

Polycarbonate Polyurethane Elastomers Synthesized via a Solvent-Free and Nonisocyanate Melt Transesterification Process

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ABSTRACT: Soluble and thermally stable polycarbonate polyurethane elastomers were synthesized through a solvent-free and nonisocyanate melt transesterification process. The conditions of this process were studied, and the optimum conditions were as follows: the catalyst dibutyltin oxide dosage was 0.125 wt %, the raw material molar (n) ratio of dimethyl 1,6-hexamethylene dicarbamate (HDC) to poly(carbonate macrodiol) (PCDL) was $n(\text{HDC})/n(\text{PCDL}) = 1:0.99$, the reactants were prepolymerized under 100°C for 1 h and then under 185°C and a high vacuum for 4 h. Three different PCDLs were selected to participate in the reaction under the conditions mentioned previously, and their structures were characterized by Fourier transform infrared spectroscopy and X-ray diffraction. The products obtained from this process were still stable under 280°C. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41377.

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INTRODUCTION

Polyurethanes (PUs) are used in a wide range of industrial applications, including foams, adhesives, and elastomers. Generally, they are formed by urethane groups originating from diisocyanates and polyols.^{1–5} Diisocyanate is highly active and can react with substances that contain active hydrogen groups; this can cause irreversible damage to the eyes and respiratory organs during manufacturing or use. Thus, there has been a lot of research on nonisocyanate polymerization processes for production use.

Currently, there are mainly several nonisocyanate PU synthesis processes being explored in the literature. First, the most widely researched process is the synthesis process of cyclic carbonate with amines.^{6–9} This was developed to synthesize PUs with cyclic carbonate oligomers or bio-oil such as soybean and amines oligomers as reactants.^{10–14} This method enables various types of PUs to be obtained, and it has a bright future in the industry. Second, the synthesis process of methylene chloride ester with diamine,^{15,16} which is not suitable for industry because of the limited supply of raw materials.^{17,18} There are two remaining synthesis processes, the acyl azide-mediated Curtius rearrangement¹⁹ and urethane diphenol with phosgene methods. These methods have significant technical drawbacks;²⁰ mainly, the degree of polymerization is low, and therefore, these methods are not viable in industry.

In 2004, a novel process for the synthesis of nonisocyanate polyurethane was proposed.²¹ This process is a melt transesterifica-

tion reaction in which the reactants are in the molten state and the side-product methanol can be recycled; this makes it environmentally friendly. The melt transurethane process involves the transformation of one urethane to another (or carbamate) in reaction with polyol in the presence of suitable catalyst. In a polymerization process, a diurethane monomer reacts with equimolar amounts of polyol in the presence of a catalyst at high temperature under melt conditions to produce PUs followed by the removal of low-boiling alcohol. Tian et al.'s²¹ research work only focused on improving the polymerization process to get high-molecular-weight polymers, but no further research on the properties of the products was proposed.

Deepa and coworkers^{22–25} have recently published articles about this method that have also focused on the synthesis process, using urethane and low-boiling alcohols such as 1,4-butanol as the reactants and titanate as the catalyst. The PU product is a kind of white powder with no soft segment in the structure. As a result, this kind of PU product does not have elastic properties.

In the PU industry, the polyester PU and the polyether PU each have strengths and weaknesses. For example, the polyester PU is prone to hydrolytic degradation during use, whereas the polyether PU has better antihydrolytic performance but may undergo oxidative degradation in several ways. Recently, considerable attention has been paid to polycarbonate polyurethane (PCPU) for its improved mechanical performance compared to

traditional PU and for its better properties in antihydrolyzation and anti-oxidation. However, there has been no detailed report on the synthesis and characterization of PCPU based on the nonisocyanate process.

In this study, the preparation conditions and the characteristics of PU synthesized from poly(carbonate macrodiol)s (PCDLs) and dimethyl 1,6-hexamethylene dicarbamate (HDC) were examined, and the basic data for industrialization were provided.

EXPERIMENTAL

Materials

All-aliphatic PCDLs with molecular masses of 1000 (PCDL T-6001) and 2000 (PCDL T-6002 and T-5652) were kindly provided by Asahi Kasei Chemical Corp. The aliphatic PCDLs can be made from dimethyl carbonate (DMC) and different diols. In PCDL T-6001 and T-6002, 6 represents 1,6-hexanediol, and 1 and 2 represents molecular masses of 1000 or 2000, respectively. For PCDL T-5652, 6 represents 1,6-hexanediol; the first 5 represents 1,5-pentanediol; the second 5 represents the amounts of 1,6-hexanediol and 1,5-pentanediol for the syntheses, which were half and half; and 2 represents a molecular mass of 2000. 1,6-Hexamethylene diamine (HDA), dibutyltin oxide (DBTO), and 1,4-butanediol (BDO) were from Aladdin Reagent. Na-MCM-41 a kind of molecular sieve based catalyst was from Shanghai Zhuoyue Chemical Corp., and the characteristics were provided by the supplier: it had a white powder appearance, the relative degree of crystallinity was 95%, the specific surface area was 877 m²/g, and the limit adsorption amount of BJH pore (dv/dD) was 3.0 nm. DMC (>99.9%) was from Anhui Tongling Chemical Industry Corp. These chemicals were used without further purification.

