Synthesis of Poly(isopropenylphenoxy propylene carbonate) and Its Facile Side-Chain Functionalization into Hydroxy-Polyurethanes

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ABSTRACT: 4-Isopropenyl phenol (**4-IPP**) is a versatile dual functional intermediate that can be prepared readily from bisphenol-A (**BPA**). Through etherification with epichlorohydrin to the phenolic group of **4-IPP**, it can be converted into 4-isopropenyl phenyl glycidyl ether (**IPGE**). On further reaction with carbon dioxide in the presence of tetra-n-butyl ammonium bromide (**TBAB**) as the catalyst, **IPGE** was transformed into 4-isopropenylphenoxy propylene carbonate (**IPPC**) in 90% yield. Cationic polymerization of **IPPC** with strong acid such as trifluoromethanesulfonic acid or boron trifluoride diethyl etherate as the catalyst at −40 °C gave a linear poly(isopropenylphenoxy propylene carbonate), poly(**IPPC**), with multicyclic carbonate groups substituted uniformly at the side-chains of the polymer. The cyclic carbonate groups of poly(**IPPC**) were further reacted with different aliphatic amines and diamines resulting in formation of polymers with hydroxy-polyurethane on side-chains. Syntheses, characterizations of poly(**IPPC**) and its conversion into hydroxy-polyurethane crosslinked polymers were presented. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 802–808

KEYWORDS: cationic polymerization; cyclic carbonate; non-isocyanate route; polyurethanes; side-chained polyurethane; synthesis; thermosetting polymers

INTRODUCTION The non-isocyanate route (NIR) for production of polyurethanes (PUs) using ring-opening reaction of polycyclic carbonates with diamines has been touted as one of the most potentially useful green chemistry routes to PUs in recent years.[1–6] This ring-opening reaction involving a cyclic carbonate with aliphatic amines will result in β-hydroxyls as side-groups on urethane main chains, and thus this route has been applied to synthesize hydrophilic PUs.[7,8] However, this NIR process generally produces PUs with low molecular weights and low T_g which have hampered its usefulness in applications. Recently, several research groups have tried further modification of side-chained hydroxyl group after ring-opening of cyclic carbonate,[9–11] while others have used tri-functional-cyclic carbonate reacting with diamines to overcome the performance deficiencies.[12] However, the quality of films or properties of polymers still have not been satisfactory, and hence this NIR strategy still needs for further improvements.

Synthesis of highly functionalized cyclic carbonate prepolymers through polymerization of vinyl-monomers bearing cyclic carbonates have been reported as yet another NIR-strategy of making crosslinked polyurethanes as means of enhancing physical properties. In 1993, G. Chen et al.[8] prepared PU-hydrogel beads for immobilization of enzymes by reacting poly(vinylene carbonate) with difunctional Jeff-amines. More recently, several other groups carried out homo and copolymerized of acrylic[13] and styrenic intermediates[14] possessing cyclic carbonates. They did result in obtaining highly functionalized polycarbonates for curing by diamines. Through these NIR approaches, highly crossliked PU-products did show improved solvent resistance and thermal stability.

Previously, Ito et al.[15] prepared 4-isopropenylphenyl ether derivatives starting from BPA and they polymerized the isopropenyl groups into a linear polymer by cationic polymerization. Subsequently, Higashimura and coworkers[16] succeeded in making poly(isopropenyl phenyl glycidyl ether), poly(**IPGE**), under strong acids such as hydroiodic acid (**HI**) as the initiator of choice at low-temperature conditions. However, no synthesis of poly(**IPGE**) through its glycidyl groups have been reported so far. In this study, we followed the same synthetic routes from BPA to make **IPGE** but we have further extended the synthesis to 4-isopropenylphenoxy propylene carbonate (**IPPC**) and poly(**IPPC**) (Scheme 1).

Additional Supporting Information may be found in the online version of this article.

