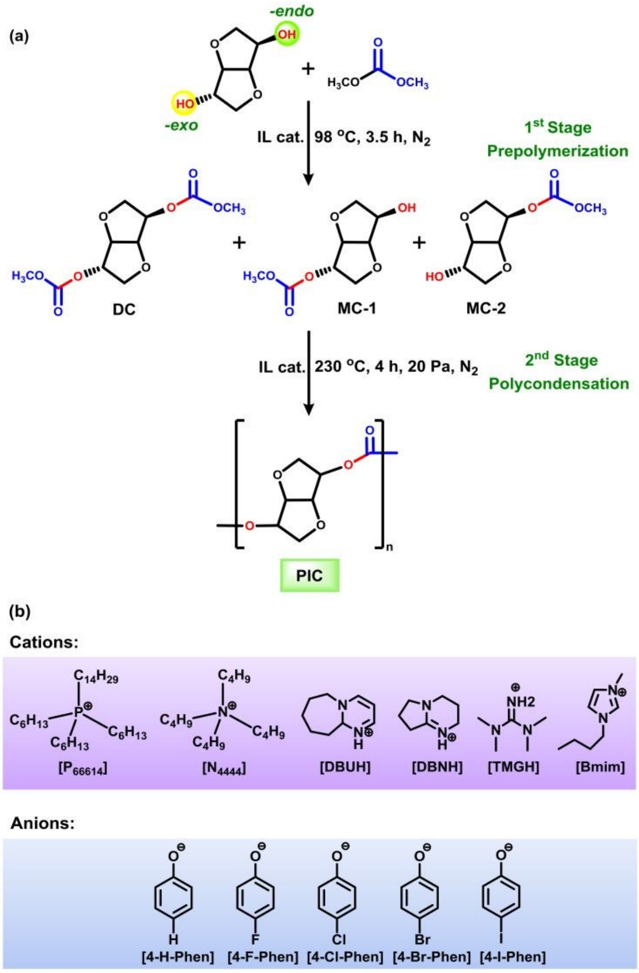

Fig. 1 (a) The melt polymerization of isosorbide and DMC; (b) The structures of IL catalysts' cations and anions used in this work.

Satisfactorily, ILs have been proven to exhibit remarkable performance in the catalytic field, and are recognized as potential replacements for metal-containing catalysts attributing to their highlighted properties of adjustability and low toxicity.[27-34] It was reported that the cation and anion of IL both could activate substrates.[35, 36] Hence, it is significant to design the structures of IL's cation and anion to promote the polymerization reaction of isosorbide and DMC. In our previous study, we discovered that phosphonium phenolate ILs were effective catalysts for the transesterification reaction of isosorbide and DMC.[37] The phenolic anion could not only form H-bonds with the -OH groups of isosorbide, but also act as a nucleophile activating DMC through interacting with the C=O groups, thus resulting in the generation of the methoxycarboxylation products [dicarboxymethyl isosorbide (DC), 2-monocarboxymethyl isosorbide (MC-1), 5-monocarboxymethyl isosorbide (MC-2)] (**Fig. 1**a).[22, 37] Concerning the melt polymerization of isosorbide and DMC, the PIC molecular weight is not only controlled by the transesterification stage but also affected by the polycondensation stage.[19] The polycondensation stage is mainly the transesterification reaction of the terminal groups of these methoxycarboxylation products causing the formation of oligomers, and then the terminal groups of the growing polymer chains are further reacting with each other continuously.[19, 37] Although the substrates' structures of the two stages are different, they all contain -OH groups and carbomethoxy groups (-OCOOCH$_3$) (**Fig. 1**a). Therefore, through modifying the structures of phenolate-based IL's anion and cation, it is possible to obtain efficient catalysts for synthesizing high-molecular-weight PICs. Because the nucleophilicity of anion and the electrophilicity of cation in IL could influence each other.[38-40]

Based on the above viewpoints, we report a one-pot DMC method for PIC synthesis using phenolic ILs as a promising class of eco-friendly catalysts, of which the highly toxic phosgene and the endocrine disruptor BPA are avoided. The excellent tunability of phenolic IL catalysts' structure facilitates the H-bond strength between IL catalyst's cation or anion and substrates to vary readily, causing the different catalytic activity of IL catalysts. As a result, the PIC molecular weight can be controlled by selecting proper IL catalysts. We also propose a plausible polymerization mechanism for PIC synthesis in the presence of phenolic IL catalysts according to the experimental results, ^{1}H NMR, ESI-MS, MALDI-TOF-MS, and DFT calculations.

Results and discussion

Effect of IL catalysts' structure on PIC synthesis

In our previous work, we developed trihexyl(tetradecyl)phosphonium 4-substituted phenolic IL ([P$_{66614}$][4-R-Phen], R = H, F, Cl, Br and I) catalysts for the transesterification reaction of isosorbide with DMC and the [P$_{66614}$][4-I-Phen] catalyst showed the highest catalytic activity (**Fig. 1**b).[37] However, for the melt polymerization of them, the substrates' structures of the two stages are different (**Fig. 1**a),[19] which means that the [P$_{66614}$][4-I-Phen] catalyst may not be the best catalyst for the whole reaction process. Thus, it is essential to investigate the influence of the anions' and cations' structures of 4-substituted phenolic IL catalysts on the polymerization reaction. For this purpose, a series of 4-substituted phenolic IL catalysts (**Fig. 1**b) were synthesized and identified by ^{1}H NMR and ESI-MS (see ESI†). Among them, the [P$_{66614}$][4-R-Phen] (R = H, F, Cl, Br and I) catalysts were used directly, which were obtained from our previous work.[37] As shown in **Fig. S1**, these

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ILs displayed excellent thermal stability and the corresponding temperatures with maximum decomposition rates ($T_{d\text{-}max}$) were all above 200 °C.[37]

Table 1 The influence of the structure of IL's anion on the pre-polymerization stage

ntry	Anion	X_{IS} (%)	S_{DC} (%)	$S_{MC\text{-}1}$ (%)	$S_{MC\text{-}2}$ (%)
1	[4-H-Phen]	94.7	51.6	26.3	22.1
2	[4-F-Phen]	97.0	68.2	19.3	12.5
3	[4-Cl-Phen]	95.0	52.7	25.6	21.7
4	[4-Br-Phen]	96.6	56.2	24.8	19.0
5	[4-I-Phen]	98.8	82.6	9.6	7.8

Reaction conditions: The molar ratio DMC/IS=7.5. Transesterification time: 3.5 h. Cat. amount is 4.4×10^{-3} equiv. mol based on IS. X_{IS} denotes isosorbide conversion at the transesterification stage calculated by GC. Transesterification products' selectivities determined by HPLC. S denotes selectivity.