Synthesis of HDC

HDC was synthesized from HDA and DMC through a reaction distillation process with Na-MCM-41 as the catalyst. The process conditions were as follows: the added amount of DMC and HDA had a $n(\text{DMC})/n(\text{HDA})$ molar ratio of 8:1, the reflux ratio was 3, the full back time was 30 min, the catalyst quality mass (m) quality $m(\text{Na-MCM-41})/m(\text{HDA})$ was 0.05%, and the reaction temperature of the reactor tower bottom was kept lower than 93°C. The reaction was considered to be completed when the outlet flow stopped and the top temperature fell. The bottom material was cooled and precipitated in water. The solid was filtered, washed with methanol, and purified by recrystallization from hot methanol several times to obtain HDC as a white crystalline solid, and the purity was greater than 99%.

Novel Process for Synthesizing PCPU

The PCPU contained PCDL as a soft segment and HDC as a hard segment without any chain extender. On the basis of the previous study, an Sn catalyst such as DBTO or stannous octoate and a Ti catalyst such as tetrabutyl titanate could both be used in the reaction as the catalysts. For this study, DBTO was used as the catalyst. The best preparation conditions of HDC and PCDL-T6002 were studied, and the product's intrinsic viscosity was tested as the main index.

HDC and PCDL were put into a polymerization reactor and melted through placement in an oil bath at 100°C with constant

stirring. Then, a certain amount of DBTO was added as a catalyst, and the polycondensation apparatus was made oxygen- and moisture-free by a nitrogen purge followed by use of a vacuum. The prepolymerization reaction was done at 100°C under room pressure for 1 h. Then, the oil temperature was elevated to a higher point. A high vacuum was applied for several hours to further condense the resulting viscous mass. At the end of the polymerization, the PCPU was obtained. There were two methods used to take samples. In one method, we did the experiment, and during the synthesis, samples were taken at different polymerization times. This method was used to research the effects of the catalyst dosage, polymerization temperature, and ratio of raw material. In the other method, we took samples each from a separate experiment. This method was used to research the effects of the polymerization time and to synthesize the products for further characterization.

Measurements

¹H-NMR and ¹³C-NMR Spectra. ¹H-NMR and ¹³C-NMR spectra of the monomers and polymers were recorded with a 500-MHz Bruker NMR spectrophotometer in CDCl₃ or dimethyl sulfoxide and with a small amount of tetramethylsilane (TMS) as an internal standard.

Inherent Viscosity ($[\eta]$). A 0.2 g/25 mL polymer solution in dichloromethane (CH₂Cl₂) was prepared. The effluxion time of the solution and solvent were measured by an Ubbelohde viscometer at 25°C, and $[\eta]$ was obtained from the following equation.

$$[\eta] = \frac{\sqrt{2(\eta_{sp} - 1)\eta_r}}{c}$$

where t is the effluxion time of the solution, t_0 is the effluxion time of solvent, η_r is the relative viscosity ($\eta_r = t/t_0$), η_{sp} is specific viscosity, $\eta_{sp} = \eta_r - 1$, and C is the concentration of the polymer solution (g/mL).

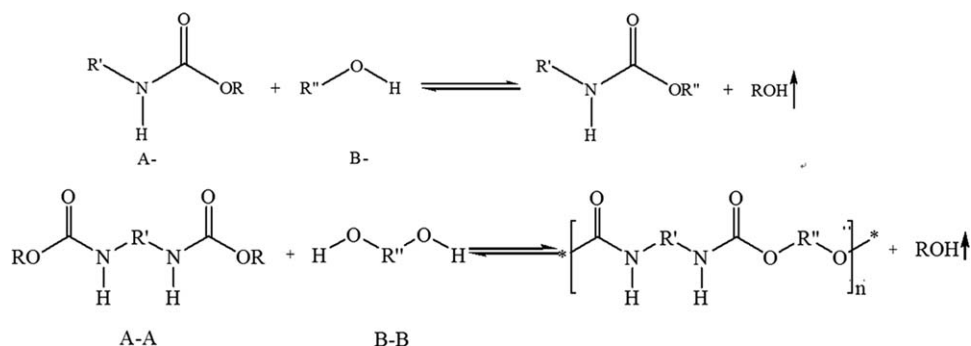
Fourier Transform Infrared (FTIR) Spectroscopy. The FTIR analysis of the PCPUs was performed on a Nicolet 6700 spectrophotometer in the mid-IR range from 4000 to 400 cm⁻¹ and with a hot-melt coating method.

X-ray Diffraction (XRD) Analysis. The X-ray patterns of samples were obtained with a Rigaku D/max2550V X-ray scatter instrument with Cu radiation at 40 kV and 100 mA from 3 to 50°.

