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Designed synthetic strategy toward poly(isosorbide terephthalate) copolymers: A combination of temporary modification, transesterification, cyclization and polycondensation

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A designed synthetic strategy to overcome the low reactivity of isosorbide (Is) and terephthalic acid (TPA) is developed for the preparation of engineering polycondensates. This method contained substitution of unreactive end groups of Is and TPA by reacting with dimethyl carbonate and 1,2-alkanediol or 1,3-alkanediol respectively, followed by transesterification, cyclization of alkylene carbonate unit, and polycondensation. Is and TPA were temporarily linked by unstable alkylene carbonate unit and then underwent cyclization with the elimination of five- or six-membered cyclic carbonate at elevated temperature, leading to a family of poly(isosorbide carbonate-co-isosorbide terephthalate)s with high T_g (169−193 °C) and high number-average molecular weight (22700−28500 g mol^{-1}). The molecular structure of the copolymer was confirmed using ^{1}H, ^{13}C and 2D NMR techniques. GC-MS, ^{1}H NMR and ^{13}C NMR were used to monitor the molecular structure revolution during the combinatorial polymerization process and a proposed mechanism was provided. Furthermore, the structure−thermal properties relations study was also conducted on a range of relevant polyesters.

Introduction

Increasing attention is nowadays given to the bio-based monomers, targeting the improvement of polycondensates properties or the replacement of petrochemical monomers.[1] Of the typical bio-based monomers, isosorbide (Is) is well known for its attractive rigidity, chirality and non-toxicity. Moreover, it is the only carbohydrate based bicyclic monomer industrially available today. These advantages lead this diol to be considered as an ideal feedstock for the synthesis of engineering plastics and, in particular, for the modification of polyesters.

Is residue has been introduced to several large-scale aromatic polyesters, such as poly(ethylene terephthalate),[2, 3] poly(butylene terephthalate),[4] and also aliphatic polyesters,[5, 6] to increase their thermomechanical stability. However, due to the low reactivity and volatility of Is, high-molecular-weight polyesters containing large amounts of Is are hard to obtain.[7] Particularly, the homopolyester of Is and terephthalatic acid (TPA), poly(isosorbide terephthalate) (PIT), though supposed to have high glass transition temperature (T_g), has been found unsuitable to be synthesized by a conventional esterification process since the unreacted terephthalic acid groups in the final PIT is very high.[7, 8] Very recently Kricheldorf et al. also tested the melt transesterification of Is and dimethyl terephthalate at a maximum temperature of 250 °C with Ti(OBu)$_4$ as a catalyst.[9] The inherent viscosity of the resulting polyester was very low (0.11 dL g^{-1}).In most reported cases, terephthaloyl chloride or succinic chloride was used to prepare Is-based homo- or co-polyesters, either *via* melt polycondensation or preferably in solution.[5, 10] Storbeck et al.[11] performed solution polycondensation of Is and terephthaloyl dichloride, reporting the highest number-average molecular weight (M_n) of PIT of 25600 g mol^{-1} up to now. However, due to the complicated processes and the toxicity of the solvent, this method is not applicable for commercial polyester manufacture and it is not environmentally friendly. Yoon et al. used ethylene glycol (EG) as an effective chain linker in the polymerization system of TPA, 1,4-cyclohexane dimethanol, and Is, which yielded an M_n in the range of 19100 to 25400 g mol^{-1}.[3] However, compared with PIT, the incorporation of EG resulted in a severe decrease to the T_g of the copolymer.

In this paper, we develop a well-designed approach to address the low reactivity problem between Is and TPA by establishing an alkylene carbonate unit as a temporary chain linker and present a new series of high number-molecular-weight PIT copolymers, namely poly(isosorbide carbonate-co-isosorbide terephthalate)s (PICTs) (Scheme 1), which have T_g values closed to PIT. To improve the reactivity of Is and TPA, dimethyl carbonate (DMC) and EG were introduced to synthesize their derivatives by substitution of the end groups with more reactive functionalities, which rendered the connection of Is and TPA by building ethylene carbonate unit during

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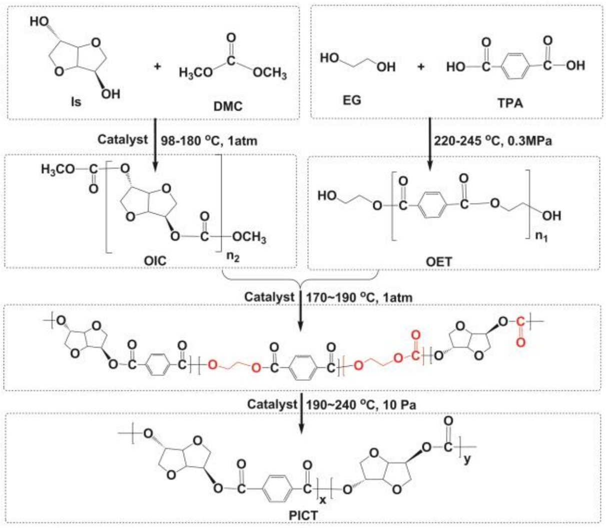
† Electronic Supplementary Information (ESI) available: [^{1}H NMR spectra of OIC and OET; GC-MS and ^{1}H NMR results of the volatile products removed from polycondensation system of $PI_{80}CT_{20}$; ^{1}H NMR spectra of oligo(1,3-propylene terephthalate)(OPT1) and oligo(1,2-propylene terephthalate)(OPT2); ^{1}H and ^{13}C NMR spectra of $PI_{80}CT_{20}$ samples prepared by the polymerization of OIC with OPT1 and OPT2 respectively; ^{13}C NMR spectra of $PI_{80}CT_{20}$ samples from OPT1 and OPT2 removed from various reaction times; the second DSC heating traces of PIC and PICTs]. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthesis of PICT via a two-step melt polymerization of Is, DMC, TPA, and EG

the subsequent transesterification. Generally, alkylene carbonate units, especially those with five or six atoms in main chain, have a negative effect on the usefulness of polymers,[12] since they are thermally unstable and readily undergo thermal decomposition by elimination of five- or six- membered cyclic carbonate.[13] However, in this paper the ethylene carbonate unit was supposed to act as an effective temporary chain linker between Is and TPA. At elevated temperature, cyclization of ethylene carbonate unit easily occurred by the elimination of cyclic ethylene carbonate (EC), leading to the formation of the target isosorbide terephthalate (IT) units.

