

Synthesis, structure, and properties of segmented carborane-containing polyurethanes

Yumeng Luo, Yafei Lu, Ning Li, Yun Li, Xiaoa Zhang, Shicheng Qi

Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing, China

Correspondence to: S. Qi (E-mail: qjsc@mail.buct.edu.cn)

ABSTRACT: Novel segmented carborane-containing polyurethane (PUR 2–5) is synthesized from hydroxyl-terminated carborane-containing prepolymer (P3) as soft segment and isocyanate-terminated carborane-containing prepolymer (P5) as hard segment by different ratio of P3 and P5. The prepared carborane-containing polyarylesters and polyurethanes (PURs) are characterized by Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR). Their mechanical properties and thermal stability are measured, while the dosage of carborane biphenol is 5–10 wt %, the tensile strength is up to 20 MPa, and thermal gravimetric analyzer (TGA) curves indicate that the carborane group effectively reduces the degradation rate of carborane-containing polyurethane, which is fairly stable above 300°C and with char yield exceeding 40%. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42227.

KEYWORDS: polyurethanes; properties and characterization; thermal properties

Received 6 September 2014; accepted 10 March 2015

DOI: 10.1002/app.42227

INTRODUCTION

PURs are one of the most versatile polymers since PURs are provided with the segmental nature of polyurethanes and the rich chemistry of isocyanates. PURs find their use in variety of applications including foams, elastomers, coatings, adhesives, and fibers. Hard segments of PURs impart strength whereas the soft segments provide flexibility.¹ The flexibility and mechanical properties of polyurethanes are greatly influenced by controlling the behavior of crystalline phase separation in soft and hard segments, and then different properties can be realized. In compliance with exceedingly versatile characteristics, such as wear-resisting, low temperature resistance, good sealing, sound insulation, biodegradable, and excellent processing performance, PURs are able to satisfy many kinds of requirements, leather, sealant, etc.

PURs, however, are well known for poor heat resistance that largely limits their use as engineering materials. Attempts to improve thermal stability of PURs have been made over a long period. There are mainly two chemical approaches to improve thermal stability of PURs. One is to adopt aromatic diisocyanates, which have good heat resistance, and another one is to introduce organic heterocyclic groups into the main chain of polymeric diols and PURs, such as isocyanurate, oxazolidone, etc. As an accepted approach, introducing organic heterocyclic groups into polyurethane backbone is popular, and the effect of

different organic heterocyclic groups on improving the thermal performance has been reported. However, most of these studies focused on either soft segment or hard segment of PURs. It is essential and important to make change in both soft and hard segment in order to reach the goal of improving thermal stability of PURs.^{2–9}

Carboranes have been one of the most extensively investigated new chemicals during last 50 years, especially dicarba-closo-dodecaboranes (carboranes for short). One of the most striking features of carboranes is the capability of two carbon atoms and ten boron atoms to adopt the icosahedral geometry in which the carbon and boron atoms are hexacoordinate. This feature of the icosahedral structure gives rise to several unusual properties, especially thermal property. According to the different locations of carbon atom on the icosahedral body, carboranes can be recognized as three isomers: 1,2-carborane, 1,7-carborane, and 1,12-carborane. Since under an inert atmosphere, when the temperature rises to 450°C slowly, 1,2-carborane will have a thermal rearrangement process and transfer into 1,7-carborane, then continue heating to over 650°C, it will become 1,12-carborane.^{10,11} Owing to the occurrence of thermal transition at high temperatures, carboranes are provided with excellent thermal properties. Thus, carboranes have been regarded as one of the most excellent organic group to improve performance of organic polymers with remarkable thermal stability due to their

stable cage-like structures and thermal isomerization shift behavior.^{12–16} Recently, our group has made some attempts with carborane groups to improve thermal stability of polyester, phenolic, and organic silicone polymers.^{17–19} As one of the application of carborane-containing polymers, adhesives based on carborane-containing PURs can be used at the temperatures of up to 500–800°C.²⁰ Nevertheless, documents about synthesis, characterization of carborane-containing PURs are seldom referenced and the researches on modifying by carboranes are rare.