Gel Permeation Chromatography (GPC) and Intrinsic Viscosity Analysis. The molecular weights of the polymers were determined by GPC in tetrahydrofuran (THF) with polystyrene as a standard. The flow rate of THF was maintained at 1 mL/min.

The intrinsic viscosity was measured with an Ubbelohde viscometer at 25°C, and dichloromethane was used as a solvent.

Thermogravimetric Analysis (TGA). The thermal stability of the materials was characterized by an SDT Q600 thermogravimeter. The sample was heated from room temperature to 700°C at a heating rate of 10°C/min under a nitrogen atmosphere at a gas flow rate of 20 mL/min. The weight loss versus temperature curves were recorded.



Scheme 1. Melt transesterification process for the synthesis of the PUs (R' and R'' represent the aliphatic and aromatic chains, respectively).

RESULTS AND DISCUSSION

Synthesis of PCPU and Optimum Conditions of the Process

HDC was prepared from HDA and DMC by a reaction distillation process whose purity was higher than 99.9%, and the NMR and FTIR data were as follows.

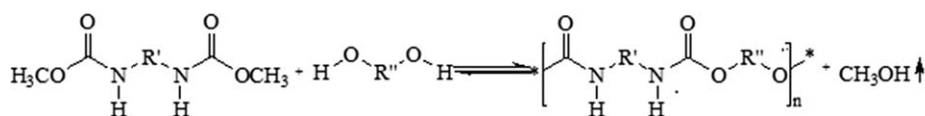
$^1\text{H-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 5.04 (b, 2H, $-\text{NH}$), 3.70 (s, 6H, $-\text{OCH}_3$), 3.17 (q, 4H, $-\text{CH}_2\text{NH}$), 1.33–1.50 (8H). $^{13}\text{C-NMR}$ (500 MHz, CDCl_3 , δ , ppm): 157.79 ($\text{C}=\text{O}$); 52.65 ($-\text{OCH}_3$); 41.47, 30.51, 26.86. FTIR (cm^{-1}): 3340 ($-\text{NH}_\text{H}$ bond); 2945, 2915, 2872 ($-\text{CH}_2$); 1691 ($\text{C}=\text{O}_\text{H}$ bond); 1531 ($-\text{NH}$); 1478, 1341, 1262, 1223, 1140, 1053, 1008, 933.

On the basis of these data, the structure of HDC as $\text{CH}_3\text{O}-\text{CO}-\text{NH}-(\text{CH}_2)_6-\text{NH}-\text{CO}-\text{OCH}_3$ was confirmed.

In Scheme 1, A represents $-\text{NCOOCH}_3$, and B represents $-\text{OH}$. The reaction types could have been the following: $\text{A}- + \text{B}-$, $\text{A}-\text{A} + \text{B}-$, $\text{A}-\text{A} + \text{B}-\text{B}$, and $\text{A}- + \text{B}-\text{B}$. Compared to the reaction of isocyanate with polyol model, this reaction can also be defined as similar to the polymerization model on the basis of infinite systems and a sequence parallel system.²⁶ The melt transurethane process involves the transformation of carbamate in a reaction with glycol in the presence of a suitable catalyst. In a polycondensation reaction, a diurethane monomer reacts with a diol monomer in the presence of a catalyst at high temperature and under melt conditions in which PUs are produced, whereas the side-product methanol is also synthesized.

Meanwhile, HDC and PCDL were used to prepare PCPU, and the process is described in Scheme 2.

During the experiment, there was no phosgene, isocyanate, or solvent, and the methanol (MeOH) could be easily moved away *in vacuo*. Thus, it was a solvent-free and nonisocyanate melt-transesterification process, and it could be applied in industrial manufacturing.



Scheme 2. Melt transesterification process between HDC and PCDL [R' represents $(\text{CH}_2)_6$, $\text{HO}-\text{R}''-\text{OH}$ represents PCDL, and R'' represents an aliphatic chain containing a carbonate group].

In our research, the experiment where the catalyst was not used rarely occurred, therefore the catalyst was necessary to be used. The relationship between the intrinsic viscosity and the polycondensation time under different amounts of DBTO catalyst is shown in Figure 1, and these experiments were carried out at a polycondensation temperature of 160°C . In Figure 1 and the following Figures 2 and 3, the point values on one curve were measured from the samples; these values were taken from one experiment at different polycondensation times. We found that when the amount of catalyst was too small, the reaction rate decreased, and certain properties, such as the viscosity and molecular weight, decreased. When the dosage was too large, side reactions occurred, the performance of the product was affected, and the color changed to yellow. We found that the best catalyst dosage was 0.125 wt %.

The curves of the intrinsic viscosity versus the polycondensation time at different polycondensation temperatures are shown in Figure 2. We observed that the catalyst retained its best catalytic activity in a certain range of temperatures. On the other hand, the side reactions were intensified; this made the product degrade at high temperatures, and the color also changed. As shown in Figure 2, 185°C was an ideal melting polycondensation temperature.

