

Synthesis and Characterization of Poly(carbonate urethane) Networks with Shape-Memory Properties

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ABSTRACT: In this study, a series of shape-memory polyurethanes were prepared from polycarbonate diol (PCDL) with a molecular weight of 2000, trimethylol propane, and isophorone diisocyanate (IPDI). The properties of crosslinked poly(carbonate urethane) (PCU) networks with various compositions were investigated. The chemical structures and thermal properties were determined with Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. FTIR analysis indicated that PCU had the structures of IPDI and PCDL and the amido formyl ester in polyurethanes. The gel content of PCU showed that PCU could

be effectively formed as crosslinked polyurethane networks. The glass-transition temperatures of the PCU networks increased slightly with decreasing soft-segment content in the networks. The values of Young's modulus in the networks at 25°C increased with decreasing soft-segment content, whereas the tensile stress and breaking elongation decreased significantly. PCU showed shape-memory effects with a high strain fixity rate. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 473–478, 2009

Key words: crosslinking; networks; polycarbonates; polyurethanes; thermal properties

INTRODUCTION

Poly(carbonate urethane)s (PCUs) are elastomer biomaterials that have been used to produce long-term implants.¹ It has been reported that they are less sensitive to biodegradation but exhibit biocompatibility characteristics similar to those of other polyurethane elastomers. It is believed that the microphase separation is due to the thermodynamic incompatibility between the different components, which are usually called soft and hard segments.² The polymers are normally characterized by a two-phase microstructure consisting of both soft and hard segments. The microstructure of polyurethanes is one of the important parameters for physical properties. Tingey and coworkers^{3,4} found that a high phase-separated polyurethane surface absorbed less pro-

tein.⁴ Other studies have demonstrated that the variation of the hard segment/soft segment ratio and changes in their associated structures also influence the biostability of the materials.⁵ The hard segment and chemistry structure influence the biodegradability of polyurethanes in the presence of enzymes or oxidants.^{6–8}

Shape-memory polymers (SMPs) have recently drawn researchers' interest because of their superior properties and potential applications in medical, industrial, electronic, and textile fields.^{9,10} Although more advanced SMPs such as shape-memory nanocomposites have been reported, block copolymers based on polyurethanes still play an important role in the area of SMPs.^{11–14} Polyurethane SMPs have attracted a great deal of attention because of their unique properties, such as a wide range of shape recovery temperatures (from –30 to 70°C), high shape recoverability, good processing ability, and excellent biocompatibility.^{15,16} These shape-memory polyurethanes basically consist of two phases, that is, the frozen phase and the reversible phase. In some cases, the crystalline soft domains form the reversible phase, with the melting temperature (T_m) of crystalline domains as the shape recovery temperature, whereas the hard domains constitute the frozen phase.¹⁷ Up to now, most shape-memory polyurethanes have been linear multiblock polyurethanes with physically crosslinked segments. However, these linear shape-memory polyurethanes cannot endure repeated changes in shape memory, and the

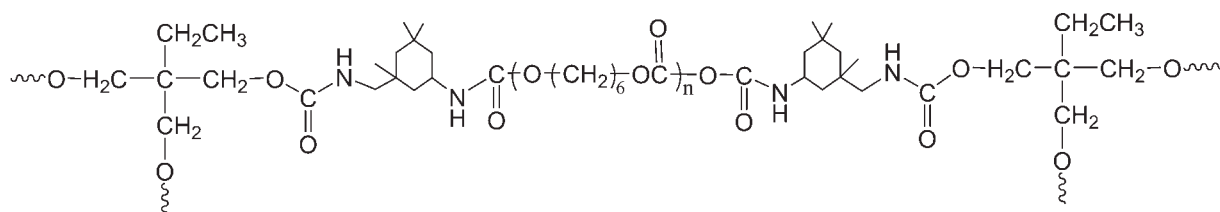
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Scheme 1 General chemical structure of PCU.

retention and recovery of the shape memory decrease after several cycles of shape-memory procedures.