The main content of this work is to adopt the method of introducing carborane group into PURs to improve thermal stability, and the highlight is to make changes in both soft and hard segment of PURs in order to ensure each segment to meet the requirement of thermal stability. P3 was prepared from carborane-containing polyarylester^{21–28} which was synthesized from 1,7-carboxyphenyl-carborane and 4,4-oxydiphenol via sulfonylation method, poly-1,4-butylene adipate (PBA), and 4,4-diphenylmethane diisocyanate (MDI) at the molar ratio of OH/NCO = 1.5, while P5 was prepared from MDI, trimethylolpropane (TMP) at the molar ratio of 3.2 : 1, and 1,2-carborane bisphenol. Afterwards, carborane-containing polyurethane (PUR 2) was obtained by P3 and P5 at the ratio of 100 : 30 by weight. The presence of P1 and 1,2-carborane bisphenol make polymer chains contain more rigid groups which possess great cohesive energy. It is the facility to form micro-phase separation between segments in the substrate, and then thermal stability is improved. Apart from the segmented structure, PURs can form highly cross-linked networks due to rich isocyanate chemistry and polyhydric alcohols in order to guarantee the thermal properties.

EXPERIMENTAL

Materials and Chemical Agents

MDI was procured by Wanhua Chemical Group Co. Benzene-sulfonyl chloride (BsCl) and 4,4-oxydiphenol were supplied by Aladdin. TMP, N,N-dimethylformamide (DMF), pyridine, chloroform, ethanol, acetone, ethyl acetate, butyl acetate, and dibutyltin dilaurate (DBTDL) were purchased from Beijing Chemical Industrial Co. PBA (molecular weight of 2000 g/mol) was purchased by Qingdao Yutian Works Co. Argon was provided by Beijing Ruyuan Ruquan Technology Company. 1,7-carboxyphenyl-carborane with measured elemental analysis values of C 50.85% (theoretical value of C 49.35%), H 5.25% (theoretical value of H 5.22%), and 1,2-carborane phenol with measured elemental analysis values of C 51.05% (theoretical value of C 50.95%) and H 6.10% (theoretical value of H 6.10%) were prepared in our laboratory.

Instruments

FTIR measurements were performed using a Nicolet Nexus 670 instrument, USA. NMR spectra were recorded at room temperature using a Bruker ARX 400 NMR spectrometer for ¹H. Solvent used for analysis was deuterated dimethyl sulfoxide (DMSO-d₆) and tetramethylsilane (TMS; $\delta = 0$ ppm) was used as the reference standard. Molecular weights (M_w and M_n) and polydispersity indexes (PDI) of the polymers were estimated by a Waters gel permeation chromatography (GPC) system (Waters, 515 HPLC Pump) using tetrahydrofuran (THF) as an eluent and refractive index (RI) detector. Tensile strength and

elongation at break were tested as a Chinese National Standard (GB/T 528–2009) using an RGT-5 electronic universal testing machine manufactured by Shenzhen Reger Instrument Co. Hardness was tested by Shore Hardness tester using Chinese National Standard (GB531-1999). Thermal stability of the polymers was verified by a Perkin – Elmer TGS – 2 analyzer using 1.5 mg of the sample in Al₂O₃ crucible under nitrogen ambience at a heating rate of 20°C/min. X-ray diffractometer with Ni-filtered Cu Ka radiation (40 kV, 30 mA) was used to obtain X-ray diffractograms of polymers at room temperature. Measurements were performed in the 2 θ ranges from 5 to 60°. The fractured surfaces of tensile samples were examined by scanning electron microscope (SEM), model JEOL:JXA-840A equipped with an electron probe microanalyzer system.

Synthesis of Carborane-Containing Polyarylates (P1, P7, and P8)

A mixture of BsCl (2.04 ml, 16 mmol) and N,N-dimethylformamide (0.20 ml, 2.6 mmol) in pyridine (5 ml) was charged into a 100 ml two-necked round bottom flask equipped with a stirring distilling tube. Afterwards, another mixture of 1,7-carboxyphenyl-carborane (1.92 g, 5 mmol) and pyridine (10 ml) was added. The substances were stirred under argon at room temperature for 30 min and then at 120°C for 10 min. Subsequently, a pyridine (10 ml) solution of 4,4-oxydiphenol (1.01 g, 5 mmol) was added, and the resultant mixture was kept in an oil bath at 120°C for 10 h. Then the resulting mixture was removed from the oil bath and evaporated under reduced pressure. The residue was poured into a mixture of chloroform and ethanol (1 : 15 by volume) for precipitation, and the precipitated polymers were isolated by filtration, ground into powder, and dried at 60°C in a vacuum oven for 10 h to give a light-brown solid powder P1 with 78% yield. Similarly, P7 and P8 were prepared by 1,7-carboxyphenyl-carborane and different bisphenols and their structural features including M_w , polydispersity and yield are shown in Table I.