The curves of the intrinsic viscosity changes with the polycondensation time under different ratios of raw materials are shown in Figure 3. When one of the reactants was in excess, the reaction proceeded to a certain level before stopping. The chain growth was slowed down or stopped because of the lack of raw materials, and the intermediate polymers were capped by functional groups. At the end of the process, there was a small system viscosity and a slow growth. Furthermore, during the vacuum process, some of the small molecules, such as HDC, were drawn out together with the gas product at a fast withdrawal rate. Therefore, the HDC used in this system needed to

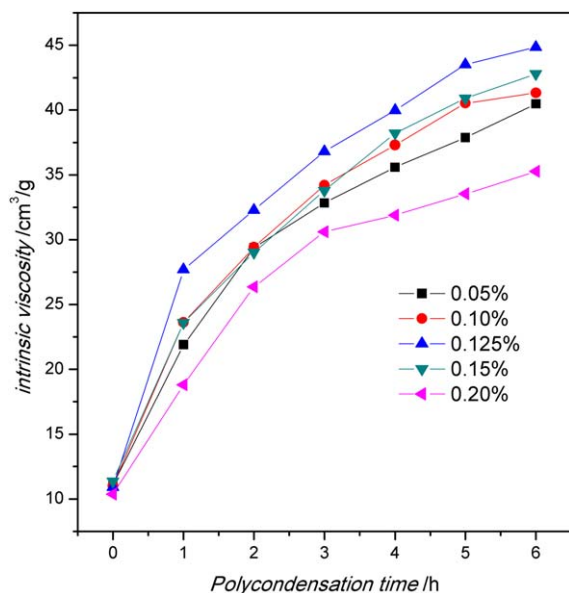


Figure 1. Intrinsic viscosity with different amounts of the DBTO catalyst [$n(\text{HDC})/n(\text{PCDL}) = 1:1$; catalyst = DBTO; prepolymerization conditions: 100°C, normal pressure, and 1 h; polymerization conditions: 160°C and high vacuum]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

be slightly in excess. As shown in Figure 3, a value of $n(\text{HDC})/n(\text{PCDL})$ of 1:0.99 was the best material ratio.

In the previous description, there are examples for one experiment at different polycondensation times. Because the reaction system was under high vacuum, samples had to be taken at ambient pressure but with the addition of nitrogen. This operation could have made the results lower than the real experimen-

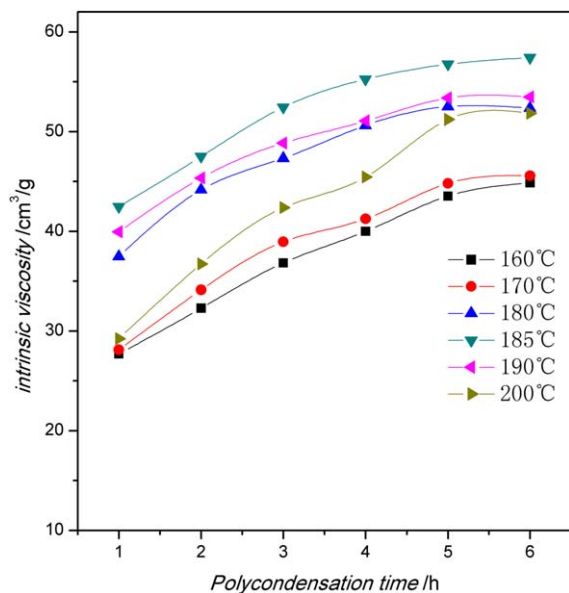


Figure 2. Intrinsic viscosity at different polycondensation temperatures [$n(\text{HDC})/n(\text{PCDL}) = 1:1$; catalyst = DBTO; DBTO catalyst dosage = 0.125 wt %; prepolymerization conditions: 100°C, normal pressure, and 1 h; polymerization condition: high vacuum]. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