The resulting PICTs have tunable T_g values from 169 to 193 °C and high molecular weight values from 22700 to 28500 g mol^{-1}. To have a clear understanding of the combinatorial polymerization process, GC-MS, ^{1}H NMR and ^{13}C NMR were used to monitor the molecular structure revolution and a proposed mechanism was provided. Furthermore, in order to have insight into the effects that Is have on polymer properties, the structure–thermal properties relations study was also conducted on a range of relevant polymers.

Experimental Section

Materials

Is was received as a gift from Roquette Chemical Co. (China). Lithium acetylacetonate (LiAcac, 99.5%) and ethylene glycol antimony were purchased from Alfa Aesar. DMC was a commercial product from Shandong Shida Shenghua Chemical Co. (China). EG and TPA were purchased from Beijing Chemical Reagents Corp. (China).

General methods

The intrinsic viscosity of the PICTs was measured in the mixed solvent of phenol and 1,1,2,2-tetrachloroethane (1:1) using an Ubbelohde viscometer thermostated at 25±0.1 °C The M_n and M_w and polydispersities (M_w/M_n) were estimated by gel permeation chromatography (GPC) performing on a Waters 1515 HPLC pump and a refractive index detector (Waters 2414) at 35 °C. Chloroform was used as the eluent (1.0 mL/min), and polystyrene standards were used to establish a calibration curve. ^{1}H NMR and ^{13}C NMR spectra were obtained on a Bruker DMX-400 NMR spectrometer. Deuterated chloroform was used as the solvent. Tetramethylsilane was used as an internal standard and as a reference for chemical shifts. The T_g of the polymers was measured by differential scanning calorimeter (DSC) on a DSC Q2000 apparatus from TA Instruments at a heating rate of 10 °C/min with nitrogen gas purging (50 mL/min). Thermogravimetric measurements were performed on a Perkin-Elmer TGA1 analyzer in a nitrogen atmosphere with a heating rate of 10 °C min^{-1} from 50 to 550 °C. The samples were carefully predried at 120 °C for 10 h in a vacuum before analysis.

Homopolycarbonate (PIC) synthesis

Poly(isosorbide carbonate) (PIC) was synthesized according to the reported procedure.[14] Typically, Is (29.22 g, 0.20 mol), DMC (135 g, 1.5 mol), and LiAcac (29.2 mg, 0.1 wt % based on Is) were charged into a 250 mL four-necked round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, reflux condenser, thermometer and feeding funnel under nitrogen atmosphere. In the transesterification stage, the reaction mixture was stirred continuously for 6 h at 98 °C. Then the temperature was gradually increased to 180 °C and after maintained at this temperature for 1 h to completely distill the methanol and unreacted DMC, methyl carbonate terminated oligo(isosorbide carbonate) (OIC) was obtained. In the polycondensation stage, the reaction temperature was increased to 240 °C gradually and vacuum (10 Pa) was applied stepwise and maintained for 5 h. Finally, the pressure was returned to atmospheric pressure using N_2 to prevent oxidative degradation. The resulting PIC sample was removed from the reactor and used for characterization without any purification.

Copolymer synthesis

The synthesis procedure of PICTs is shown in Scheme 1. A series of PICTs were prepared and they were described by the abbreviation PI_xCT_y, where x and y subscripts indicated the relative molar feed percentages of Is and TPA, respectively. A typical copolymerization procedure for $PI_{80}CT_{20}$ was as follows. In the transesterification stage, methyl carbonate terminated OIC and hydroxyl terminated oligo(ethylene terephthalate) (OET) were obtained respectively. OIC was synthesized according to the transesterification stage of homopolymerization described above. As for OET, TPA (8.3 g, 0.05 mol), EG (6.8 g, 0.11 mol) were charged into a 100 mL micro reactor. The reactor was heated to 220 °C under a vapor pressure of 0.3 MPa and subsequently the water produced from esterification reaction was distilled out within 2 h with increasing temperature (240-245 °C). Then the mixture was cooling to 180 °C at which temperature the excessive EG was effused under a fairly low vacuum for 30 min and the OET was obtained. Then using ethylene glycol antimony as catalyst (0.005 g), two oligomers (OET and OIC) were mixed at 170 °C for 30 min at room pressure and then maintained at 190 °C for 1.5 h under vacuum to guarantee the complete elimination of ethylene carbonate. Then it gradually increased to 240 °C in 3 h under a high vacuum (10 Pa). After maintained at this temperature for 1 h, the $PI_{80}CT_{20}$ copolymer was obtained and used for characterization without any purification.