To fulfill the various needs regarding the physical properties and enhancement of the shape-memory effect, in this study, we introduced a new shape-memory crosslinked PCU network prepared from polycarbonate diol (PCDL), trimethylol propane (TMP), and isophorone diisocyanate (IPDI). Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA) were used to analyze the prepared PCU. The shape-memory effects were also investigated with stress-controlled thermocyclic tensile tests.

EXPERIMENTAL

Materials

IPDI was purified by vacuum distillation, whereas PCDL with a number-average molecular weight of 2000 was carefully dried *in vacuo* at 100°C for 24 h. The OH value of PCDL, determined by the conventional neutralization titration method, was found to be 56.8 mg of KOH/g. TMP was recrystallized from ethyl acetate. Dimethylformamide (DMF) was freshly distilled by vacuum distillation after drying under anhydrous magnesium sulfate for 24 h. Dibutyl tin dilaurate was used as the catalyst. All other reagents were obtained from Tianjin Chemical Reagents Co. (Tianjin, China) and used as received.

Synthesis of the PCU networks

A 500-mL, round-bottom, four-necked separation flask, equipped with a mechanical stirrer and a thermometer, was used as a reactor to prepare PCU. First, PCDL (6.00 g) was charged into the dried flask

for 3 h at 95°C *in vacuo* to decrease the water content. Then, calculated amounts of IPDI, dibutyl tin dilaurate, and DMF were added, and the reaction was continued for about 10 h at 60°C under nitrogen. After that, TMP in DMF was added dropwise to the reaction mixture and reacted at 80°C for 24 h. The solid content of the product was about 30%.

Films, which were prepared through the casting of PCU solutions into a mold, were stored in an oven to evaporate the solvent at 80°C for 48 h. The film thickness was approximately 0.3 mm. The general structure of PCU is shown in Scheme 1, and the details of the PCU samples are listed in Table I.

Sample preparation

The PCU films were processed into disc-shaped specimens with a diameter of 10 mm for gel content tests and into dumbbell-shaped specimens with a 30-mm length for the tensile and thermomechanical tests.

Gel content

The gel content of the specimens was determined by immersion in dichloromethane for 24 h at room temperature and was calculated with the following formula:

$$\text{Gel content (\%)} = \frac{m_t}{m_0} \times 100\% \quad (1)$$

where m_0 and m_t are the weights of the original sample and the dried sample after swelling, respectively.

FTIR spectroscopy

FTIR spectra of PCU were taken with a Nicolet model 60SXR (Nicolet Instruments Co., Madison, WI) in the absorbance mode.

TABLE I
Details of the PCU Samples

Network	IPDI (mmol)	PCDL (mmol)	TMP (mmol)	Soft-segment content (wt %)	TMP content (mol %)	Gel content (%)
PCU1	7.2	3	2	75.7	16.4	Not determined
PCU2	7.8	3	2.3	74.8	17.6	90.3
PCU3	9.0	3	3.0	71.4	20.0	90.8
PCU4	10.8	3	4.0	67.1	22.5	92.3

DSC

The thermal behavior was studied by DSC with a Mettler DSC 40 system (Mettler-Toledo GmbH, Giesen, Germany). Indium metal was used for calibration. The PCU networks were dried to a constant weight before DSC measurement. The specimens (5 mg) were heated in sealed aluminum pans and scanned from -100 to 120°C , then cooled to -100°C , and finally heated to 120°C with heating and cooling rates of $10^\circ\text{C}/\text{min}$. All experiments were performed in a flow of dry N_2 .

TGA

TGA testing was carried out with a PerkinElmer (Walham, MA) Pyris 1 thermal analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under pure nitrogen. The temperatures ranged from the ambient temperature to 500°C . The weight of the samples was kept within 10 mg.