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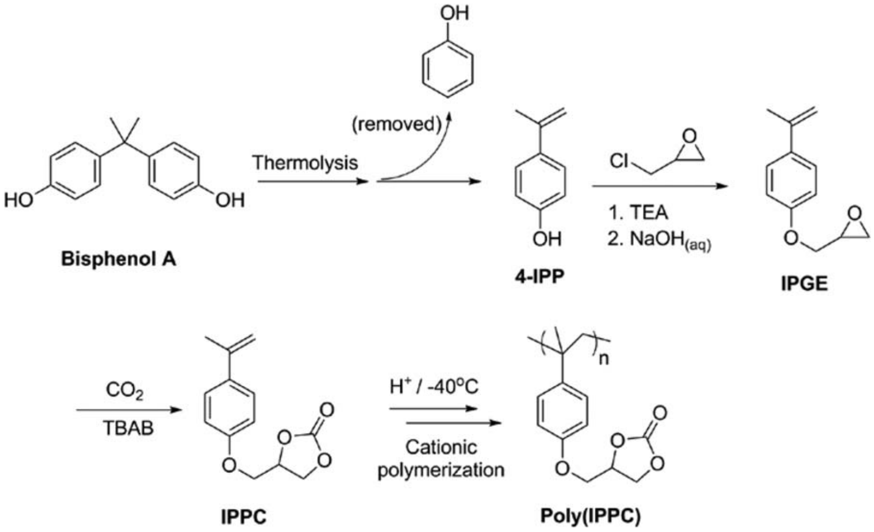
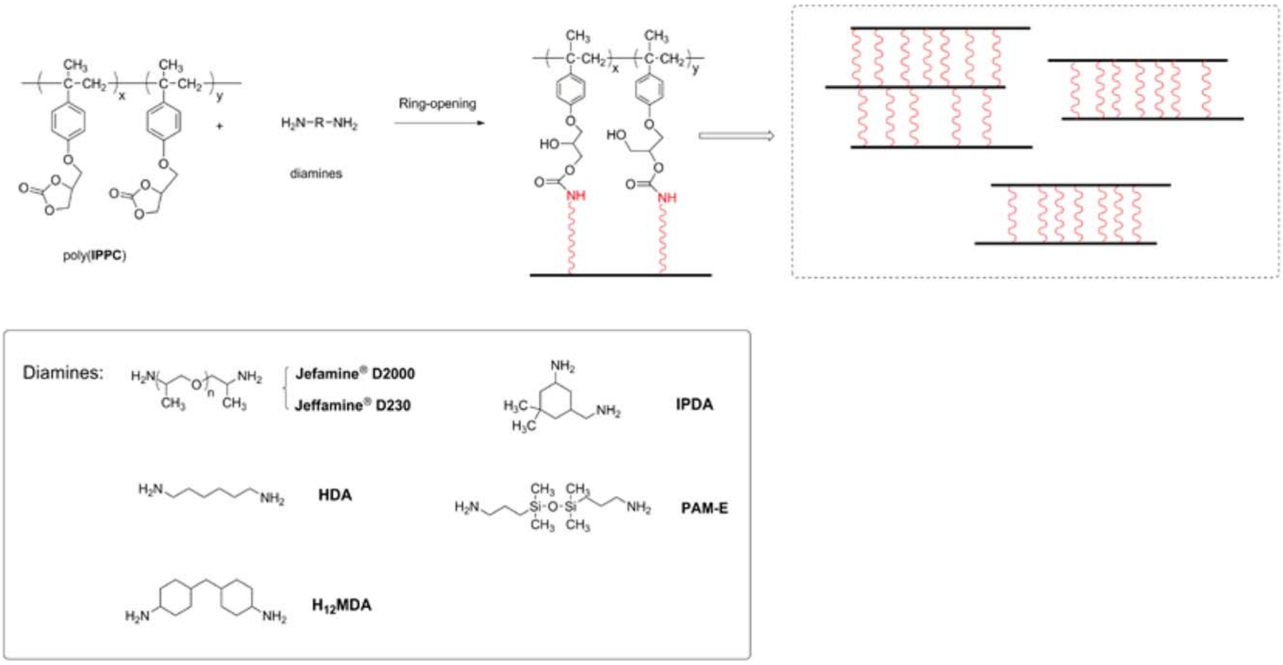


SCHEME 1 Synthesis and polymerization of **IPPC** and poly(**IPPC**) from bisphenol A.

Through the highly functionalized crystalline polymer predecessor, poly**(IPPC)**, as our key PU hard-component raw material in this report, PU films were prepared readily with interesting characteristics. (Scheme 2).