Results and Discussion

Synthesis and Molecular Characterization of the PICT copolymer

It has been frequently reported that the two secondary hydroxyl groups of Is are relatively unreactive and chemically nonequivalent, which often leads to polymers with unsatisfactory molecular weights.[5, 15] The endo-hydroxyl group is usually less reactive under melt polymerization conditions, which is thought to be due to steric

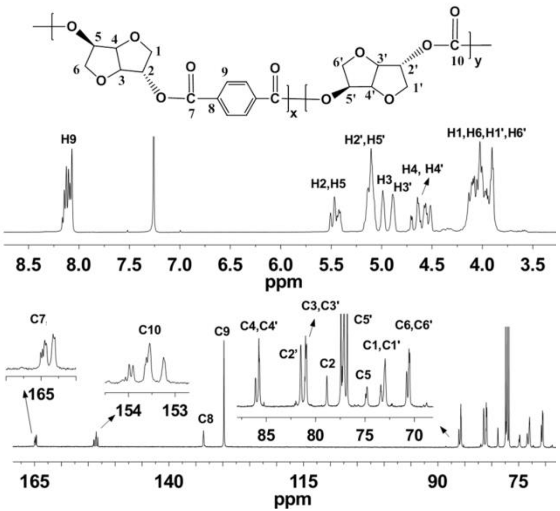


Fig. 1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of $PI_{80}CT_{20}$

hindrance and/or the intramolecular hydrogen bonding formed between the endo-hydroxyl proton and the oxygen atom in the neighboring ring.[15] To overcome these drawbacks, OIC was firstly synthesized by the transesterification of Is with an excess of DMC according to our previous report.[14] Transforming the secondary hydroxyl groups into more reactive methyl carbonate functionalities, this derivative of Is shows much higher reactivity and has been used as an intermediate for the synthesis of a series of high-molecular-weight Is-based polymers.[14, 16] Meanwhile, during this stage, OET was also prepared by esterification reaction of TPA in excess of EG. The structures of OIC and OET are confirmed by ^{1}H NMR in Fig. 1S (Supporting Information (SI)). Negligible signals attributing to the hydroxyl groups of Is and the carboxyl groups of TPA are observed, indicating the complete substitution of them by methyl carbonate groups and ethylene glycol groups respectively.

In the following process, the mixture of OIC and OET was stirred at 170 °C for 30 min to establish the ethylene carbonate linkage between Is and terephthalate moieties by the transesterification between the reactive groups of OIC and OET (discussed later in detail). Subsequently, cyclization of ethylene carbonate unit was executed under a high vacuum to form IT unit. Since the ethylene carbonate unit also readily undergoes thermal degradation with the formation of ether groups in the copolymer by elimination of CO_2[17] at high temperatures, the reaction temperature of cyclization was raised and maintained at 190 °C for 1.5 h to render the complete removal of EC, and then gradually increased to 240 °C for polycondensation. As the incorporation of terephthalate could increase the melt viscosity of the resulting polymers, longer reaction times were used in the synthesis of copolymers with higher terephthalate contents to facilitate the complete elimination of the byproduct. Using these designed conditions, copolymers with high molecular weight were obtained and their compositions and characteristics are listed in Table 1.

The resulting PICT copolymers were obtained with intrinsic viscosities between 0.49 and 0.55 dL g^{-1}, number-average molecular weights confined in the 22,700−28,500 g mol^{-1} interval, and dispersities in the 1.48−1.59 range. It is worth noting that the molecular weights of the PICT copolymers slightly decay with the increasing feed ratio of TPA. Two reasons may be responsible for this trend. Firstly, since the copolymer chain has a stiff and immobile conformation, high content of terephthalate increases the melt viscosity of polymers, which impedes the removal of the byproducts and growth of the molecular weights in the later stage of polycondensation. Secondly, high feed ratio of TPA means high content of primary hydroxyl end in the initial system. These primary hydroxyl groups could readily promote the alcoholysis of OIC and lead to the emerging of the less reactive Is end groups, which would have negative effects on the ultimate molecular weight of the copolymer (this will be discussed later in detail).

The chemical structure and composition of newly synthesized PICT copolymer samples were evaluated using ^{1}H NMR and ^{13}C NMR spectra. The ^{1}H NMR spectra corroborated the chemical structure of the copolymers with all signals being correctly assigned to the different protons contained in their repeating units. Representative NMR spectra of $PI_{80}CT_{20}$ are shown in Fig. 1.The peaks of the Is moiety in IT unit at δ 4.08, 5.47, 4.99, 4.71, 5.41, and 4.02 ppm were assigned to hydrogen atoms 1, 2, 3, 4, 5, 6, respectively, while those in isosorbide carbonate (IC) unit at δ 4.05, 5.10, 4.88, 4.56, 5.09, and 3.90 ppm were assigned to hydrogen atoms 1', 2', 3', 4', 5',

Table 1 Characteristics of PIC and PICTs synthesized with various Is/T ratios.

Sample code [a]	Is/T [b]	IsC/IsT [b]	[η] [c]	M_n [d]	M_w [d]	M_w/M_n [d]	T_g [e] (°C)
PIC	100/0	100/0	0.56	28,800	43,200	1.51	167
$PI_{95}CT_5$	94/6	94/6	0.55	28,500	42,200	1.48	169
$PI_{90}CT_{10}$	89/11	88/12	0.53	25,300	38,100	1.50	171
$PI_{80}CT_{20}$	77/23	70/30	0.54	25,700	40,900	1.59	177
$PI_{70}CT_{30}$	67/33	51/49	0.51	24,100	37,600	1.55	182
$PI_{60}CT_{40}$	56/44	22/78	0.49	22,700	34,100	1.50	193
$PI_{80}CT_{20}$ [f]	78/22	72/28	0.47	20,900	32,000	1.53	173
$PI_{80}CT_{20}$ [g]	77/23	70/30	0.51	23,500	36,900	1.57	175

[a] Sample codes denote the feed ratio of Is to TPA. [b] The composition ratio determined by ^{1}H NMR results. [c] Intrinsic viscosity (dL g^{-1}) measured in 1,1,2,2-tetrachloroethane (1:1) at 25 °C. [d] M_n and M_w determined by GPC. [e] T_g measured by DSC. [f] using 1,2-propylene diol instead of EG. [g] using 1,3-propylene diol instead of EG.