Initially, the cation in IL was fixed as the [P_{66614}] cation, of which the anions were grafting the atoms of H, F, Cl, Br, and I to the para-position of phenolic ion, respectively. To study the influence of the composition of transesterification products on PIC molecular weight, the transesterification time was set to 3.5 h instead of 13 h.[37] Because DC was the main transesterification product under the condition of excessive transesterification time.[37] The results are listed in **Table 1** and **Fig. 2**a, indicating that the whole polymerization reaction can be catalyzed effectively by the phenolate-based ILs. Moreover, the typical ^{1}H NMR spectra of the different stages of the isosorbide moiety construction change obviously with the reaction process, implying the growth of polymer chains (**Fig. S2**). The GPC results are consistent with the ^{1}H NMR analysis and indicate that the molecular weight of PIC (M_n and M_w) is also changed with the variation of phenolic anion structure (**Fig. 2**a and **Table S1**). This can be explained as follows. The different IL's anion structure leads to the variation of the nucleophilicity of 4-substituted phenolic anion in IL. As reported by our previous work, the O atom of the phenolic anion can form H-bond interactions with the -OH groups in isosorbide.[37] Thus, the change of IL's anion structure could result in the variation of the H-bond strength. For instance, the bond lengths of H-bond are 1.538, 1.539, and 1.557 Å for [4-H-Phen], [4-F-Phen], and [4-I-Phen], respectively.[37] Furthermore, the halogen group could undertake the negative charge of the oxygen atom of phenolic anion, improving the halogen-oxygen interaction of phenolic anion with isosorbide.[41-43] Naturally, when IL catalyst has a different anion structure, the proportion of the transesterification products (DC, MC-1, and MC-2) is also different at the same reaction condition (**Table 1**). At the transesterification stage, the catalytic activity order of [P_{66614}][4-R-Phen] catalysts (R = H, F, Cl, Br and I) is consistent with our previous work.[37] At the polymerization stage, the different contents of various PIC precursors are a significant factor for the difference of the PIC molecular weight, owing to the three methoxycarboxylation compounds with different reactivity.[19] With the catalysis of [P_{66614}][4-I-Phen], the obtained PIC exhibits the highest molecular weight (M_n = 16500 g/mol and M_w = 28400 g/mol) (**Fig. 2**a). From this point, we can conclude that a high content of DC is really conducive to the growth of polymer chains.

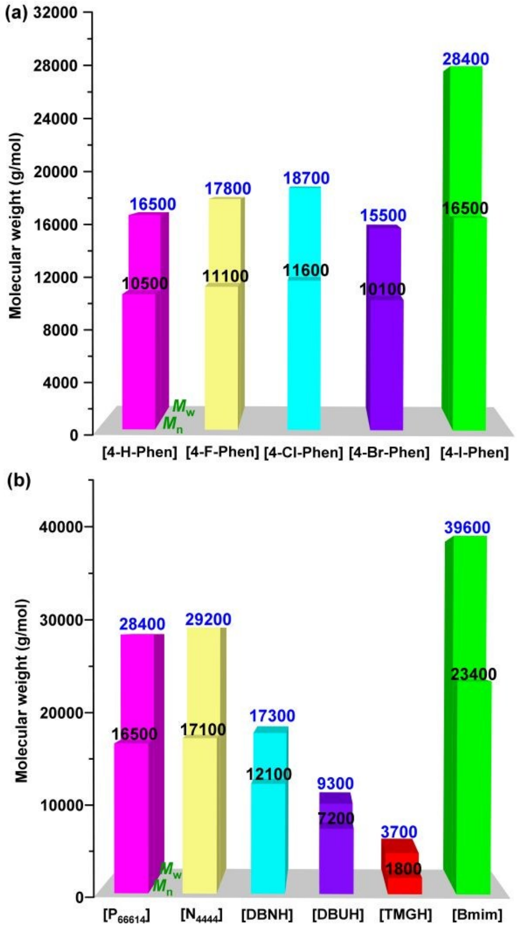

Fig. 2 PIC molecular weight catalyzed by IL catalysts (a) cation fixed as [P_{66614}] and the anions with different structures; (b) anion fixed as [4-I-Phen] and the cations with different structures.

Obviously, [4-I-Phen] is an appropriate anion in this polymerization reaction according to the above experimental results. So, does the cation have a significant effect on this reaction? For this purpose, the effect of IL's cation structure on the PIC molecular weight was discussed. As illustrated in **Fig. 2**b and **Table S1**, the structure of IL's cation also has a great influence on PIC molecular weight. With the presence of [Bmim][4-I-Phen], the M_n and M_w can attain to 23400 g/mol and 39600 g/mol, respectively. When IL's cation structure involves [P_{66614}] or [N_{4444}], the proportion of DC is obviously more than that catalyzed by [Bmim][4-I-Phen] (**Table 2**, entry 1-2, 6). However, the molecular weight of PIC catalyzed by the IL catalyst including [P_{66614}] or [N_{4444}] is lower than that catalyzed by [Bmim][4-I-Phen]. It means that a high proportion of DC is a prerequisite but not the unique factor in synthesizing high-molecular-weight PIC. One possible reason is that [P_{66614}]