EXPERIMENTAL

Materials. Bisphenol-A, (+/−)epichlorohydrin, methanesulfonic acid, trifluoromethanesulfonic acid, boron trifluoride diethyl etherate and tetra-*n*-butylammonium bromide (TBAB) were purchased from Alfa Aesar. Isophorondiamine (IPDA), and 1,6-hexanediamine (HDA) were purchased from Acros. 4,4'-Methylene biscyclohexylamine (H_{12}MDA) was purchased from Aldrich. Jeffamine M600 (polyether amine, $M_w = 600$ g/mol), Jeffamine D230 (polyether diamines, $M_w = 230$ g/mol), D2000 (polyether diamines, $M_w = 2000$ g/mol), and 1,3-Bis(3-aminopropyl)−1,1,3,3-tetramethyldisiloxane (PAM-E, $M_w = 260$ g/mol) were supplied from Great Eastern Resins Industrial of Taichung, Taiwan. Acetonitrile was purchased from Aencore and purified by distillation under reduced pressure over calcium hydride (Acros) and stored over molecular sieves (water-content is lower than 100 ppm before each polymerization reaction). All other solvents in the experiments were commercial products used without further purification.



SCHEME 2 Ring-opening reaction of poly(IPPC) with high ratio diamines curing. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 1 The Results of Polymerization of IPPC

Entry	Initiator Type	$[M_0]$ mmol/L	[I] mmol/L	M_n ($\times 10^4$)[a]	M_w ($\times 10^4$)[a]	PDI	T_m (°C)[b]	T_g (°C)[b]	Yield
1	CF_3SO_3H	0.45	0.012	1.15	2.50	2.2	184	170	83%
2	CF_3SO_3H	0.45	0.016	0.84	1.88	2.3	194	156	90%
3	CF_3SO_3H	0.45	0.022	0.47	1.40	3.0	193	152	88%
4	CF_3SO_3H	0.45	0.025	0.65	0.95	1.5	190	152	80%
5	CH_3SO_3H	0.45	0.024	0.33	0.93	2.8	180	132	44%
6	CH_3SO_3H	0.45	0.035	0.34	0.83	2.5	185	n/a	26%
7	CH_3SO_3H	0.45	0.050	0.44	1.03	2.3	193	135	31%
8	CH_3SO_3H	0.45	0.076	0.33	0.83	2.6	183	140	27%
9	BF_3OEt_2	0.45	0.015	1.59	3.55	2.2	n/a	n/a	83%
10	BF_3OEt_2	0.45	0.017	1.22	2.97	2.4	n/a	n/a	88%
11	BF_3OEt_2	0.45	0.023	1.52	2.34	1.5	190	n/a	85%
12	BF_3OEt_2	0.45	0.029	0.83	1.79	2.2	189	139	52%

[a] Measured by GPC under NMP solvent system.

[b] Measured by DSC at a heat rate of 10 °C/min.

Preparation of 4-Isopropenyl Phenol from Bisphenol A

The preparation of 4-isopropenyl phenol was according to the Schnell method[17] and our previous modified procedure.[18] BPA (0.5 mol) and traced $NaOH_{(s)}$ (0.2 g) was added to a reaction flask, and then the pyrolysis was carried out at 230–250 °C under 15 mmHg. The resulting mixtures of 4-isopropenyl phenol and phenol were collected in a receiving flask. Then, traced $NaOH_{(s)}$ (0.2 g) was again added to the mixed products, and the mixture immediately underwent a fractionation at 150 °C under 20 mmHg to remove phenol. This was followed by heating the remaining IPP and IPP oligomers at temperatures of 230–250 °C under the 15 mmHg to produce IPP. Yields of 4-IPP were between 85–92% stored in anisole as the IPP stabilized solution to prevent its oligomerization.

Preparation of 4-Isopropenylphenoxy Propylene Carbonate (IPPC)

The solution of 4-IPP (0.12 mol 4-IPP in 30 mL anisole), epichlorohydrin (0.24 mol) and triethylene amine (0.012 mol) was added into a 250 mL three-neck flask.[19] The reaction solution was heated and stirred vigorously at 90 °C under dry nitrogen atmosphere. After 1 h, the reaction was cooled to 40 °C, and then 5*N* $NaOH_{(aq)}$ (25.2 mL) was slowly added to the solution. The mixture was further stirred for 2 h at 40 °C. The organic layers were washed with 2*N* $NaOH_{(aq)}$ and DI-water until the solution became neutral. The excess epichlorohydrin and anisole were removed by fractionation under reduced pressure. Finally, 17.0 g (75%) of the IPP-glycidyl ether (**IPGE**) was obtained by recrystallization using ethanol. Mp= 25–26 °C (lit.[19] 44–45 °C).