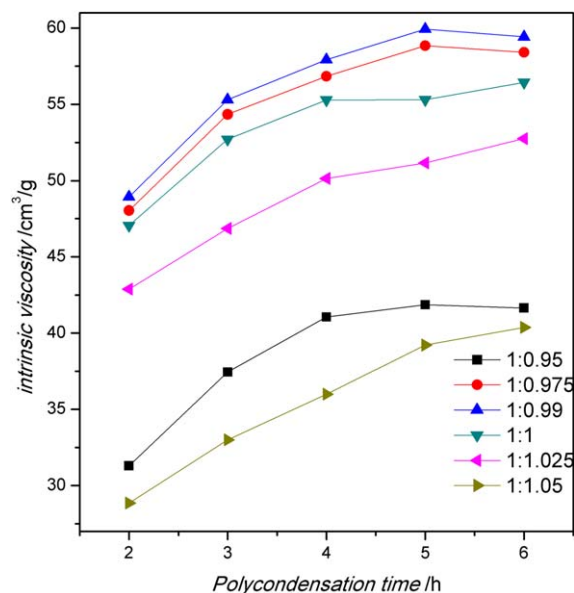


Figure 3. Intrinsic viscosity with different ratios of the raw materials (catalyst = DBTO; DBTO catalyst dosage = 0.125 wt %; prepolymerization conditions: 100°C, normal pressure, and 1 h; polymerization conditions: 185°C and high vacuum). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tal values. The curves of the intrinsic viscosity versus the polycondensation time are shown in Figure 4. This figure shows that when the polycondensation time was greater than 4 h, the system viscosity began to decrease slowly because of thermal degradation or side reactions. $[\eta]$ had its maximum at 4 h, but this maximum was not observed in Figures 1–3. This shows how sampling during the reaction could make the value smaller but could still be useful for exploring the optimum process

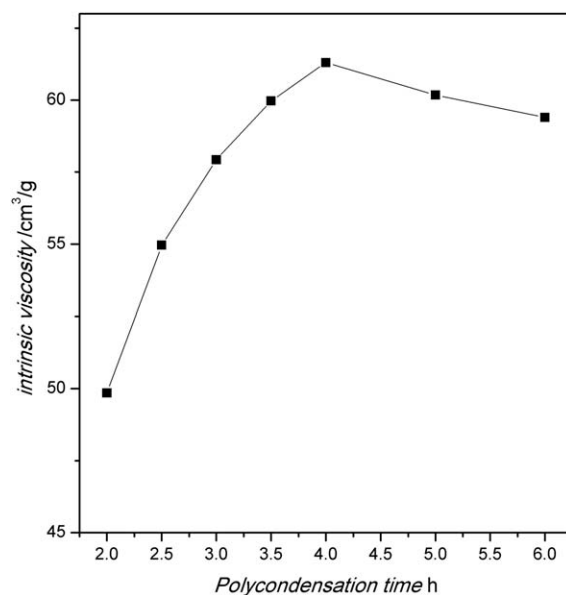


Figure 4. Intrinsic viscosity changes with the polycondensation time [$n(\text{HDC})/n(\text{PCDL}) = 1:0.99$; catalyst = DBTO; DBTO catalyst dosage = 0.125 wt %; prepolymerization conditions: 100°C, normal pressure, and 1 h; polymerization conditions: 185°C and high vacuum].

Table I. Monomers, Appearance, Intrinsic Viscosities, Molecular Weights, and Crystallinity of the PUs

Sample	Diurethane	Diol	Polycondensation time (h)	Appearance	$[\eta]$ (dL/g)	M_n^a	M_w^a	M_w/M_n
PU-B ^b	HDC	BDO	0.5	White	—	43,822	58,941	1.34
PCPU-1	HDC	T-6001	2.5	White, elastomeric	0.61	47,272	60,243	1.27
PCPU-2	HDC	T-6002	4.0	White, elastomeric	0.60	51,019	79,145	1.55
PCPU-3	HDC	T-5652	4.0	Pale yellow, elastomeric	0.56	34,746	56,823	1.63

M_w , weight-average molecular weight.

^aMolecular weights were determined by GPC in THF at 30°C with polystyrene standards for calibration.

^bPolyurethane made from HDC and BDO.

conditions. As shown in Figure 4, 4 h for polycondensation was better.

On the basis of the previous information, the optimum conditions were summarized as follows: the catalyst (DBTO) dosage was 0.125 wt %, the raw material ratio of HDC to PCDL was $n(\text{HDC})/n(\text{PCDL}) = 1:0.99$, and the reactants were prepolymerized at 100°C for 1 h and then under 185°C and high vacuum for 4 h.

The influence of the diol's starting molecular weight on the reaction time to obtain a similar molecular weight was also considered. Three different PCDLs were selected and studied in this synthesis system under the conditions mentioned previously in this article, as shown in Table I. The average molecular weight was in the range 30,000–50,000, and the dispersion coefficient was less than 1.8 with a concentrated distribution. For PU-B, PCPU-1, and PCPU-2, the polycondensation time for each synthesis reaction was different, even though they had similar molecular weights. It was found that a low-starting-molecular-weight [BDO (90) < T-6001 (1000) < T-6002(2000)] polyol reacted more easily with HDC so that the polymerization time was lower. This was likely due to the steric hindrance caused by the long-chain molecules curling, which increased the difficulty for them to react. Therefore, the diol starting molecular weight

had an effect on the reaction time. In the following experiments, these three different PCPUs were characterized.

FTIR Analysis of the PCPUs

The PCPU-1, PCPU-2, and PCPU-3 samples were characterized by FTIR spectroscopy,^{27,28} and their spectra are shown in Figure 5. We showed that the final products synthesized from different PCDLs were almost identical substances.