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or [N_{4444}] cation has a long alkyl chain, resulting in an increase of steric hindrance interacting with the bulky carboxymethyl moiety of methoxycarboxylation products (DC, MC-1 or MC-2).[44] Consequently, its catalytic activity of polycondensation stage could be weaker than that of [Bmim][4-I-Phen]. This can be proved by the DFT calculations below. The protic ILs ([DBNH][4-I-Phen], [DBUH][4-I-Phen], and [TMGH][4-I-Phen]) present inferior catalytic activity in the prepolymerization stage, leading to the low conversion of isosorbide and the low contents of prepolymers (**Table 2**, entry 3-5). As a result, the PIC molecular weight is lower than that catalyzed by aprotic ILs (**Fig. 2**b). According to previous literature,[45, 46] generally, the ability to form H-bond of protic IL is stronger than that of aprotic IL. Therefore, the inferior catalytic activity of protic ILs could be related to the fact that the proton of IL's cation can form strong H-bond interactions with the oxygen atom of C=O in DMC and is difficult to disintegrate from the complex. Thus, it makes methoxycarboxylation products difficult to generate, especially, DC (**Table 2**, entry 3-5). The results of DFT calculations, given below, can verify the abovementioned deduction. Next, further investigations were carried out utilizing the [Bmim][4-I-Phen] catalyst.

Table 2 The influence of the structure of IL's cation on the pre-polymerization stage

Entry	Cation	X_{IS} (%)	S_{DC} (%)	S_{MC-1} (%)	S_{MC-2} (%)
1	[P_{66614}]	98.8	82.6	9.6	7.8
2	[N_{4444}]	98.1	70.8	16.2	13.0
3	[DBNH]	44.9	-	72.6	27.4
4	[DBUH]	43.6	-	74.6	25.4
5	[TMGH]	3.2	-	80.0	20.0
6	[Bmim]	96.6	53.8	25.3	20.9

Reaction conditions: The molar ratio DMC/IS=7.5. Transesterification time: 3.5 h. Cat. amount is 4.4×10^{-3} equiv. mol based on IS. X_{IS} denotes isosorbide conversion at transesterification stage calculated by GC. Transesterification products' selectivities determined by HPLC. S denotes selectivity.

Effect of prepolymer composition on PIC synthesis

Undoubtedly, [Bmim][4-I-Phen] is a proper IL catalyst in this polymerization reaction according to the abovementioned experimental results. Then, does the proportion of prepolymers have a significant effect on PIC molecular weight? To this end, the influences of DMC/IS molar ratio and the transesterification time on the polymerization reaction were interrogated with the catalysis of [Bmim][4-I-Phen], respectively. As depicted in **Fig. 3**a, the molar ratio of DMC to isosorbide indeed has an important impact on the PIC molecular weight. When the DMC/IS molar ratio increases from 1.5 to 7.5, the PICs M_n and M_w increase from 9600 g/mol and 18100 g/mol to 23400 g/mol and 39600 g/mol, respectively. However, as the DMC/IS molar ratio exceeding 7.5, the M_n and M_w of PIC gradually decrease to 14400 g/mol and 23800 g/mol (DMC/IS molar ratio: 15), respectively. To the best of our knowledge, no one has made a clear explanation for this phenomenon. To solve this puzzle, the selectivity of intermediate products (DC, MC-1, MC-2) and isosorbide conversion were analyzed (**Fig. 4**). With the increase of DMC/IS molar ratio, the amount of DC in the total transesterification products is significantly enhancing and that of MC-1 (MC-2) is considerably reducing (**Fig. 4**a). After DMC/IS molar ratio reaching to 7.5, the increase of isosorbide conversion is not apparent. These results reveal that the PIC molecular weight is not always increasing with the DC amount enhancement. Similarly, the influence of transesterification time is consistent with the above result (**Fig. 3**b and **4**b).

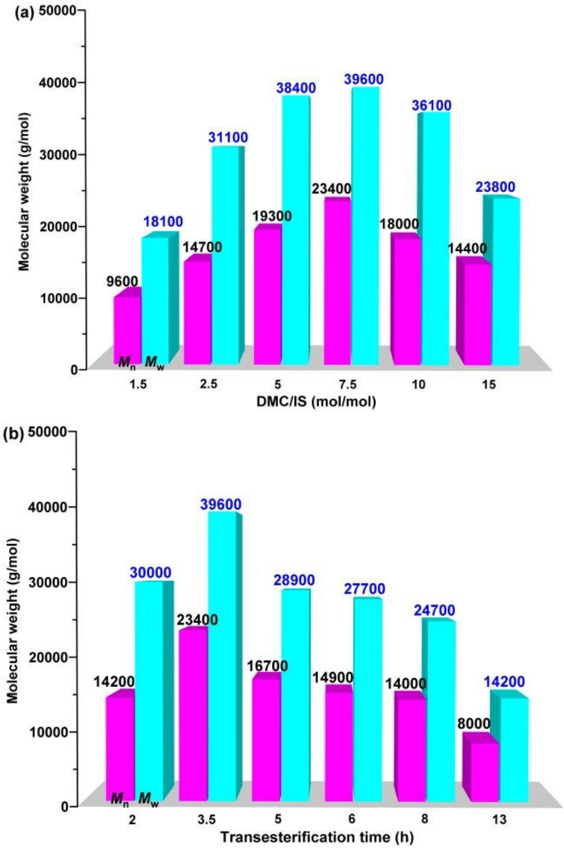

Fig. 3 Effect of (a) molar ratio of DMC to isosorbide; (b) transesterification time on PIC molecular weight catalyzed by [Bmim][4-I-Phen].