Then, **IPGE** (0.025 mol), toluene (60 mL) and TBAB (0.01 mol) were added into a three-neck flask, and the mixture was then purged with carbon dioxide gas at 80 °C for 8 h while being monitored by FTIR. The reaction was terminated when the epoxy absorption at 910 cm^{-1} disappeared completely. The catalyst was then removed by extraction and the product was isolated by crystallization using ethanol. The white solid product (5.27 g; 90%) was isolated. Mp= 107–108 °C. FTIR (KBr): $v = 1797$ (C=O of carbonate), 1621, 1606 (C=C of isopropenyl) cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6, δ): 2.07 (s, 3H, CH_3), 4.19–4.40 (m, 2H, CH_2), 4.65 (d, 2H, OCH_2), 4.98(s, 1H, C=CH^a), 5.15 (m, 1H, CH), 5.32 (s, 1H, C=CH^b), 6.91–6.94 (m, 2H, Ar—H), 7.43–7.45 (m, 2H, Ar—H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 21.49, 65.95, 67.50, 74.76, 110.91, 114.35, 126.49, 133.49, 141.70, 154.76, 157.47. HRMS (EI, *m/z*): $[M+H]^+$ Calcd for $C_{13}H_{14}O_4$, 234.0892; Found, 234.0895.

Cationic Polymerization of IPPC

The 2.00 g (8.5 mmol) of **IPPC** was dissolved in acetonitrile (20 mL), and the solution was added into a 50 mL round-bottom flask with magnetic stirrer under a nitrogen purge. The resulting mixtures were then slowly cooled by acetone/liquid nitrogen bath and kept at −40 °C. CF_3SO_3H was injected into the reaction solution by a syringe, and the solution was stirred for 2 h. Finally, the solution was poured into an ethanol containing dilute ammonium hydroxide. The precipitated polymer product was collected by filtration (see Table 1 for the weights of acid added and resulting yield).

Curing Reaction of Poly(IPPC) with Amines via Ring-Opening of Cyclic Carbonate

Poly(**IPPC**) (0.5 g; $M_w = 23{,}000$ g/mol) and diamines [~0.8 equivalnet relative to poly(IPPC)] were dissolved in 4.5 g of *N*-methyl-2-pyrrolidone (NMP). The solution of the reaction mixture was heated at 100–130 °C for 12 h. Then, the resulting solution was poured into a circle Teflon mold of 4.0 cm (Diameter) in size, which was placed into an oven at 60 °C for about 24 hours to remove NMP. The melt-product was shaped into PU film to get the final films for testing.

Characterization

Fourier transform infrared (FTIR) were recorded over the range from 4000–450 cm^{-1} using a Perkin-Elmer Spectrum One FTIR spectrometer. NMR spectra were recorded on a Varian Inova 400 NMR in DMSO-d_6 and the chemical shifts were calibrated by setting the chemical shift of DMSO-d_6 at 2.49 ppm. Melting points were measured using a BÜCHI B-540 melting-point apparatus operated at a heating rate at raising rate of 3 °C/min. Electron ionization (EI) mass spectra were recorded using a Finnigan/Thermo Quest MAT 95XL apparatus. Differential scanning calorimetry (DSC) scans were obtained using a Seiko SII model SSC/6200 under a nitrogen atmosphere at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was performed with a Seiko SII model SSC/5200 at a heating rate of 10 °C/min under nitrogen atmosphere. Gel permeation chromatography (GPC) was conducted on a Viscotek^{TM} MBLMW-3078 utilizing MBHMW-3078 column and utilizing N-methyl-2-pyrrolidone (NMP) as mobile phase at rate of 1.0 mL/min under 40 °C. The molecular weight of polymer products was calibrated by using polystyrene as the standard. Mechanical properties of the product were performed on a Universal Shimatsu HT-8504 by a 20.0 × 10.0 mm^2 sample film with a testing rate set at 100 mm/min.

RESULTS AND DISCUSSION

Synthesis and Characterization of IPPC

4-Isopropenylphenoxy propylene carbonate (**IPPC)** was prepared from 4-isopropenyl phenyl glycidyl ether (**IPGE**) according to the CO_2-carbonylation method reported by Heinrich et al.[19] In the first step of our synthetic sequence, 4-IPP and epichlorohydrin were mixed in anisole in the presence of triethylamine as the catalyst, and the solution was stirred at 90 °C for converting phenolic group into the epoxide intermediate. After 1h, the reaction was then cooled to 40 °C followed by treatment with 5N $NaOH_{(aq)}$ to effect the ring-closure in formation of glycidyl ether intermediate. After the isolation and recrystallization of the products in methanol, **IPGE** was isolated in 75% yield (Mp = 25–26 °C). This melting point was lower than previous literature data (lit.[19] 44–45 °C) and the dis-agreement may be due to (+/−) epichlorohydrin was used as the epoxidation agent in our run as the starting material, which was different from the Heinrich's method[19]. After that, **IPGE** was treated with CO_2 in toluene solution using TBAB[20,21] as catalyst, and the carbonylation further transformed **IPGE** into the corresponding carbonate at 80 °C under the monitoring of FTIR (Fig. 1). The isolated yield of **IPPC** was 90% (Mp = 107–108 °C) and its chemical structure was firmly established by its ^{1}H-NMR (Supporting Information Fig. S1) and HRMS analyses.