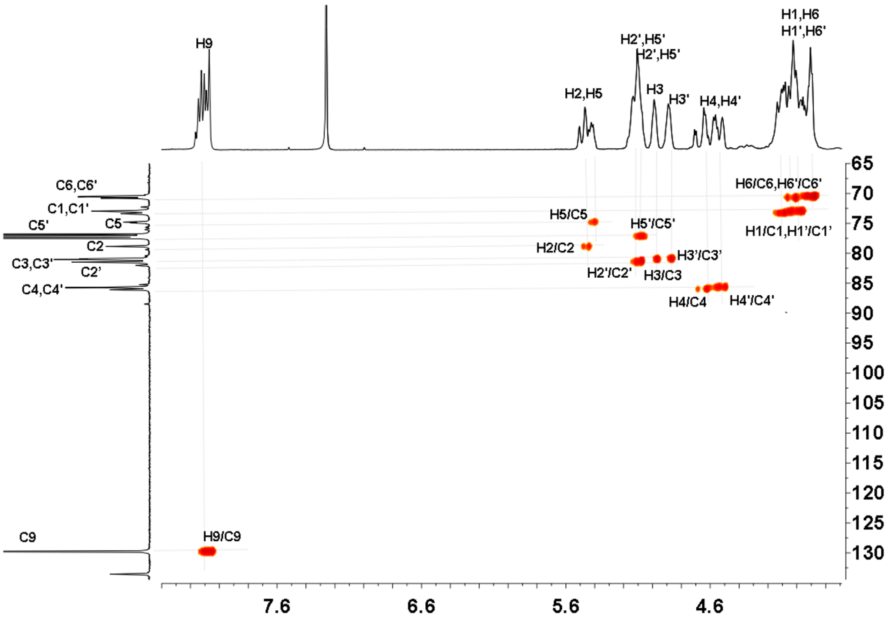


Fig. 2 Correlation spectrum (COSY) of $PI_{80}CT_{20}$

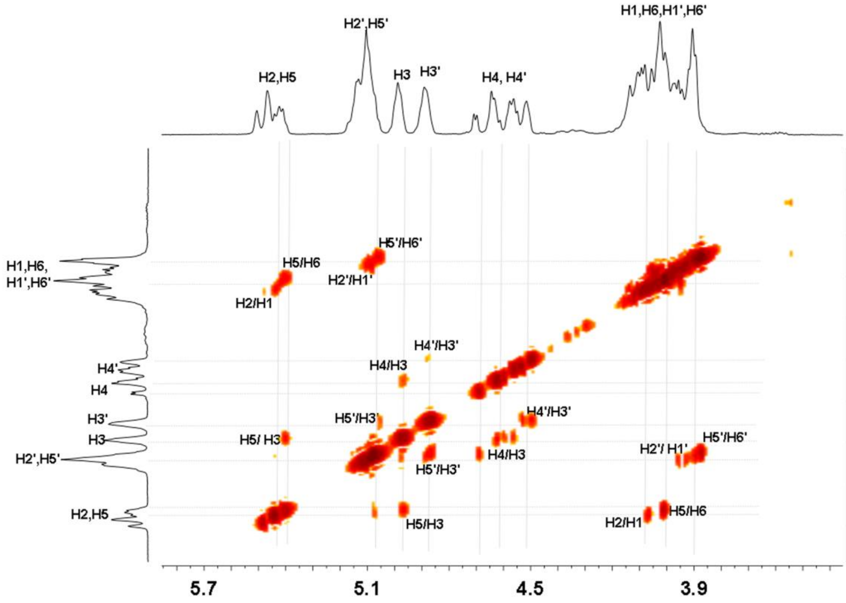


Fig. 3 Heteronuclear single-quantum correlation spectrum (HSQC) of $PI_{80}CT_{20}$

6', respectively. Integration of the proton signals arising from terephthalate moieties led to the proportions of IT unit, while the proportion of IC unit was calculated by subtracting the proportions of IT from that of the Is moiety. Data provided by this analysis are given in Table 1, showing that all the PICTs had composition very close to those of their corresponding feeds.

The peak assignments were confirmed by two-dimensional (2D) NMR spectroscopy. Various NMR techniques, including correlation spectroscopy (COSY) and heteronuclear single-quantum correlation spectroscopy (HSQC), were used to determine the sequence of specific protons and carbon atoms in PICTs. Fig. 2 shows the COSY spectrum of $PI_{80}CT_{20}$, identifying the presence of each moiety in units. The existence of Is moiety in IT unit was confirmed by cross peaks H2/H1, H4/H3, H5/H3, and H5/H6 in the COSY spectrum, whereas the existence of Is moiety in IC unit was confirmed by cross peaks H2'/H1', H4'/H3', H5'/H3', and H5'/H6'. Because of the V-shaped structure of Is and its two five-membered rings, correlation signals H2/H3 and H2'/H3' were not detected. However, cross peak H5/H3 and H5'/H3' were observed in the spectrum, as they were in the same plane. On the basis of the above results, the proton signals were then assigned to the corresponding ^{13}C signals in the HSQC spectrum shown in Fig. 3. The peaks in the ^{13}C NMR spectrum of $PI_{80}CT_{20}$ at δ 73.4, 78.8, 80.9, 86.0, 74.8, 70.9 ppm and δ 73.0, 81.5, 80.8, 85.7, 76.8, 70.4 ppm were assigned to carbon atoms 1, 2, 3, 4, 5, 6 and 1', 2', 3', 4', 5', 6', respectively. These assignment were confirmed by correlation signals H1/C1, H2/C2, H3/C3, H4/C4, H5/C5, H6/C6 and H1'/C1', H2'/C2', H3'/C3', H4'/C4', H5'/C5', H6'/C6' at δ 4.08/ δ 73.4, 5.47/78.8, 4.99/80.9, 4.71/86.0, 5.41/74.8, 4.02/70.9 and 4.05/73.0, 5.10/81.5, 4.88/80.8, 4.56/85.7, 5.09/76.8, 3.90/70.4 ppm, respectively, in the HSQC spectrum.