Tensile tests

The mechanical properties of the PCU were determined with a model M350-10AX (Tensometric Messtechnik GmbH, Wuppertal, Germany) tensile tester equipped with a 100-N cell at room temperature and at a high temperature. The tensile tests were performed with a crosshead speed of 12 mm/min. The results were statistically averaged values of five measurements.

Shape-memory properties

To examine the shape memory of PCU, specimens equipped with a temperature-controlled chamber were used to measure the stress and strain at various temperatures. The test procedure was as follows: (1) deformation (ε_m) was applied to the sample at a constant crosshead speed of 10 mm/min at a high temperature (T_2); (2) the sample was cooled to a low temperature (T_1) with a constant load, and in this process of cooling, the strain of recovery was $\varepsilon_m - \varepsilon_u$; (3) the sample was kept at T_1 for 5 min after the load was removed; and (4) the temperature was raised from T_1 to T_2 and maintained at T_2 for 10 min, and the strain of the remnant was ε_p . Under these conditions, the strain fixity rate (R_f) and the strain recovery rate (R_r) were calculated as follows:^{17,18}

$$R_f (\%) = \varepsilon_u \times 100 / \varepsilon_m \quad (2)$$

$$R_r (\%) = (\varepsilon_m - \varepsilon_p) \times 100 / \varepsilon_m \quad (3)$$

where ε_m is default tensile strain in a cyclic thermomechanical experiment, ε_u is fixed tensile strain after unloading a sample in a cyclic thermomechanical experiment, and ε_p is recovered tensile strain in a cyclic thermomechanical experiment.

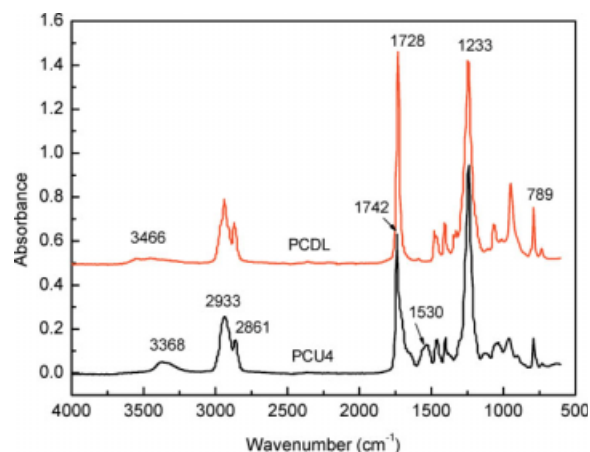


Figure 1 FTIR spectra of the prepared PCU4 and PCDL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Synthesis of shape-memory polyurethane PCU networks

The shape-memory polyurethane networks were prepared from PCDL with a molecular weight of 2000, IPDI, and TMP as a crosslinker. The urethane network formation was monitored by the decline of the isocyanate signal at 2250 – 2275 cm^{-1} in the IR spectra of the reaction mixtures. The results for the gel content of the samples are shown in Table I. The gel content of PCU was above 90%. PCU4 with a gel content of 92.3% could effectively be formed as crosslinked PCU. No significant effect of the soft-segment content on the gel content was observed.

FTIR analysis

The FTIR spectrum of PCU4, presented in Figure 1, shows that absorption peaks of crosslinked PCU4 at 1742 and 1530 cm^{-1} were responsible for the carbonyl groups and the C–N bonds in PCU4, respectively. Although the peak at 1728 cm^{-1} in PCDL was due to C=O of ester groups, it was narrower than that in PCU4. The 1233-cm^{-1} band was assigned to ester C–O–C stretching in the polycarbonate segments. Meanwhile, the peaks at 2933 and 2861 cm^{-1} were attributed to C–H in IPDI and PCDL. The 789-cm^{-1} band was assigned to ester O=C–O blending in PCDL. However, no peak appeared at 3460 cm^{-1} in PCU4, whereas the 3466-cm^{-1} band appeared in PCDL, and this meant that no free O–H stretching remained in the crosslinked PCU4. TMP completely reacted with isocyanate groups in IPDI. In addition, a broad peak due to N–H bonds appeared at 3368 cm^{-1} in PCU4.