As shown in Figure 5, at 3390 or 3324 cm^{-1} , there were vibration peaks of the NH affected by the presence of the intermolecular interactions. The NH stretching (III_{NH}) at 3322 cm^{-1} was assigned to this group involved in hydrogen bonding, and at 3392 cm^{-1} (II_{NH}), it was related to the NH group involved in hydrogen-bonding interactions in the amorphous phase, mainly with the carbonate carbonyls. As shown in Figure 6, the shoulder peak at 3460 cm^{-1} was related to the NH group not involved in hydrogen bonding (I_{NH}).

The peaks at 2937 and 2860 cm^{-1} corresponded to the CH_2 anti-symmetry and symmetry stretching vibration peaks. The strong peak at 1743 cm^{-1} corresponded to the free $\text{C}=\text{O}$ bond of the carbonate and urethane groups. The peak of $\text{C}=\text{O}$ at 1683 cm^{-1}

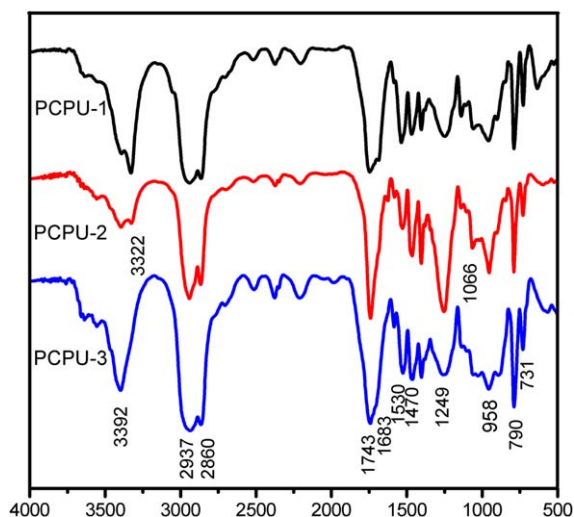


Figure 5. FTIR spectra of three samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

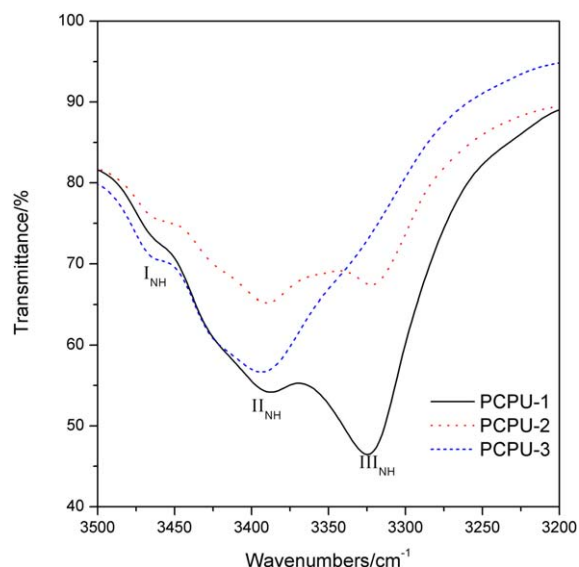


Figure 6. FTIR spectra for the NH stretching regions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Fitting Peak Area Percentages (As) for the Three NH Peaks

A (%)	PCPU-1	PCPU-2	PCPU-3
$A_{(I\text{NH})}/A_{\text{total}}$	0.168	0.306	0.381
$A_{(II\text{NH})}/A_{\text{total}}$	0.318	0.301	0.398
$A_{(III\text{NH})}/A_{\text{total}}$	0.514	0.393	0.221
R^2	0.995	0.995	0.998

joined with the hydrogen bonds in urethane; the strong and sharp peak at 1530 cm^{-1} was the joint frequency of the symmetry bent vibrations of the N—H bond. The 1470-cm^{-1} peak was the symmetrical bent vibrations of CH_2 ; the 1249-cm^{-1} peak was the antisymmetrical vibrations of the O—C=O in the soft segment of PCDL. The 1066-cm^{-1} peak was the stretching vibrations of the C—O—C of urethane. The 958-cm^{-1} peak was the symmetrical vibrations of C—O—C of the carbonate.

Because there also was carbonyl groups in the PCDL structure, the stretching peaks of the NH groups were selected to analyze the formation of hydrogen bonds. In Figure 6 of the spectra of the wave-number region from 3200 to 3500 cm^{-1} , the use of Gauss to fit the curves and calculate. The results are shown in Table II, and it can be seen that the I_{NH} % area of PCPU-1 was at a minimum; this could represent the maximum extent of hydrogen bonding. The II_{NH} associated with disordered hard domains (II_{NH} % area) showed the highest intensity for PCPU-3; this could have been related to stronger phase mixing on the interface between the hard and soft segments.

XRD Analysis of the PCPUs

The longer the polyhydric alcohol chain was, the better the PU's flexibility was, and the easier it was for the soft segment to cluster. Furthermore, by means of hydrogen bonds between soft and hard segments in the PCPUs, microphase separation occurred.