Proposed reaction mechanism for combinatorial polymerization process

To make a clear understanding of the combinatorial process and the role that ethylene carbonate unit plays in the preparation of PICTs, the polymerization process of OIC and OET was monitored by ^{1}H NMR and ^{13}C NMR spectroscopy on $PI_{80}CT_{20}$ samples removed at various times as the reaction progressed (Fig. 4). When dealing with the transesterification of OIC and OET, a general question is the detailed mechanism by which they may take place: by direct exchange between inner functional groups (i.e., located inside the chain)(called here inner-inner, Scheme 2a), or by attack of outer functional groups (i.e., reactive chain ends) on inner groups (called here outer-inner, Scheme 2b) or on outer groups (called here outer-outer, Scheme 2c), as shown in Scheme 2.[17]

In this system, since both OET and OIC contain reactive chain ends, the initial exchange reaction is most likely to occur by attack of the hydroxyl groups of OET (sequence B') on the carbonate groups inside or outside of OIC (alcoholysis, outer-inner in Scheme 2b or outer-outer in shown and 2c). This is confirmed by the NMR results after 30 min of reaction (Fig. 4a and 4b), in which the signals 2a, 3a and 4a assigned to sequence B' disappears and are substituted by

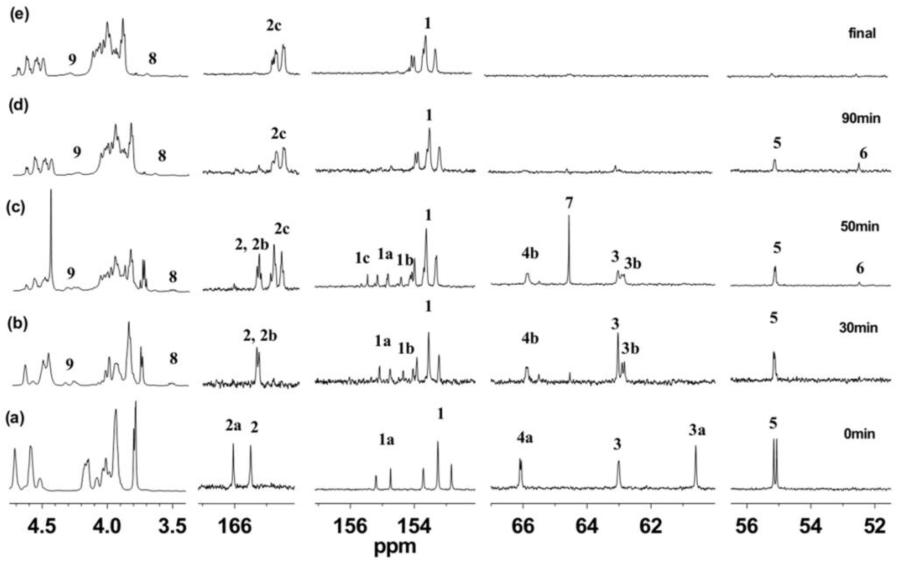
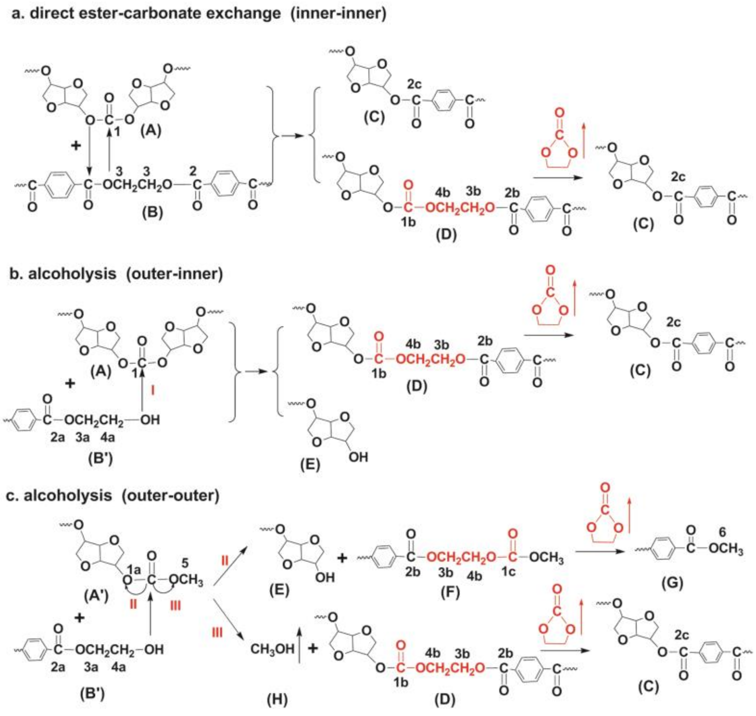
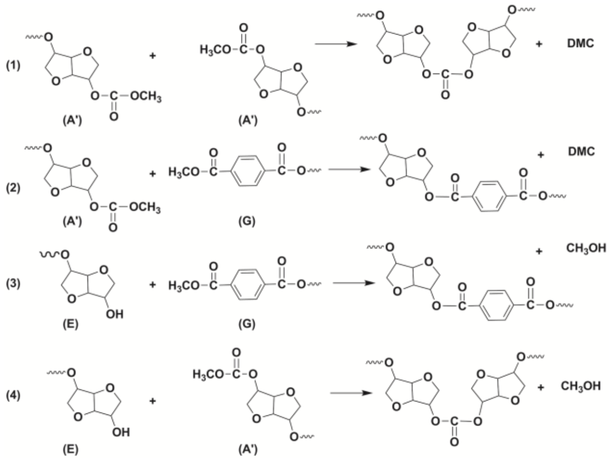


Fig.4 ^{1}H NMR and ^{13}C NMR spectra of $PI_{80}CT_{20}$ samples removed from various reaction times