Thermal properties of PCU

The thermal behaviors of PCU and PCDL were investigated with DSC. The DSC curves of PCU

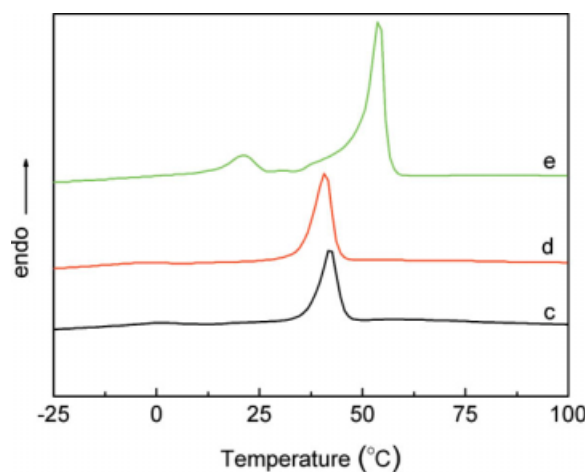


Figure 2 DSC thermograms of (c) PCU3, (d) PCU4, and (e) PCDL on the first heating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

showed a small melting peak upon first heating at about 40°C (Fig. 2), whereas no recrystallization exotherm upon cooling or a melting endotherm upon second heating was observed when the samples were cooled at a cooling rate of 10°C/min (Fig. 3). However, the DSC curves of PCDL showed two melting peaks upon first heating and three melting peaks upon second heating. All curves of PCU in Figure 3 exhibited only one glass transition during the second heating. The glass-transition temperatures (T_g 's) were taken at the midpoint of the heat capacity change during the second heating in DSC and are listed in Table II. It can be seen from Figure 3 and Table II that T_g of PCU was in the range of -34.4 to -40.7°C. Therefore, PCU was semicrystalline and had hard and soft segments forming two

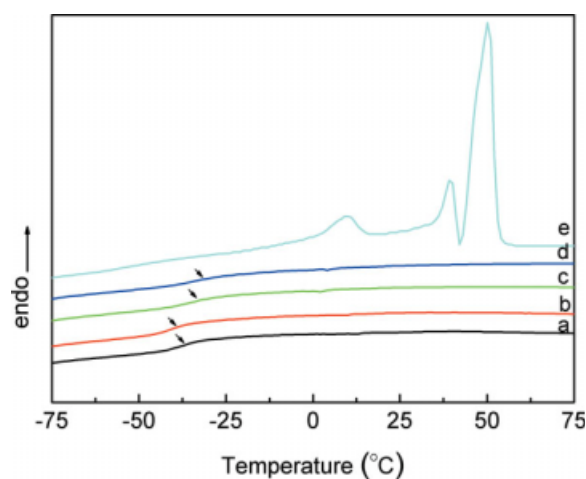


Figure 3 DSC thermograms of PCU with the different soft-segment contents on the second heating: (a) PCU1, (b) PCU2, (c) PCU3, (d) PCU4, and (e) PCDL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Thermal Properties of the PCUs and PCDL

Network	T_m (°C) ^a	T_g (°C) ^b
PCDL	54.3	—
PCU1	42.0	-38.0
PCU2	41.8	-40.7
PCU3	42.1	-35.5
PCU4	41.4	-34.4

^a On the first heating.

^b On the second heating.

domains. T_g of PCU increased with the reduction of the soft-segment content in the network; however, T_m of PCU was almost constant, about 42°C upon the first heating in DSC, which is near the body temperature of human beings, 37°C. T_m of PCDL (54.3°C) during the first heating was much higher than T_m of PCU. The hydroxyl telechelic PCDL reacted with IPDI to form polyurethane, which hindered the mobility of PCDL blocks and hence decreased the crystallinity and T_m of PCDL blocks in PCU.