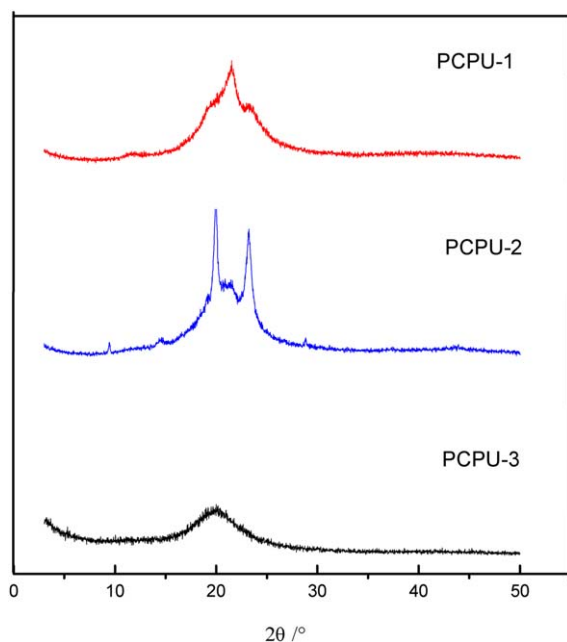


Figure 7. XRD spectra of three samples. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

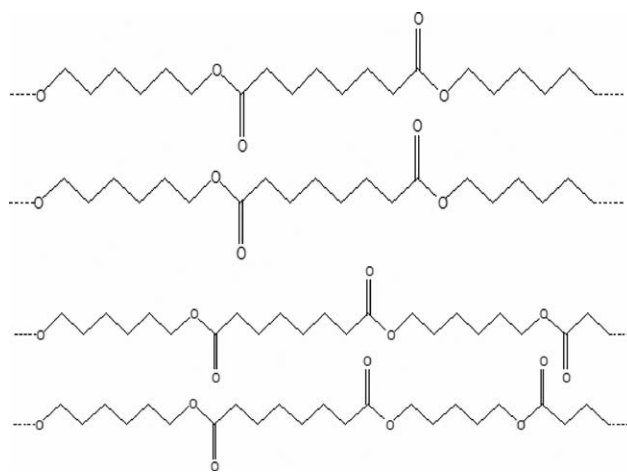


Figure 8. Soft segments in the PCPUs (top: soft segments in PCPU-1 and PCPU-2 and bottom: soft segments in PCPU-3).

The three samples were characterized by XRD, and their spectra are shown in Figure 7.

Figure 7 showed that PCPU-1's curve had sharp diffraction peaks at 21.5° , the PCPU-2's curve had sharp diffraction peaks at 19.9 and 23.2° , and the PCPU-3's only had a round shape peak at 19.8° but no sharp diffraction peak. Therefore, PCPU-1 and PCPU-2 had a certain degree of crystallinity. For PCDL T-6001 and T-6002, the only difference between them was the molecular weight. Compared to the literature,²⁹ there were also two sharp diffraction peaks at 19.9 and 23.2° in PCDL T-6001 and T-6002's XRD curves. As shown in Figure 8, the soft segments in PCPU-1 and PCPU-2 were more ordered and were called the crystalline soft segment. However, the chain length of the PCPU-2's soft segment was longer than PCPU-1's, so the soft segment in PCPU-2 crystallized more easily, and this result can be seen in Figure 7. However, for PCPU-1, there was only one sharp peak at 21.5° ; this showed that there was an ordered structure in PCPU-1's hard segment. So, there was microphase separation in PCPU-1 and PCPU-2. As shown in Figure 8, even the chain length of the PCPU-3's soft segment was as long as that of PCPU-2's; the structure was not as ordered as PCPU-2's, and this showed that the soft segment was an amorphous soft segment. PCPU-3 had no sharp diffraction peaks in its XRD curve; this was related to low crystallinity, so we considered that there was a strong phase mixing.

TGA of the PCPUs

The thermal stabilities of these samples were analyzed by TGA, as shown in Figure 8, and the data of the special temperature points are reported in Table III.

As shown in Figure 9, polymer decompositions occurred in different temperature ranges, and there were two steps of mass loss; one was the major loss step, and the other was a small loss step. The main loss could be seen as the degradation of the hard segment and soft segment, mainly the mixing phase. Then, the hard-phase degradation finished first. Thus, the second small loss step was due to soft-phase degradation only.

The increase in the hard-segment molecular weight lengthened the distance between the hard-segment microdomains and

Table III. TGA Data for the PCPUs

Sample	Interval of weight loss (°C)	Weight loss (%)	Temperature of initial weight loss (°C)	Temperature of the maximum rate of weight loss (°C)	Residue at 700°C (%)
PCPU-1	25-401	92.44	285	347	0.24
	401-700	7.32	401	439	
PCPU-2	25-389	93.55	287	352	0.51
	389-700	5.94	389	436	
PCPU-3	25-407	97.92	282	348	0.74
	407-700	1.34	407	431	

reduced the hydrogen-bond formation ability between the hard segments. This led to a decrease in the initial weight loss temperature in the first step. At the same time, the increase in the hard-segment microdomain was arranged well, and this resulted in ordered microdomains and made crystallization easier, so that the initial weight loss temperature in the second step was enhanced. The effect of the hard-segment molecular weight was a competitive result of the previous two roles. As shown in Table III, the effect of the increase in the hard-segment molecular weight on the weight loss temperature was negligible, and the special temperatures for the three samples were similar.