Scheme 2 Proposed exchange reactions between OIC and OET



Scheme 3. Various reactions in the polycondensation process

the peaks 2b, 3b and 4b assigned to sequence D (Scheme 2b and 2c), while the intensity of the peak 3 corresponding to sequence B shows little changes (inner-inner, Scheme 2a). There are three alcoholysis approaches (path I, II and III in Scheme 2b and 2c) that may occur during the reaction. This is inferred from the ^{1}H NMR spectrum that the new peaks 8 and 9 due to the protons of Is end groups (sequence E) (path I or path II) appear and from the GC-MS result (Fig. 2S, SI) that a new peak assigned to methanol (path III) appears. Generally, these approaches are almost equally likely to occur, as the environments around the carbonyl groups are similar. However, from the results calculated by the ^{1}H NMR spectrum (Table 2), the fraction of the sequence B' consumed by path III (Scheme 2c) is much higher than that consumed by path I and II (Scheme 2b, Scheme 2c), indicating that the sequence B' is more likely reacted with sequence A' by path III in Scheme 2c. This is owing to the constant removal of CH_3OH byproduct of path III accelerating the forward reaction. It is worth noting that, after the transesterification of OIC and OET, ethylene carbonate unit is established and acts as a linker between Is and terephthalate moieties (sequence D).

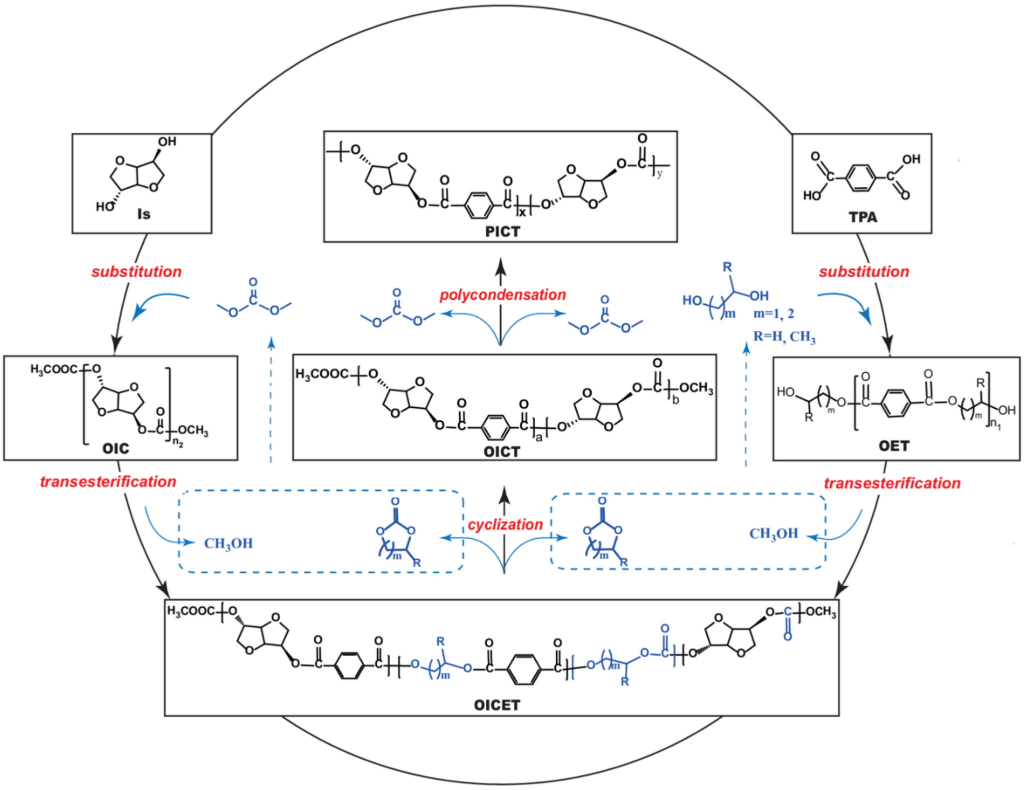
After 50 min of reaction, due to the elevated temperature (190 ^oC) and the low thermal stability of ethylene carbonate unit, cyclization of ethylene carbonate unit in sequences D and F begins, which leads to the formation of target IT unit (Sequence C) and sequence G in the copolymer. This could be deduced from the decreasing intensity of the peaks 3b and 4b (sequence D), the appearance of peaks 2b, 6 and 7 corresponding to the carbonyl carbon of sequence C, the methyl carbon of sequence F and the alkyl carbon of cyclic ethylene carbonate (EC) respectively. Meanwhile, it can be observed that the intensity of peak 3 at 63.0 ppm assigned to sequence B is decreased (Fig. 4c), indicating that the inner-inner exchange reactions between sequences A and B occur simultaneously during this stage (Scheme 3a). By this direct ester-carbonate exchange sequences D are generated and then they would undergo thermal decomposition by the elimination of cyclic EC as mentioned above. The cyclic EC could be removed from the system under high vacuum, which in turn accelerates the inner-inner exchange reactions between sequences A and B towards the formation of sequence C and D. Since the fraction of carbonate moieties is higher than ethylene glycol in the system (calculated by the feed ratio of OIC and OET), this circle could repeat itself by constant removal of EC until the sequence B is totally consumed. This is confirmed by the NMR results after 90 min of reaction (Fig. 4d), in which the peaks in the range of 62-66 ppm (Peaks 3, 3b, 4b and 7) corresponding to the ethylene and the peaks 1b and 1c due to the sequences D and F almost disappear.