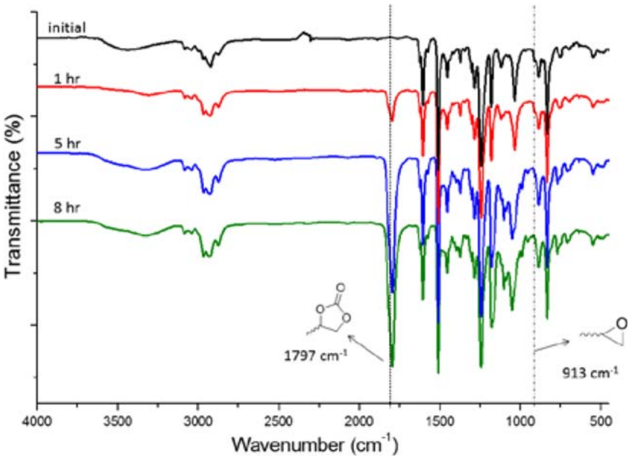


FIGURE 1 FTIR monitoring conversion of epoxy into cyclic carbonate functions from **IPGE** by CO_2-carbonylation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis, Characterization and End-Group Stabilization of Poly(IPPC)

In our cationic polymerization experiments of **IPPC**, both methylene chloride and toluene used in previous Higashimura's synthesis of poly(**IPGE**)[16] as the solvents were found to be unsatisfactory in our case because of their poor solubility for **IPPC** under the low-temperature condition. It was found that the polymerization of **IPPC** is best done in acetonitrile at −40 °C. Furthermore, highly strong acid initiators seemed essential in the cationic polymerization of **IPPC**. Based on effectiveness and selectivity of the polymerization, trifluoromethanesulfonic acid has been found to be the best acid initiator among all initiators tried so far. Trifluoromethanesulfonic acid gave 83–90% isolated yields of homopolymer at −40 °C in 1.5 h. As ^{1}H-NMR spectrum of poly(**IPPC**) shown in Supporting Information Figure S2-a, all original vinylic protons of poly(**IPPC**) disappeared. All proton chemical shifts of the new product in the NMR spectrum could be assigned as indicated in Supporting Information Figure S2. The molecular weight of final poly(**IPPC**) were found to be ranging from 8000 to 35,000 g/mol (with DP of 1.5–3.0), which appear to be determined by the amount of trifluoromethanesulfonic acid added. The plots of the polymer's M_w versus catalyst concentration were exhibited in Figure 2, where a straight line could be drawn only in the runs of trifluoromethanesulfonic acid. In boron trifluoride diethyl etherate and methanesulfonic acid initiated polymerizations both showed comparatively lower efficiency of initiators and thus giving higher molecular weights of poly(**IPPC**) but their polymer products seem to be less structurally regioselective as those from trifluoromethansulfonic acid as indicated in molecular weight data (Supporting Information Fig. S3) with thermal analysis data shown in Table 1. The most optimal concentration of trifluoromethanesulfonic acid was found at 0.012 mmol/L (Run 1, Table 1) since it gave high molecular weights of the product in 1.5 h and highest glass transition temperature (T_g) of poly(**IPPC**) at 170 °C (M_w = 25,000) among all runs. In Run 5 to 8 initiated by methanesulfonic aicd, the T_g has been recorded as low as 130 °C which seems correlated to its small M_w (8000–10,000). In TGA analysis, the 5% weight loss (T_d) of most poly(**IPPC**)s were found to be at around 260 °C.