Interestingly, it seems to mean that an excessive amount of high reactive DC has a negative effect on the PIC molecular weight. The most plausible reason is that DC is more prone to occur a decarboxylation reaction at high temperatures. Decarboxylation reactions could indeed occur for some dialkyl carbonates at high temperatures in the presence of catalysts.[47] For supporting this hypothesis, TG-MS and ^{1}H NMR spectroscopy were employed. As exhibited in **Fig. S3**a, TG-MS curves demonstrate that DC, MC-1, and MC-2 all can release CO_2 (m/z 44) at 190 ^oC. Furthermore, as shown in **Fig. S3**b and **Fig. S4**, the ^{1}H NMR spectra indicate that DC, MC-1, and MC-2

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all can undergo methylation at a high temperature (the single peak at about 3.4 ppm belongs to the hydrogen in methoxy group -OCH_3 of isosorbide moiety according to the previous report).[22] Hence, the carbomethoxy group (-$OCOOCH_3$) of DC (MC-1 or MC-2) could suffer methylation in the presence of a catalyst, which leads to -$OCOOCH_3$ transforming into -OCH_3 and releasing CO_2 at the same time. Additionally, the end -OCH_3 could cause the polymer chain to be terminated. Thus, excessive content of DC is easier to terminate the polymer chain growth, on account of that DC has two -$OCOOCH_3$ groups. Consequently, an excessive amount of high reactive DC has a negative effect on the PIC molecular weight. The optimum proportion of prepolymers for PIC synthesis depends on reaction conditions and catalyst type.

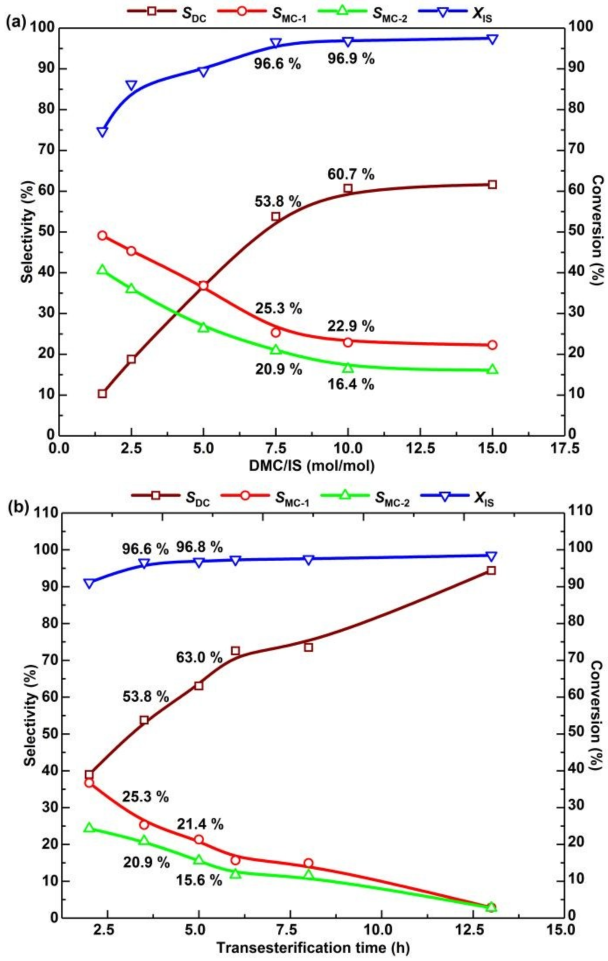

Fig. 4 Effect of (a) molar ratio of DMC to isosorbide; (b) transesterification time on IS conversion at transesterification stage and prepolymers' selectivities.

Subsequently, to explore the maximum molecular weight of PIC in the presence of [Bmim][4-I-Phen], we also studied the influences of polycondensation temperature and time on the polycondensation reaction under the optimum prepolymer composition (**Fig. S5**). A high polycondensation temperature is indispensable to reduce melt viscosity for polymer chain growth.[15] However, the thermal degradation of PIC and side reactions would play a dominant role when the polycondensation temperature was too high or the polycondensation time was too long.[14] Through conditional optimization, the maximum molecular weight of PIC is M_n = 28500 g/mol and M_w = 50300 g/mol (**Fig. S5**).

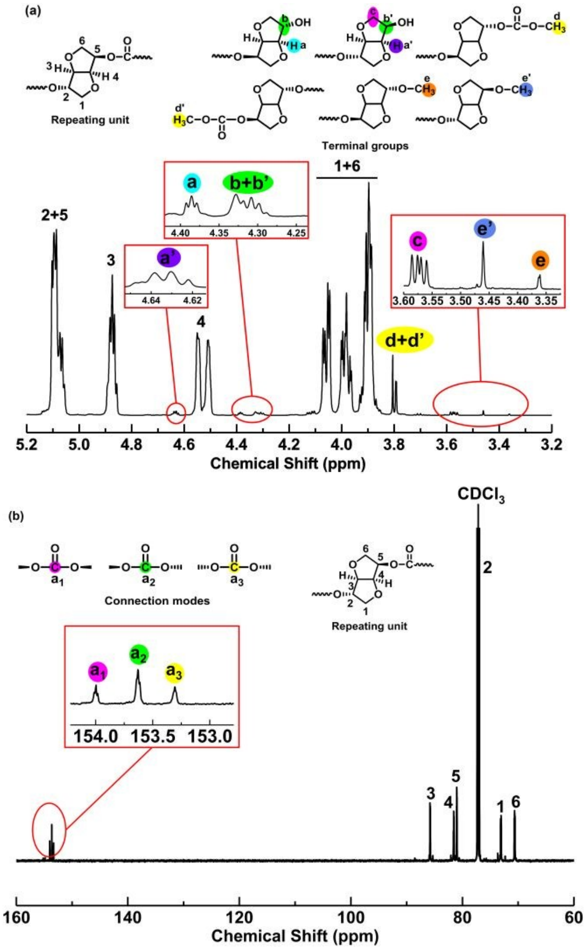

Fig. 5 Typical (a) ^1H NMR, and (b) ^{13}C NMR spectra of PIC prepared by [Bmim][4-I-Phen].