After 90 min of reaction (transesterification and cyclization), from the ^{1}H NMR spectrum, the copolymer is essentially constituted of five components (sequences A, A', C, E, and G, Scheme 3): sequences A and C located inside the copolymer chain and sequences A', E and G as the chain ends. For the subsequent process, the outer-inner transesterification does not occur easily, since the methyl carbonate (A') cannot attack carbonyl carbon within the polymer chain and the relatively low reactivity and large steric hindrance of Is impedes the attack of its end hydroxyl group to the inside chain. Although the methyl carboxylate end groups of G could react with carbonate groups of sequence A by interchange reactions,[18] the products are sequences C and A' without formation of any new sequences. For such reasons, the polycondensation may preferentially occur at the end groups (Scheme 3). Due to sequences A' and G possess active chain ends, the reactions (1) + (2) readily occur, which would result in a rapid growth of the polymer chain. As shown in Fig. 4d and 4e, the main difference between NMR spectra of the sample at 90 min and the final sample is the decreasing intensity of peak 5 and 6 corresponding to the end groups of A' and G respectively. For reactions (3) + (4), since the sequence E possesses less reactive end groups of Is, the rate of the reactions is slow and they are the rate controlling steps. Therefore the content of less reactive Is end groups is the determining factor and would have negative effects on the ultimate molecular weight of the copolymer. This also explains why the molecular weights of the PICT copolymers slightly decay with the increasing feed ratio of TPA in Table 1, as the increasing feed ratio of TPA leads to the increasing content of less reactive end groups of Is in the copolymer (Table 2).

Table 2 Various ratios related to sequence B' from ^{1}H NMR

Sample code	$f_{A'}/f_{B'}$ [a]	$f_A/f_{B'}$ [b]	$f_E/f_{B'}$ [c] (%)	P_{III} [d] (%)
$PI_{95}CT_5$	10.0	25.0	7	93
$PI_{90}CT_{10}$	4.5	13.0	10	90
$PI_{80}CT_{20}$	2.0	5.6	16	84
$PI_{70}CT_{30}$	1.2	3.2	21	79
$PI_{60}CT_{40}$	0.8	2.1	34	66

[a] The ratio of the fraction of sequence A' to that of sequence B'.
[b] The ratio of the fraction of sequence A to that of sequence B'.
[c] The ratio of the fraction of sequence E to that of sequence B'.
[d] The percentage of sequence B' reacted by path III



Scheme 4 Proposed mechanism for the synthesis of PICT

Deduced from the above analysis, we put forward a proposed mechanism for the combinatorial process, as shown in Scheme 4. First, Is and TPA are reacted with DMC and EG respectively, giving to OIC and OET oligomers. Second, a hydroxyl group of OET attacks the carbonyl carbon atom on the chain end of OIC via transesterification, generating OICET with ethylene carbonate unit as a chain linker between Is and terephthalate moieties. Third, due to the low thermal stability of the ethylene carbonate unit, OICET would undergo thermal decomposition by the elimination of cyclic EC, leading to the formation of oligomer (OICT) with a majority of reactive methyl carbonate end groups. Finally, the methyl carbonate end groups can be readily reacted by generating the highly volatile DMC via polycondensation, leading to high molecular weight PICT copolymer. During the whole process, the ethylene carbonate unit acts as an effective temporary chain linker between TPA and Is. Moreover, since the byproduct cyclic EC can readily proceed a transesterification reaction with another byproduct methanol, reverting back to EG and DMC with mighty small side reactions,[19, 20] this route can be regarded as a green and sustainable method for the preparation of PICT.

To examine the universality of the above strategy, other alkylene diols, such as 1,2-propanediol or 1,3-propanediol, were also used to replace EG for the synthesis of $PI_{80}CT_{20}$ (Fig. 5S and 6S, SI). Similarly, the alkylene carbonate units formed during the transesterification proved to be effective as temporary chain linkers and could be readily removed as five- or six-membered cyclic carbonates under high vacuum. The structure of the resulting copolymers was confirmed by ^{1}H and ^{13}C NMR spectra and they have M_n and T_g values closed to that of $PI_{80}CT_{20}$ discussed above (Table 1). When 1,4-butanediol was used, butylene carbonate unit was hard to be eliminated as cyclic carbonate in the reaction temperature range due to its relative higher thermal stability. Thus 1,4-butanediol could not be used for the synthesis of PICT. [16]

Thermal properties

The effect of the structure and composition on the thermal behavior of the resulting copolymers is an issue of prime importance for the evaluation of these copolymers as potential thermoplastic materials. Therefore DSC and TGA were used to evaluate the basic thermal properties of the copolymers and the fundamental data are listed in Table 3.

Fig. 9S shows the second heating DSC scans of all the samples, carried out at 10 °C min^{-1} after a 5-min isotherm at 240 °C to remove the thermal history. At this scan rate, due to the bulky and twisted structure of Is which assists in hindering the crystallization

Table 3 Thermal properties of the PICTs and PIC

Sample code	T_g (°C)^a	T_d^o (°C)^b	$T_{d\text{-}max1}$ (°C)^c	$T_{d\text{-}max2}$ (°C)^c	W^{res}(%)^d
PIC	167	353	374	--	2.9
$PI_{95}CT_5$	169	362	388	--	3.2
$PI_{90}CT_{10}$	171	364	388	--	5.0
$PI_{80}CT_{20}$	177	367	395	431	7.4
$PI_{70}CT_{30}$	182	374	402	432	8.2
$PI_{60}CT_{40}$	193	405	429	--	12.7

[a] Glass transition temperatures measured using DSC. [b] Initial decomposition temperature obtained from the onset temperature at the end of the initial plateau region using TGA.. [c] Temperature of the maximum rate of decomposition estimated from the derivative line of the TGA thermogram. [d] Residual weight%