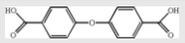
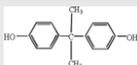
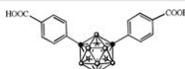
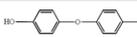
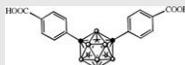
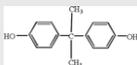
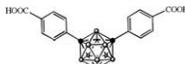
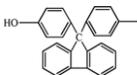
Carborane-free polyarylate (P2) was prepared by sulfonylation method as well.²⁰ The M_w , polydispersity and yield of P2 are listed in Table I.

Synthesis of Carborane-Containing Hydroxyl-Terminated Prepolymer (P3)

Carborane-containing hydroxyl-terminated prepolymers (PUAs) were prepared via single-step procedure employing MDI and PBA at the molar ratio of NCO/OH = 1 : 1.5. PBA (60.00 g) was degassed and dried in a 500 ml four-necked round bottom flask equipped with mechanical stirrer, reflux condenser, thermometer, and argon inlet under high vacuum at 110°C for 2 h. When the flask was cooled to 65°C, MDI (6.00 g), DBTDL (0.4 wt %), and a solution of carborane-containing polyarylate (P1, 1 wt %) in DMF (10 ml) were charged into the flask together. As the viscosity of the solution increased, ethyl acetate which had been out of water was added to dissolve the mixture, finally acetone was added with continuous stirring to form a homogeneous pale brown viscous turbid solution, and carborane-containing PUA (P3) was given with 93% yield.

Without adding carborane-containing polyarylate (P1), carborane-free PUA (P4) was prepared by a procedure similar

Table I. Monomers Used, M_w , Polydispersity and Yield of Carborane-Containing Polyarylates

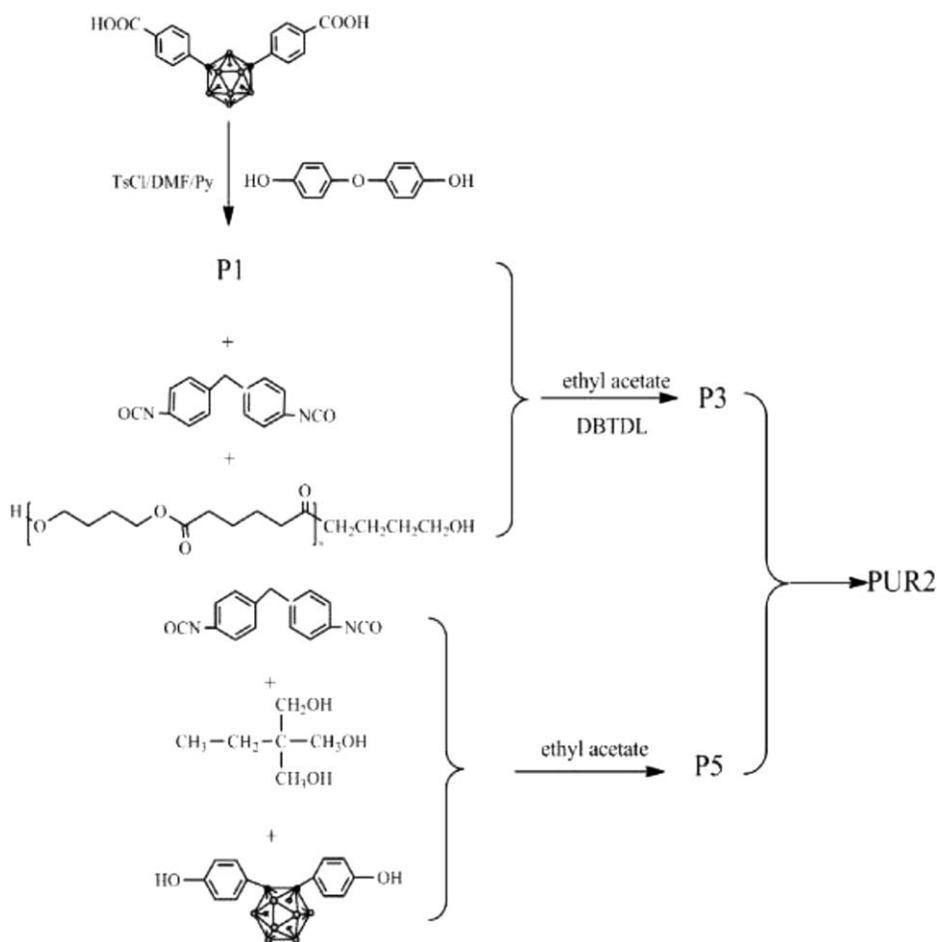
Polyarylates	Dicarboxylic acids	Bisphenols	M_w	M_w/M_n	Yield (%)
P2			1.2×10^4	0.91	87
P1			7.5×10^3	1.88	78
P7			2.4×10^3	1.29	74
P8			1.6×10^3	2.68	73