PIC structure characteristic and thermal properties

The structure characteristic of the synthesized PIC, catalyzed by [Bmim][4-I-Phen], was identified by ^1H NMR and ^{13}C NMR spectra (**Fig. 5**). From the ^1H NMR spectra, the proton signals of repeating unit and the terminal groups (-OH, -$OCOOCH_3$, and OCH_3) could be identified (**Fig. 5**a), which are completely in conformity with the previous literature.[19, 48] From proton signals of the terminal groups, the relative contents of various terminal groups could be determined.

Taking the effect of the polycondensation temperature as an example, the relative contents of terminal groups change obviously with the polycondensation temperature increasing. With the growth of molecular weight, the content of the terminal -OH increases and the amount of the terminal -$OCOOCH_3$ decreases (see **Table 3** and **Fig. S5**a). This is because the reactivity of the terminal -$OCOOCH_3$ is higher than that of the terminal -OH,[19] which leads to the terminal -$OCOOCH_3$ participating in polycondensation faster. Additionally, the reduction of the terminal -$OCOOCH_3$ amount is also related to the decarboxylation reaction of the -$OCOOCH_3$. As shown in **Fig. S6**, the decomposition temperatures at 5% weight loss ($T_{d-5\%}$) of DC and the PIC sample are about 180 °C and 313 °C, respectively, which means that the thermal stability of the PIC sample is higher than DC. The -$OCOOCH_3$ group turns to be stable at the end of long polymer chains. As a result, the content of -$OCOOCH_3$ is higher than that of -OCH_3 (**Table 3**). Due to the steric effect, the catalyst tends to attack the terminal *exo*-$OCOOCH_3$ easier than *endo*-$OCOOCH_3$, which leads to the *exo*-$OCOOCH_3$ to be consumed faster in the polycondensation reaction.[49] Meanwhile, the decarboxylation reaction of the terminal -$OCOOOCH_3$ occurs continuously at high polycondensation temperature. As a result, the ratio of the terminal *endo*-OCH_3/*exo*-OCH_3 is also always more than 1 (**Table 3**). We also discover that the ratio of the terminal *endo*-OH/*exo*-OH is always greater than 1.5, which could be attributed to the reason that the reactivity of the terminal *endo*-OH and *exo*-OH are non-identical.[10] This is similar to that the molar ratio of MC-1/MC-2 is always greater than 1 (**Table 1** and **2**).[37]

Table 3 The influence of polycondensation temperature on the relative contents of terminal groups of PIC

Entry	*PT* (°C)	Terminal groups (%)				
		-OH		-OCH_3		-$OCOOCH_3$
		exo	*endo*	*exo*	*endo*	
1	180	11.2	18.1	1.1	2.0	67.6
2	220	15.1	23.0	1.1	2.9	57.9
3	230	19.2	27.3	1.3	3.0	49.2
4	250	18.5	29.0	1.2	3.5	47.9
5	260	19.4	29.2	1.9	5.1	44.4
6	270	22.7	34.8	2.0	4.5	35.9
7	280	20.6	36.8	1.5	5.4	35.8

Reaction conditions: DMC/IS=7.5. Transesterification time: 3.5 h. Polycondensation time: 4 h. Cat. amount is 4.4×10^{-3} equiv. mol based on IS. The relative amount of terminal groups determined by ^1H NMR. The peak integration at δ 4.87 ppm in a repeating unit normalized to be 1. *PT* denotes polycondensation temperature. Total -OH = *exo*-OH + *endo*- OH; Total -OCH_3= *exo*- CH_3 + *endo*- OCH_3

As presented in **Fig. 5**b, the peaks of the ^{13}C NMR spectrum are in good accord with the carbon atoms of the PIC repeating unit.[14] The signals of carbonates in the PIC repeating units can be detected at 154.0, 153.6 and 153.3 ppm and the relative peak ratio of them is 1:2:1, which are attributed to the three connection modes of *endo-endo* (a_1), *endo-exo* (a_2) and *exo-exo* (a_3), respectively, suggesting PIC is a random polymer.[48]

Thermal properties are of great significance for the processing and application of polymers. The results mentioned above indicate that the influence of polycondensation temperature on PIC molecular weight is pronounced. Therefore, the thermal behaviors of these PIC samples were evaluated by the TGA and DSC analyses (**Fig. S7**). These PIC samples all display a one-step decomposition process (**Fig. S7**a). Moreover, the decomposition temperature of these PIC samples at 5% weight loss ($T_{d-5\%}$) and the thermostability of PIC can be improved with the increasing of PIC molecular weight (**Fig. S7**a, c and **Table S2**). For instance, $T_{d-5\%}$ enhances from 314 °C to 345 °C, with the M_n and M_w of PIC increasing from 11500 g/mol and 23800 g/mol to 24800 g/mol and 45100 g/mol. When the molecular weight is high enough, $T_{d-5\%}$ increases slowly.[19] The DSC curves reveal that these PIC samples are all amorphous state because of the absence of a single sharp molten peak. This result is perfectly consistent with the information provided by the ^{13}C NMR spectra. Glass transition temperature (T_g) of PIC also tends to be high with increasing PIC molecular weight, for example, the T_g enhances from 128 °C to 160 °C, with the M_n and M_w of PIC increasing from 11500 g/mol and 23800 g/mol to 28500 g/mol and 50300 g/mol (**Fig. S7**b-c and **Table S2**). These results indicate that PIC has excellent heat resistance.