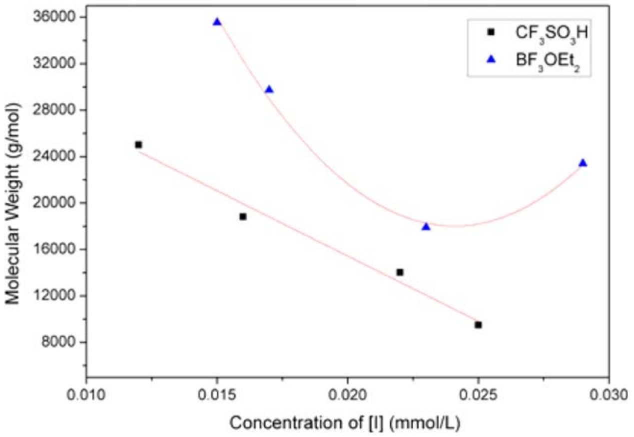


FIGURE 2 Correlation between molecular weights of poly **(IPPC)s** with catalyst concentrations [I]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Under closer inspection of ^{1}H-NMR spectra of all prepared poly(**IPPC**), the polymers showed several tiny NMR peaks of olefin protons located at 4.99, 5.33, and 4.88 ppm in the NMR, which were assigned to the terminal exo- and endo-protons, respectively[16] (Supporting Information Fig. S2-b). In order to stabilize the polymers from further chemical complications such as acid initiated disproportionations,[18] cumene hydroperoxide (80% solution) treatment of poly(**IPPC**) in the presence of $CuCl_2$ was carried out to effectively oxidize these terminal groups leading to new carbonyl functions as the terminal group.[22] Without this oxidation treatment, poly (**IPPC**) has been observed to undergo acid-catalyzed equilibrations resulting in lower molecular weight distributions.

Amination of Poly(IPPC) for Its Side-Chain Functionalization into Hydroxy-Polyurethanes

In an attempt to introduce β-hydroxy-polyurethane side-chains into poly(**IPPC**) via amination of its cyclic carbonate groups, we added aliphatic mono- or diamines as the reagents in various equivalent ratios relative to cyclic carbonate of poly(**IPPC**) to promote ring-opening reactions. These functionalizations were done primarily on the poly(**IPPC**) with $M_w = 23{,}000$ g/mol, the trifluoromethanesulfonic acid initiated polymers (entry 2, Table 1).

As a typical run, 0.5g of poly(**IPPC**) dissolved in 3.5 g NMP was treated with 1.03 g of Jeffamine M600, a mono-polypropylene etheramine of 600 g/mol molecular-weight. The relative molar equivalent of poly(**IPPC**) to Jeffamine M600 is calculated to be approximately 1/0.8 and the reaction was done at 130 °C with vigorously stirred for 12 h. As shown in Figure 3, the IR spectra indicated that the intensity of the initial carbonate carbonyl absorption at 1799 cm^{-1} reduced substantially after 6 h, while the new carbonyl groups of urethane intensified with the new absorption at 1710 cm^{-1}. In Figure 4, the GPC spectra of the resulting adduct concurrently showed a distinct molecular-weight increase.

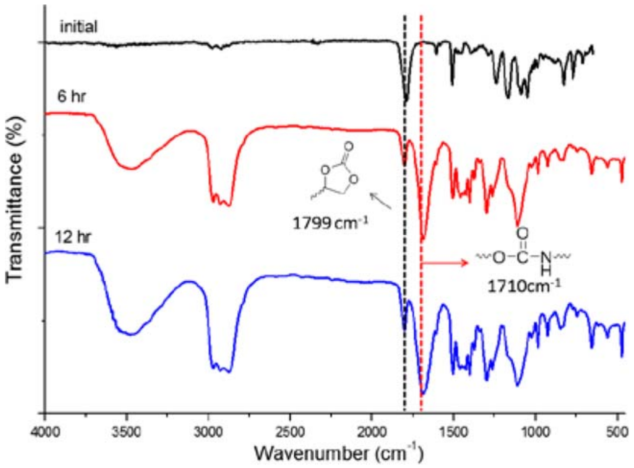


FIGURE 3 FTIR of ring-opening reaction of cyclic carbonate from poly(**IPPC**) by Jeffamine M600. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In a similar thermoset PU synthesis, poly(**IPPC**) dissolved in NMP, was added to polypropylene ether diamine of 2000 molecular weight (Jeffamine D-2000) with the relative ratio of 1/0.8 equivalent weight at 130 °C. After the resulting solution was vigorous stirred for 12 h, the solution was poured into a Teflon mold for the solvent removal under reduced pressure. By doing so, a highly crosslinked PU with new urethane absorption at 1710 cm^{-1} in FTIR spectra was obtained. The product, **NIPU-A** (Table 2), exhibited as a light yellow opaque film with only slight cyclic carbonate and urea-absorption detected in its FTIR spectrum. (Fig. 5). Another interesting phenomenon was observed in the run where the relative equivalent ratios of Jeffamine D2000 to poly(**IPPC**) was decreased to 1/0.6 or lower, respectively. In all those runs, insoluble crosslinked polymeric products formed rapidly. For example, **NIPU-B** (Table 2) was obtained in the run with 50% equivalent ratio of Jeffamine D2000