to that used for preparation of P3. A light yellow and translucent solution of P4 was obtained in 94% yield.

Synthesis of Carborane-Containing Isocyanate-Terminated Prepolymer (P5)

TMP (2.64 g, 0.02 mol) was charged into a 100 ml round flask, followed by addition of 10 mL of butyl acetate. The water in the mixture was removed by decompressing at 55°C for 30 min. Subsequently, MDI (9.28 g, 0.64 mol) and ethyl acetate (10 ml) were

charged into a four-necked round bottom flask (250 ml) equipped with reflux condenser, mechanical stirrer, thermometer, and argon inlet. Under argon environment, TMP-butyl acetate solution was added drop-wise into the flask for 1.5 h at 65°C. During this period, 1,2-carborane bisphenol (5 wt % of the mass of the reactants of P5) with ethyl acetate (10 ml) were added into the flask. And then the mixture was rigorously stirred at 75°C for 2 h. Finally, the product was cooled to room temperature and discharged to get a homogeneous pale yellow viscous translucent

**Figure 1.** Synthetic route of PUR 2.

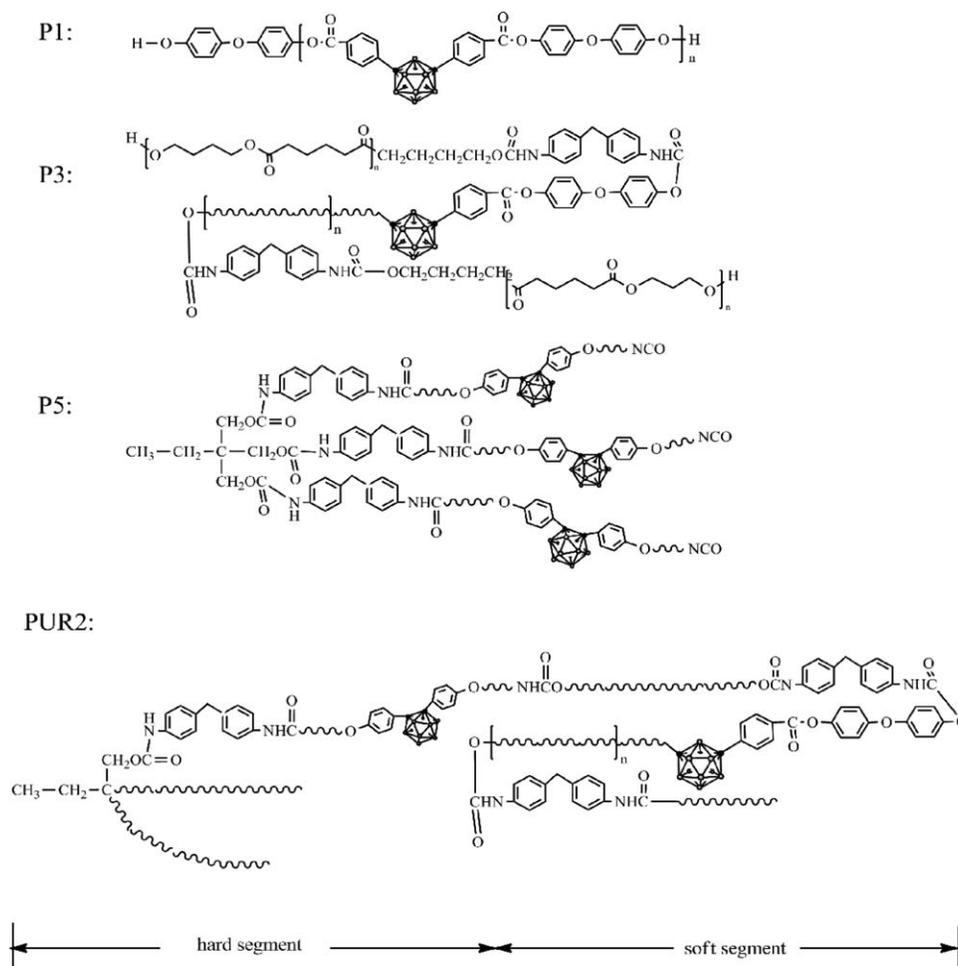


Figure 1. (Continued)

solution. Carborane-containing isocyanate-terminated prepolymers (PUB) was prepared successfully. The yield of carborane-containing PUB (P5) was 93%.

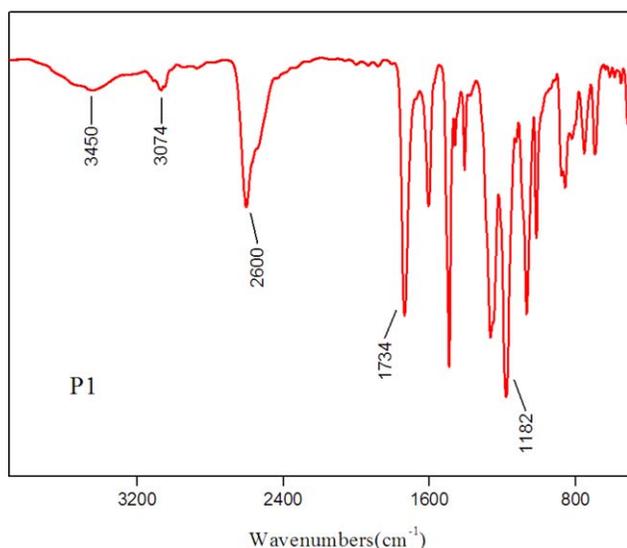


Figure 2. FTIR spectrum of P1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Without adding carborane-containing polyarylate, carborane-free PUB (P6) was prepared by a procedure similar to that used for preparation of P5. A light yellow and translucent solution of P6 was obtained in 94% yield.

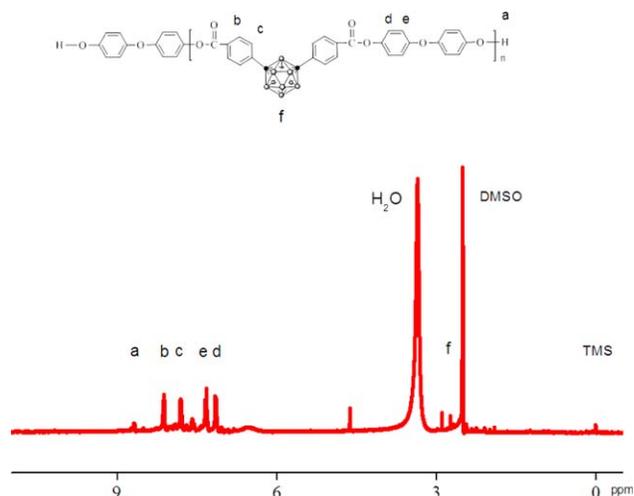


Figure 3. ^1H NMR spectrum of P1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