Figure 10 shows the differential thermogravimetry (DTG) curves of the three samples. The small weight loss at 170°C, which could not be seen in the TGA curve, might have been due to the loss of absorbed water. There were overlapped peaks for PCPU-1 and PCPU-2; this could have indicated that the separation of the two phases was not complete if we assumed that the two peaks represented the two steps of the thermal decomposi-

tion. At the same time, there was almost no second step peak for PCPU-3; this showed that the thermal decomposition of PCPU-3 was almost one-step, so the extent of phase mixing was high. In conclusion, PCPU-1 and PCPU-2 had microphase separation, but PCPU-3 did not. The results were consistent with previous results.

CONCLUSIONS

In this study, the synthesis of all-aliphatic PCPU elastomers with good properties was achieved. We did this through a novel melt transurethane process for the preparation of PUs under solvent- and isocyanate-free conditions. There was no phosgene, no isocyanates, no chemical hazards, and low-boiling methanol, which could be easily removed in this process. This technology could be applied in industrial manufacturing. The optimum reaction conditions when DBTO was used as the catalyst were studied as follows: the catalyst (DBTO) dosage was 0.125 wt %, the raw material ratio of HDC and PCDL was $n(\text{HDC})/n(\text{PCDL}) = 1:0.99$, and the reactants were prepolymerized at 100°C for 1 h and then at 185°C and a high vacuum for 4 h. As a result, the products' number-average molecular weight

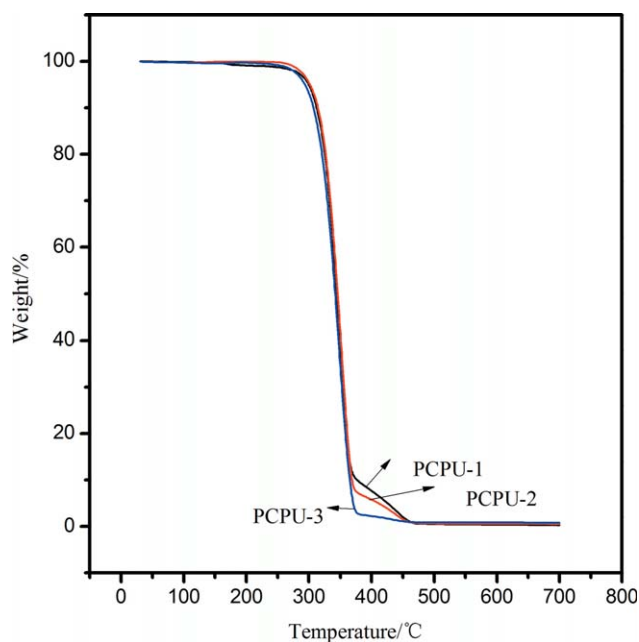


Figure 9. Thermogravimetry curves of the PCPUs under an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

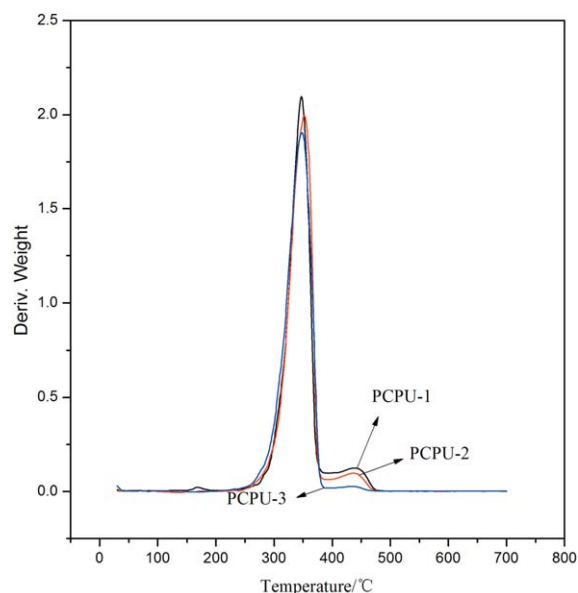


Figure 10. DTG curves of the PCPUs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(M_n) was in the range 30,000–50,000, and the dispersion coefficient was less than 1.8 with a concentrated distribution.

The FTIR measurement showed the structure of the three PCPUs. XRD measurements showed that the product synthesized from a single symmetric orderly structure PCDL had sharp diffraction peaks. TGA showed that the PCPU products could be fully thermal degraded with a similar initial decomposition temperature, and there were two steps of mass loss. The polymers prepared in this investigation were polycarbonate-based PUs with no isocyanate groups, and they were very stable.

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