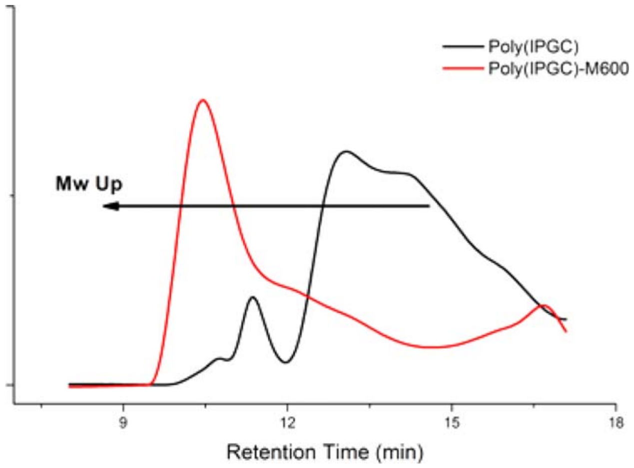


FIGURE 4 GPC analysis of poly(**IPPC**) and poly(**IPPC**)-M600. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 The Results and Analyses of NIPU Synthesized from Poly(IPPC) and Different Diamines

Sample	Diamines	Eq. ratio of Diamine	Wt % of Diamine	T_m (°C)[a]	T_g (°C)[a]	$T_{d5\%}$ (°C)[b]	Tensile Strength (MPa)	Elongation (%)
NIPU-A	D2000	80%	77%	n/a	n/a	297	0.26	71.2
NIPU-B	D2000	50%	68%	207	n/a	295	0.36	89.2
NIPU-C	HDA	80%	17%	181	n/a	234	n/a	n/a
NIPU-D	H12-MDA	80%	26%	n/a	85	246	n/a	n/a
NIPU-E	IPDA	80%	23%	n/a	98	240	n/a	n/a
NIPU-F	D230	80%	28%	194	83	260	n/a	n/a
NIPU-G	D2000/D230	80%/20%	76%/2%	n/a	143	253	1.3	9.6
IONIPU	PAM-E	80%	31%	208	n/a	190	2.4	26.2

[a] Measured by DSC at a heat rate of 10 °C/min.

[b] Temperature corresponding to 5% weight loss by themogravimetry at a heat rate of 10 °C/min in the atmosphere of nitrogen.

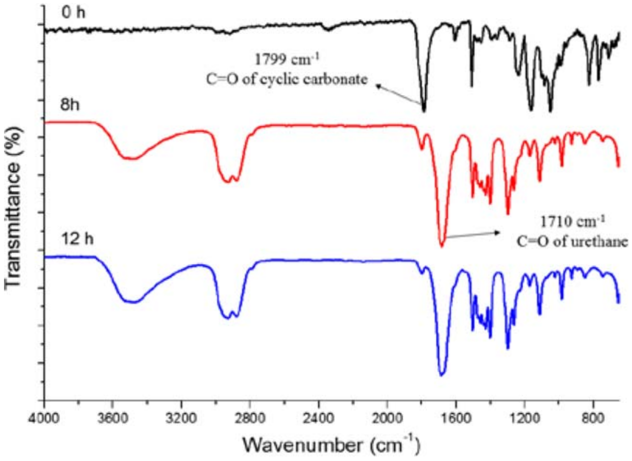


FIGURE 5 FTIR of curing reaction of poly(**IPPC**) via ring-opening of cyclic carbonate by Jeffamine D2000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

additon, and this product seemed much harder than **NIPU-A**, but its tensile stress is much poorer. The different rates of crosslinked product formations from same diamine but in different molar ratios are intriguing (Fig. 6). In parts, the reason of insolubility may be because of less soluble cross-linked poly(**IPPC**) that still possessed higher rigid-cyclic carbonate groups in the products. On the other hand, another probable reason may be due to the result of forming a fence-like polymer product between two homo-poly(**IPPC**) chains and diamines as shown in Scheme 2 particularly when high concentrations of diamines were added all at once to poly (**IPPC**). In SEM and AFM analysis of D2000 cured sample of **NIPU-A**, the results appear to support the postulated morphologies comprising of numerous fence-like structures. (Supporting Information Fig. S4-S5).