The thermal stability of PCU4 was studied with TGA in nitrogen. The thermal degradation process of PCU4 was classified into one step. Its initial temperature was about 250°C, based on a 5% mass loss, whereas the temperature with fastest mass loss was about 350°C, with excess 80% mass loss. PCU4 showed very effective charring ability according to the TGA and differential thermogravimetry (DTG) data (Fig. 4).

Mechanical properties

The mechanical properties of PCU were measured with tensile tests at different temperatures and are listed in Table III. The TMP content in the feed is a linear function of the crosslinking density of PCU

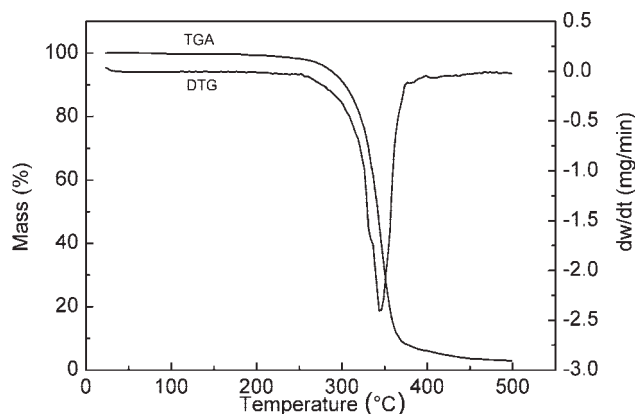


Figure 4 Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) curves of PCU4 at heating rate of 10°C/min.

TABLE III
Mechanical Properties of the PCUs at Different Temperatures

Network	Test temperature (°C)	Young's modulus (N/mm ²)	Tensile stress (MPa)	Break elongation (%)
PCU2	25	34 ± 1.2	35.9 ± 1.5	550 ± 40
PCU3	25	52 ± 3.2	34.8 ± 1.5	450 ± 40
PCU4	25	160 ± 30	26.3 ± 1.5	240 ± 50
PCU4	50	57 ± 3.2	5.0 ± 1.5	280 ± 50

and is inversely proportional to the average molecular weight between crosslink points. At room temperature (25°C), the values for Young's modulus of PCU increased, but the break elongation decreased with the increase in the crosslinking density. In comparison with the effect of the crosslinking density on the mechanical properties, a high soft-segment content led to low Young's modulus and a high break elongation. The values for the tensile stress and Young's modulus of PCU4 at 25°C were higher than those at 50°C, but the break elongation was slightly lower.

Shape-memory properties of PCU

The shape-memory properties of PCU3 and PCU4 were quantitatively characterized with thermocyclic tensile experiments. In the course of the thermocyclic experiments, each sample was stretched at $T_2 = 50^\circ\text{C}$ over T_m of PCDL blocks and fixed at ϵ_m (100%) at $T_1 = -20^\circ\text{C}$. After the fixation time, the sample was driven back to a zero load and heated up to T_2 for the recovery time before the next thermocycle started. This completed one thermocycle ($N = 1$), leaving a residual strain (ϵ_r), at which the next cycle ($N = 2$) started. The results of the cyclic tensile tests are listed in Table IV. PCDL blocks in PCU acted as switching segments, and T_m of PCU was the transition temperature for the shape-memory effect. The crosslinked points acted as hard domains to keep the permanent shape. Values for R_r varied significantly between the first and second cycles because of the flow of amorphous chain segments, plastic deformation of hard segments, and relaxation effects. PCU4 showed a slightly higher value for R_r than PCU3 because PCU4 had higher gel content and TMP content. After the second cycle, the values determined for R_r became almost constant. The semicrystalline PCDL segments efficiently recrystallized to sustain the temporary shape in the thermo-

cyclic tensile tests when the material in the deformed temporary shape was cooled below the transition temperature. The values for R_f were found to be higher than 97% for all cycles because semicrystalline PCDL domains in the networks were beneficial for shape fixation. PCU4 demonstrated the macroscopic shape-memory properties shown in Figure 5. The initial PCU4 was an opaque strip-