Possible polymerization mechanism

Although a possible mechanism has been proposed for the transesterification reaction of isosorbide and DMC catalyzed by quaternary phosphonium phenolate ILs in our previous work,[37] the polymerization mechanism of the polycondensation stage is still unclear. Herein, a plausible anion-cation synergistic catalytic polymerization mechanism was proposed according to the previous report,[14, 37, 50] the experimental results, and DFT calculations (**Scheme 1**). As mentioned above, the polycondensation stage is mainly the transesterification reaction of methoxycarboxylation products (DC, MC-1, and MC-2) causing the formation of oligomers, and then the growing polymer chains are reacting with each other continuously. The ^1H NMR spectra were employed for investigating the interactions of methoxycarboxylation products with [Bmim][4-I-Phen]. The C-2 hydrogen of the [Bmim] cation was anticipated to accelerate electrophilic activation of DC through an H-bond, which was similar to the previous literature.[14, 50] This inference was supported by the C-2 hydrogen signal of the [Bmim] cation shifting from δ 9.30 to 9.15 ppm, when the molar ratio of [Bmim][4-I-Phen] to DC decreased from 1:0 to 1:4 (see **Fig. S8**a). Simultaneously, the proton of [4-I-Phen] anion moved from δ 7.03 and 6.17 ppm to 7.21 and 6.40 ppm (see **Fig. S8**b). This was contrary to the anticipated downfield shift of the C-2 hydrogen of [Bmim] cation and upfield shift of the hydrogen of [4-I-Phen] anion induced by forming a new H-bond, which ascribed to the strong intramolecular H-bonds in IL substituted by the relatively weak H-bonds of the C-2 hydrogen of [Bmim] cation with the oxygen of C=O in DC.[14, 51, 52] Additionally, the interactions of MC-1 or MC-2 with [Bmim][4-I-Phen] were also explored, respectively. As expected, the oxygen of C=O in MC-1 could also form an H-bond with the C-2 hydrogen of [Bmim]

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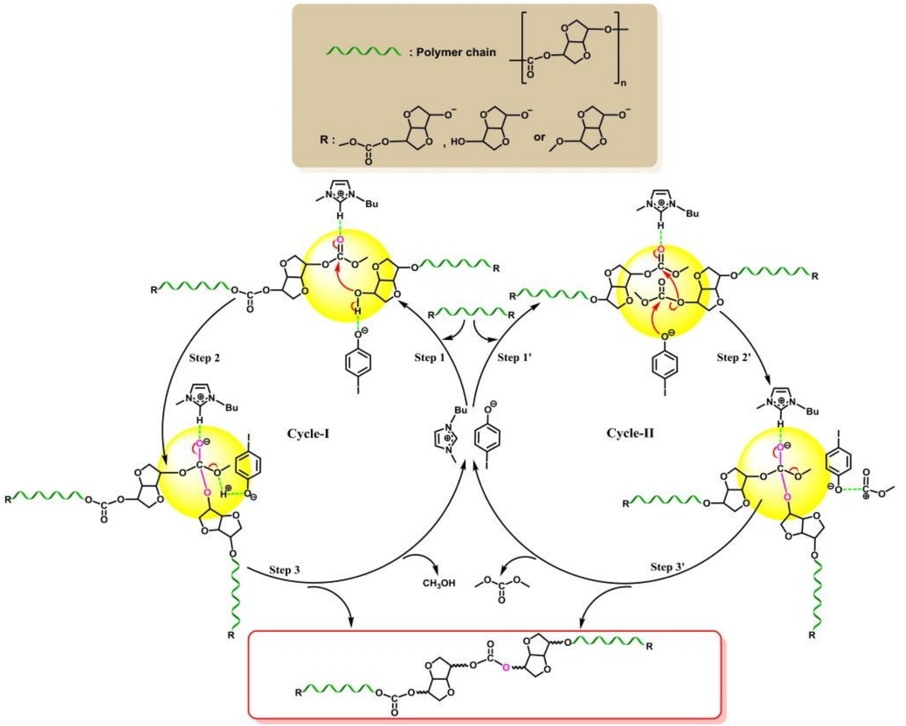
cation, which made carbon of C=O more susceptible to be attacked. This proposal was also verified by the C-2 hydrogen signal of the [Bmim] cation moving from δ 9.30 to 9.16 ppm, when the molar ratio of MC-1 to [Bmim][4-I-Phen] increased from 0:1 to 5:1 (see **Fig. S9**a). Meanwhile, the proton of [4-I-Phen] anion shifted from δ 7.03 and 6.17 ppm to 7.13 and 6.30 ppm (see **Fig. S9**b). Upon addition of [Bmim][4-I-Phen], the hydrogen signal of the *endo*-OH in MC-1 at δ 2.48 ppm could not be probed, suggesting the *endo*-OH in MC-1 could also be activated through forming an H-bond with the O of [4-I-Phen] (see **Fig. S10**a), which made the nucleophilicity of the oxygen of *endo*-OH increased.[37] Undoubtedly, there is a similar result for MC-2 (see **Fig. S10** and **S11**b).

Furthermore, the key intermediates of the early polymerization stage were successfully captured employing ESI-MS and MALDI-TOF-MS (**Fig. 6** and **Table S3-S4**). As



Scheme 1 Plausible melt polymerization mechanism of polycondensation stage.