Since **NIPU-A** cured by Jeffamine D2000 yielded a very soft film which is lack of mechanical properties, we have carried out similar syntheses of **NIPU** by addition of several short-chained diamines such as HAD, H_{12}MDA, IPDA, and D-230 (**NIPU-C, -D, -E, and -F,** respectively) under 100 °C for 6 h for comparison as shown in Table 2. All these NIPUs turned into highly rigid PU films. However, when 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, PAM-E, were applied in equivalent ratio of 0.8 to poly(**IPPC**) as the curing agent, and we obtained an elastic hybrid PU's film (**IONIPU**). Clearly, siloxane-based diamines could impart necessary flexibility to

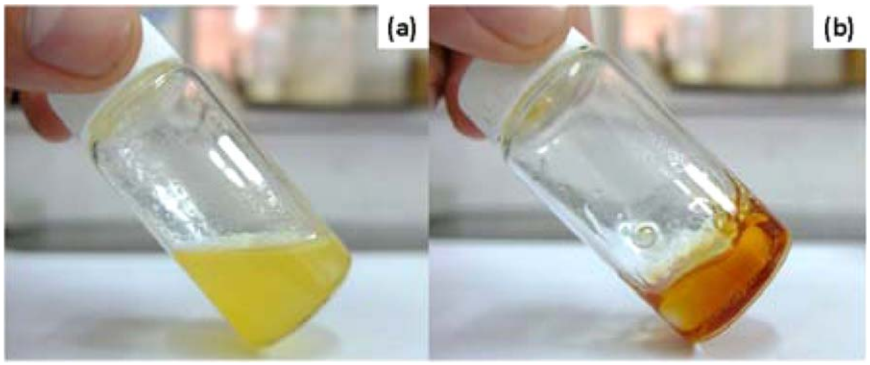


FIGURE 6 Fluidity of cured poly(**IPPC**) with D2000 in ratio of (a) 1/0.8 (b) 1/0.3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

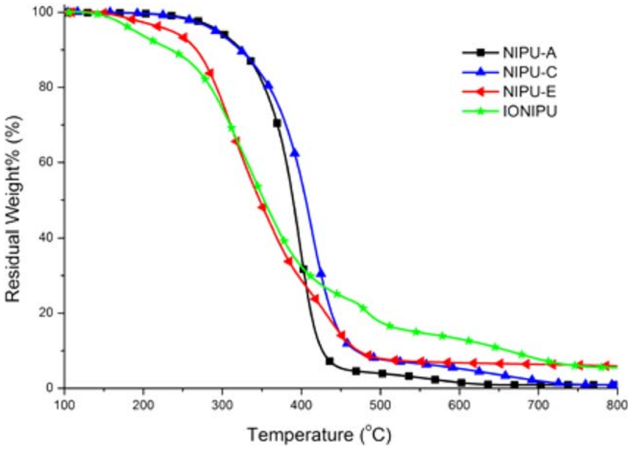


FIGURE 7 TGA thermograms of the crosslinked NIPUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the crosslinked polymers with an improved elongation (25%). In the TGA analysis, the 5 wt % degradation temperature ranges from 190 to 297 °C for these crosslinked PUs, and PUs which were cured by polyether diamines had a much higher degradation temperature. (Fig. 7).

CONCLUSIONS

The poly(**IPPC**) which structurally possesses a linear repeating *p*-substituted-methylstyrene backbone has been newly synthesized from bisphenol-A as the starting raw material. Homopolymers of poly(**IPPC**) in a medium molecular weight range (9500–25,000 g/mol) with isolated yield of over 80% could be realized with trifluoromethanesulfonic acid as the initiator at −40 °C. These polymers are characterized by possessing side-chained propylene cyclic carbonates groups at *para*-position of each phenylene ring. They possess high T_g of up to 170 °C along with a T_m of 180–190 °C, which reflects its structural homogeneity. The side-chained cyclic carbonate of poly(**IPPC**) can be easily functionalized into polyurethanes using ring-opening reactions with aliphatic amines at around 100 °C. Furthermore, when poly(**IPPC**) was modified into polyurethane at a high equivalent ratio of diamines relative to cyclic carbonate, the resulting polymers stay as stable solution throughout the reaction. Hence, the ease of urethane formation from poly(IPPC)-diamine reaction and non-gelling phenomenon of the crosslinked PU in NMP both will provide substantial processing advantages for film-making or coating operations. Further research on the formulation optimization is in progress to enhance the physical properties of the crosslinked PUs and PU foams through poly(**IPPC**) with various diamine combinations.

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