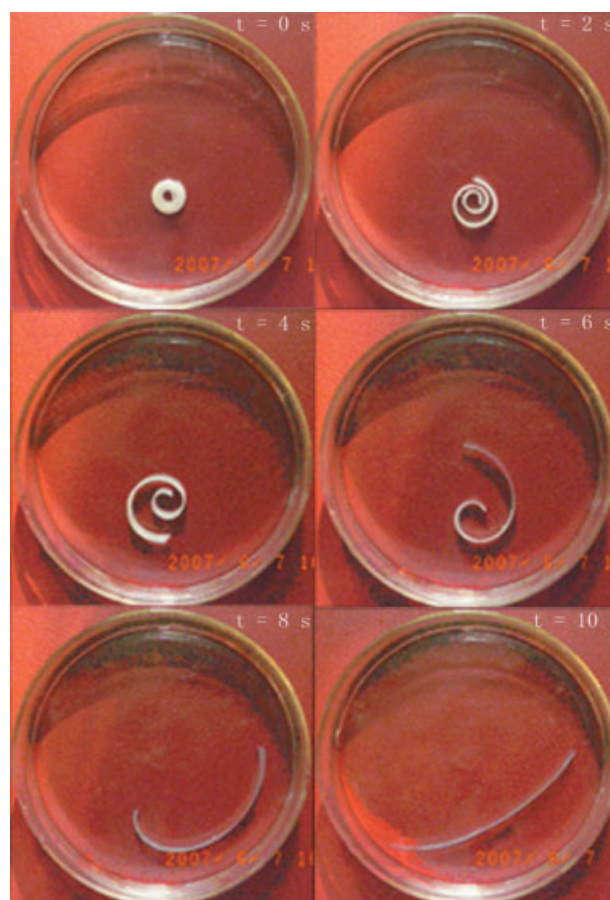


Figure 5 Shape-memory photographs of PCU4 showing the transition from temporary to permanent shape in 10 s at 50°C. The initial strip-shaped film was deformed into a snail-like shape as a temporary shape in water at 50°C; it was cooled to room temperature, and the external force was withdrawn. The PCU4 in the temporary shape was put into water at 50°C, and it recovered its permanent shape again in 10 s. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE IV
 R_r and R_f Values of the PCUs

Network	R_r (%)		R_f (%)	
	$N = 1$	$N = 2-5$	$N = 1$	$N = 2-5$
PCU3	80	91 ± 1.4	98	98 ± 2.5
PCU4	82	92 ± 0.8	97	97 ± 1.0

shaped film at room temperature. When the sample was heated to 50°C above T_m of PCU4, it was deformed to a snail-like temporary shape under an external force; it then maintained the deformed shape, was quenched to room temperature for 4 h, and then was unloaded. As a result of PCDL domain recrystallization, it was rigid enough to fix the temporary shape without an external force. When it was reheated to 50°C, the original shape was recovered again by the elastic force generated during the deformation state in only 10 s.

CONCLUSIONS

In this study, crosslinked shape-memory PCU samples were first prepared, and their thermal, mechanical, and shape-memory properties were investigated. The obtained results were as follows:

1. The high gel content indicated that crosslinking could effectively occur in PCU. Thermal analysis showed that the soft segment affected the T_m and T_g values of the soft segments. In addition, crosslinking reduced the mobility and crystallization of the soft segments, and this subsequently led to a decrease in the T_m values and an increase in the T_g values of the soft segments.
2. PCU showed a shape-memory effect. The chemical crosslinking bonds in the network were beneficial to permanent shape fixation. The

semicrystalline PCDL domains in the networks were beneficial to temporary shape fixation.

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