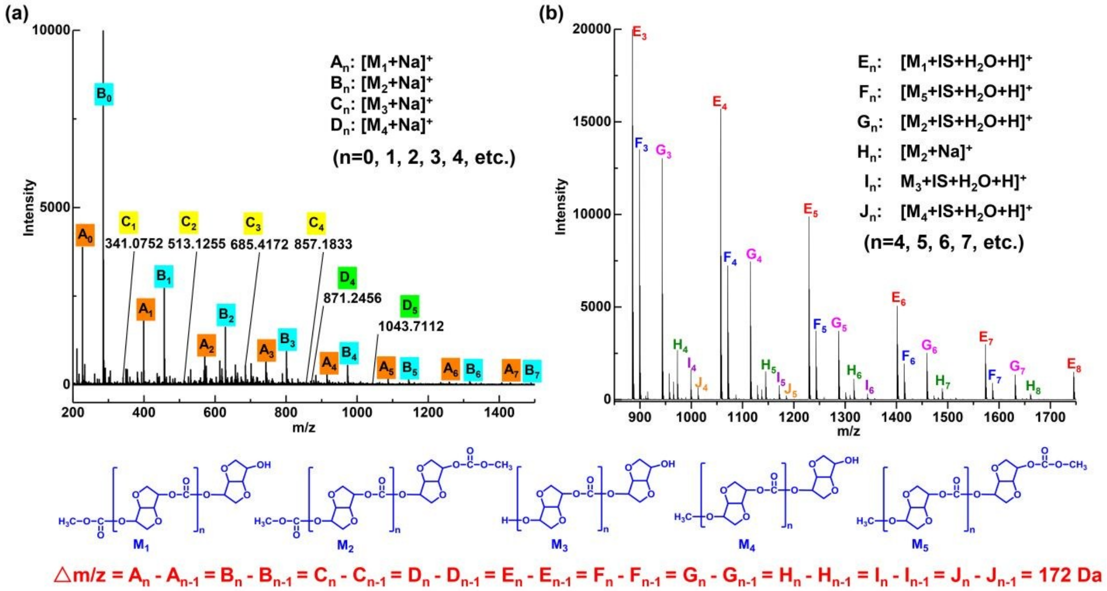


Fig. 6 (a) ESI-MS spectrum of PIC oligomers obtained at 160 °C; and (b) MALDI-TOF-MS spectrum of PIC oligomers obtained at 180 °C.

presented in **Fig. 6**a, the intervals of Δm/z =172 Da is the PIC repeating unit mass and the oligomers mainly feature Na^+ adducts. The end groups of -OH, -$OCOOCH_3$ and -OCH_3 could be detected, which are perfectly consistent with the above ^1H NMR results. We also analyzed the end group types of PIC oligomers using the analysis technique of MALDI-TOF-MS (**Fig. 6**b and **Table S4**). The oligomers mainly feature the adducts of isosorbide molecule, H_2O molecule, and H^+, which may be due to the residual isosorbide with strong moisture absorbability. The types of end groups are in full accord with the above results.

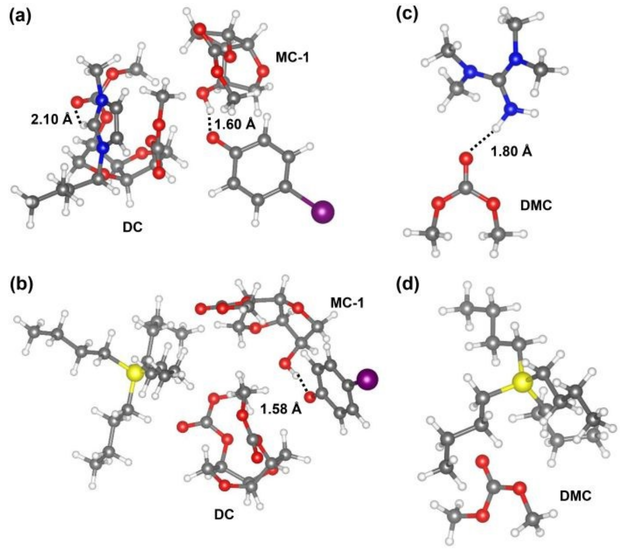


Fig. 7 Optimized structure of (a) [Bmim][4-I-Phen] interaction with DC and MC-1; (b) [P_{4444}][4-I-Phen] interaction with DC and MC-1; (c) [TMGH] cation interaction with DMC; (d) [P_{4444}] cation interaction with DMC. C atom (dark grey), H atom (light grey), O atom (red), N atom (blue), I atom (purple), P atom (yellow).

To further confirm the proposed polymerization mechanism, DFT calculations were implemented for investigating the interactions between IL and the transesterification products. The amount of DC is close to the total amount of MC-1 and MC-2 under the optimal conditions catalyzed by [Bmim][4-I-Phen]. Therefore, the interactions among [Bmim][4-I-Phen], DC and MC-1 were selected to geometry optimizations and energy calculations at the B3LYP/6-311+G* level using the Gaussian 09 program (see ESI†). As expected, the C-2 hydrogen of [Bmim] cation could form a weak H-bond (bond length: 2.10 Å) with the oxygen of C=O in DC and the [4-I-Phen] anion could form a strong H-bond (bond length: 1.60 Å) with the hydrogen of *endo*-OH in MC-1 (**Fig. 7**a) at the same time. By analogy, the polymer chain with the terminal -OH or terminal $OCOOCH_3$ also could form H-bonds with [Bmim][4-I-Phen]. As a result, the dual H-bonds are high-efficient to promote the polymerization progress. For comparison, the interactions among [P_{4444}][4-I-Phen], DC and MC-1 were also surveyed. There are only weak van der Waals forces between [P_{4444}] cation and the DC molecule, due to the long alkyl chain of [P_{4444}] cation resulting in the increase of steric hindrance. The [4-I-Phen] anion of [P_{4444}][4-I-Phen] still could form a strong H-bond (bond length: 1.58 Å) with the hydrogen of *endo*-OH in MC-1 (**Fig. 7**b). However, at the polymerization stage, the terminal -$OCOOCH_3$ proportion of the prepolymers is more than the terminal -OH, resulting in a greater probability of the terminal -$OCOOCH_3$ reacting with each other than that with -OH. At this point, the cation of IL plays a vital role in activating the terminal -$OCOOCH_3$ for the polymer chain growth, and the [Bmim] cation shows a better catalytic effect for the polymerization stage obviously, which is in accord with the abovementioned result of catalyst activity evaluation. To clarify the inferior catalytic activity of protic ILs, the interaction of DMC with [TMGH] cation or [P_{4444}] cation has also been investigated (**Fig. 7**c-d). As expected, the hydrogen atom in -NH_2 of [TMGH] cation could form a strong H-bond (bond length: 1.80 Å). There are only weak van der Waals forces between [P_{4444}] cation and the DMC molecule. In other words, the interactions between IL's anion or cation and substrates should keep a balance for its anion-cation synergistic catalysis. Therefore, the cation of phenolic ILs and substrate with a moderate H-bond strength is beneficial to synthesis PIC with a higher molecular weight.