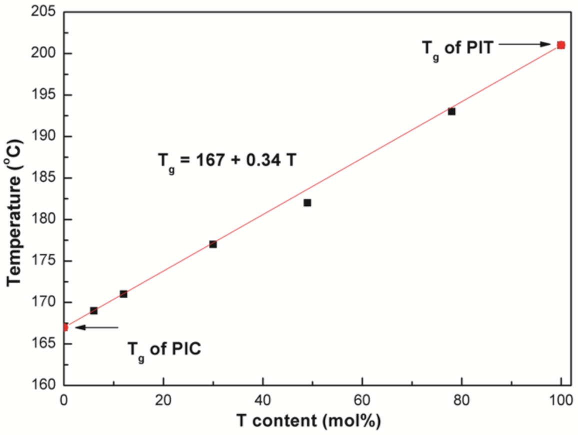


Fig. 5 Relationship between the terephthalate (T) content and T_g of the PICTs

of the polymer chain[21], none of the PICTs shows the ability to crystallize. Therefore all the PICTs have perfectly amorphous characteristics and a unique and well-identified glass transition is observed in all systems. Despite the negative effect of Is on crystallization, its rigid structure nature endows the resulting copolymers with high T_g values. As shown in Table 3, a remarkable feature of the PICTs is that they have T_g values in the range of 169 to 193 °C, which is much higher than that of bisphenol A polycarbonate and can meet the requirement for highly thermal resistance products. Furthermore, due to the invariance of the terephthalate content in the PICTs, the T_g of the PICT samples is almost directly proportional to the terephthalate content, with minimum and maximum values corresponding to their respective PIC homopolycarbonate and PIT homopolyesters. As shown in Fig. 5, the estimated T_g value of PIT is about 201 °C, which is closed to the reported result with same M_n.[11]

The thermal stability of the PICTs was comparatively examined by TGA taking PIC as the reference. TGA traces of the PICTs are depicted in Fig. 6, and thermal data provided by this analysis are presented in Table 3. The samples were dried at 120 °C for 10 h in a vacuum before analysis to allow an exact evaluation of the temperatures of initial decomposition (T_d^o) and the maximum rate of decomposition (T_d^{max}).

Like the results for T_g, the decomposition of the PICTs samples shows a great relationship with the composition, as shown in Table 3. PIC can be thermally stable up to 350 °C, while the PICTs start to decompose above 360 °C with T_d^{max} values steadily increasing with the content of terephthalate units. The same trend is also observed for the residual weight, and these results are in accordance with our previous report which demonstrated that PIT had higher thermal stability than PIC.[16] Moreover, as shown in Fig. 6(b), with the increasing content of terephthalate units, the thermal degradation mechanism of the copolymers ranges from one main step to two steps and finally back to one main step. This is also caused by the increasing content of terephthalate units, which leads to the evolution of decomposition of the PICTs from degradation of carbonate component to degradation of ester component. The temperatures of the two maximal decomposition rates at approximately 390 °C and 430 °C are mainly attributed to weight loss of IC and IT units respectively. Generally, a T_d^{max} of 390-430 °C is sufficiently high to enable the general application for PICTs in the plastics industry. Furthermore, the valuable conclusion drawn from this thermogravimetric study is that, instead of reducing their thermal stability, the insertion of terephthalate units to the copolymers contributes to a significant increase in their decomposition temperatures, which could be useful from the perspective of recycling and reusing the polymer waste to prevent or reduce environmental pollution.

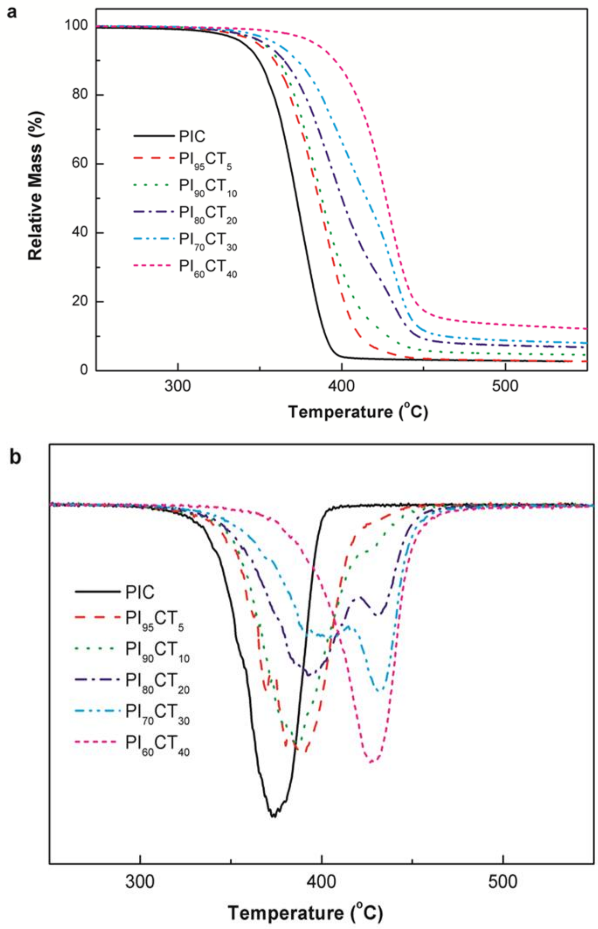


Fig. 6 TGA curves of (a) PIC and PICTs and (b) the derivatives of remaining weight versus temperature

Conclusions

For the first time, a well-designed strategy is demonstrated to solve synthetic problems associated with melt polymerization of Is and TPA due to their low reactivity. The strategy involves substitution of unreactive end groups of Is and TPA, followed by transesterification, cyclization of alkylene carbonate unit, and polycondensation. Alkylene carbonate unit acts as an effective temporary chain linker between Is and TPA and its subsequent elimination leads to a unique family of poly(isosorbide terephthalate) copolymers with very high thermal resistance and high molecular weight. All the PICTs had a really high T_g which increased linearly with the terephthalate content, allowing for the fine-tuning of T_g over a wide range. Moreover, concerning the difficulty for the synthesis of polycondensates from less reactive diols and diacids, this synthetic strategy provides an alternative choice for polymerization methodology and might have potential application for sophisticated polymer synthesis.

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Designed synthetic strategy toward poly(isosorbide terephthalate) copolymers: A combination of temporary modification, transesterification, cyclization and polycondensation

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After a combination of temporary modification, transesterification, cyclization and polycondensation, a series of high-M_n and high-T_g poly(isosorbide terephthalate) copolymers were synthesized