Briefly, the mechanism of the polymerization stage (**Scheme 1**) could be described as follows: for cycle-I, initially, the oxygen of C=O in DC (MC-1 or MC-2) forms an H-bond with the C-2 hydrogen of [Bmim] cation, which makes the carbon of C=O in DC (MC-1 or MC-2) more easily to be attacked by the nucleophile. The hydrogen of -OH in MC-1 or MC-2 forms an H-bond with the oxygen of [4-I-Phen] anion, which makes the oxygen of -OH in MC-1 (MC-2) exhibit stronger nucleophilicity. As a consequence, the carbon of C=O in DC (MC-1 or MC-2) is attacked by the oxygen of -OH in MC-1 or MC-2 more easily (**Step 1**). With the electron transfer, an unstable complex is formed (**Step 2**). Subsequently, with the electron further transfer and the electrostatic interactions, the highly volatile methanol generates at high temperature and high vacuum more easily. Spontaneously, the oligomer produces and [Bmim][4-I-Phen] regenerates (**Step 3**). For cycle-II, first, the carbon of C=O in DC (MC-1 or MC-2) is activated through the formation of an H-bond between the oxygen of C=O in DC (MC-1 or MC-2) and the C-2 hydrogen of [Bmim] cation. In the another molecule of DC (MC-1 or MC-2), the carbon of C=O is activated by the nucleophile of [4-I-Phen] anion, which makes the oxygen of -$OCOOCH_3$ beside the furan ring could attack the pre-activated carbon of C=O in DC (MC-1 or MC-2) molecule more readily (**Step 1'**). With the electron transfer, an unstable complex is formed and the $COOCH_3$ positive ion is dissociated out (**Step 2'**). Afterward, with the electron further transfer and the electrostatic interactions, the highly volatile DMC generates more easily at high temperature and high vacuum.[53] Spontaneously, the oligomer produces and [Bmim][4-I-Phen] regenerates (**Step 3'**). Then, the terminal -OH and -$OCOOCH_3$ of oligomers repeat the above similar catalytic cycles (cycle-I and cycle-II), resulting in the increasing of PIC molecular weight. It should be mentioned that the terminal -$OCOOCH_3$ of polymer chain transforming into -OCH_3 can lead to this end of polymer chain stopping chain growth.

Conclusions

In summary, a strategy for PIC synthesis with adjustable molecular weight from the biorenewable isosorbide and the CO_2-derived DMC catalyzed by phenolic ILs has been developed. Noteworthily, the excellent tunability of phenolic IL's structure facilitated the H-bond strength of the cation and anion of IL with substrates to vary readily, causing different catalytic activity of IL catalysts. Concerning PIC synthesis, the catalytic activity of aprotic IL catalysts was superior to protic IL catalysts. Based on the ^{1}H NMR analysis and DFT calculations, we discovered the cation of phenolic ILs and substrate with a moderate H-bond strength was beneficial to synthesis PIC with a higher molecular weight. Additionally, an IL's anion-cation synergistic catalytic mechanism has been proposed, which reveals that nucleophile electrophile dual activation by H-bonds and charge-charge interactions in catalyzing PIC formation. Further significance of this study is that we provide a guidance of developing other IL catalysts for preparing higher molecular weight polycarbonates with the biorenewable building blocks, thus expediently creating various polymeric materials with desired properties.

Experimental

Synthesis of ILs

IL catalysts were synthesized through the acid-base neutralization reaction according to the previous literature.[54-56] For instance, synthesis of [DBUH][4-I-Phen], an ethanol solution of 4-I-Phen was dropwise added into an equimolar amount of DBU in an ice–water bath. Then the mixture was stirred for 48 h at room temperature. Subsequently, the solvent was removed by reduced pressure distillation and then the IL was vacuum-dried for 24 h at 55 ^{o}C.

Synthesis of PIC

PIC was prepared via the one-pot melt polymerization based on the previous study.[19] Isosorbide (10 g, 0.0684 mol), DMC (46.23 g, 0.5132 mol), and the catalyst (4.4×10^{-3} equiv. mol, based on IS) were mixed for the reaction. The transesterification reaction time was set as 3.5 h. At the polycondensation stage, the temperature was gradually heated to 180 ^{o}C and kept 1 h. Then, the reaction temperature and vacuum degree were increased gradually to 230 ^{o}C and less than 20 Pa, respectively. Meanwhile, the mixture was stirred continuously for 4 h at this temperature. Finally, the obtained powder was vacuum-dried at 55 ^{o}C for 24 h.

Characterization methods

^{1}H NMR and ^{13}C NMR spectra were collected in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) using a Bruker AVANCE III HD 600 MHz NMR spectrometer with tetramethylsilane (TMS) as the internal reference. Mass spectra data were recorded on a Bruker micrQTOF-Q II mass spectrometer or an Autoflex III Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) (Bruker, Germany) fitted with alpha-cyano-4-hydroxycinnamic acid (α-CCA) as the MALDI matrix. TG-MS data were collected on a Setaram Labsys Evo TGA 1600 thermal gravimetric analyzer and a mass spectrometer (MS, Tilon grp technology limited). The selectivities of carboxymethyl compounds were measured on a SHIMADZU LC-20AT HPLC with a differential refraction detector (RID) and an InertSustain C18 chromatographic column.[37] The molecular weights of PICs were identified using an Agilent PL-GPC 50 gel permeation chromatography (GPC). Polystyrene and the moving phase of dimethylformamide (DMF) were used to establish the calibration curve. Thermogravimetric Analysis (TGA) was performed on a Diamond TG/DTA6300 thermal analyzer with a heating rate of 10 ^{o}C/min under an N_2 atmosphere. The glass transition temperature was measured on a Mettler Toledo DSC 1 differential scanning calorimeter (DSC) with a heating rate of 10 ^{o}C/min and a nitrogen flow rate of 50 mL/min.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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Phenolic ionic liquid's structure is capable of being designed readily to control the molecular weight of isosorbide-derived polycarbonate.