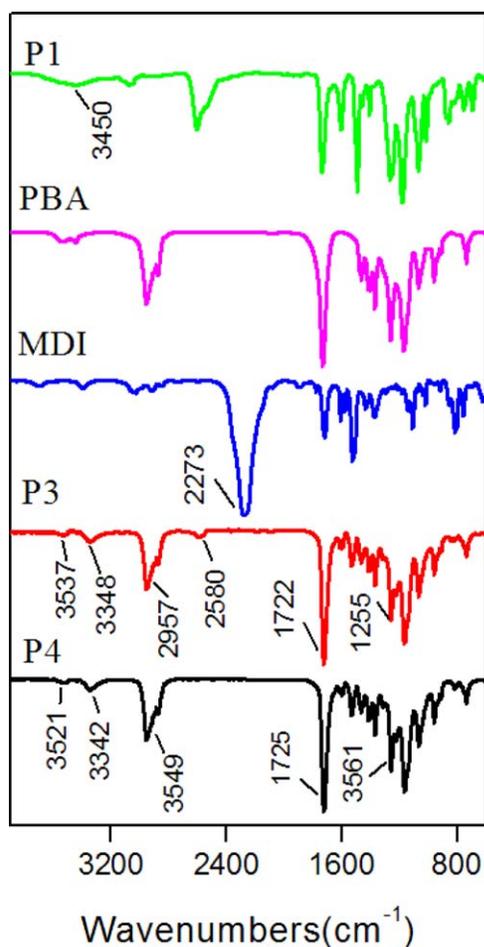


Figure 4. FTIR spectra of PUA (P3) and P4. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Synthesis of PUR 2

P3 and P5 were mixed at a certain proportion of 100 : 30 by weight. Then, the mixture was poured onto the treated mold,

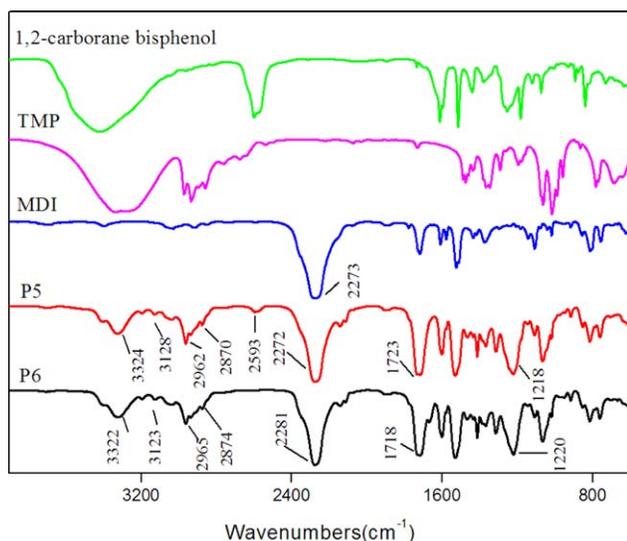


Figure 5. FTIR spectra of PUB (P5) and P6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

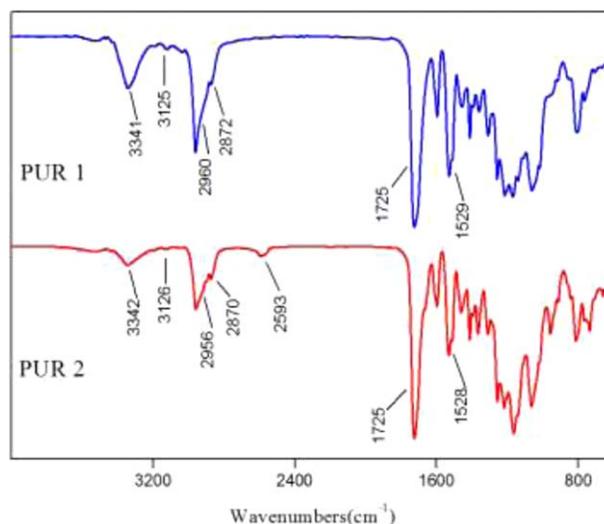


Figure 6. FTIR spectra of PUR 2 and PUR 1. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

and put horizontally at room temperature. After 72 h, the product PUR 2, which was a white opaque membrane-like substance, was given. At the same time, carborane-free PUR 1 with the appearance of colorless, transparent membrane-like was prepared from P4 and P6.

RESULTS AND DISCUSSION

Characterization of Carborate-Containing Polyarylate (P1)

P1 was synthesized by condensation polymerization of 1,7-carboxyphenyl-carborane and 4,4'-oxydiphenol, as outlined in Figure 1 (also the total synthetic route of PUR 2 is shown). The obtained polymers were characterized with multiple spectroscopic methods, and giving satisfactory analysis data corresponding to its expected molecular structures. The FTIR spectrum of P1 is shown in Figure 2. The absorption bands around 3074 cm^{-1} (aromatic C–H), the bands at 1182 cm^{-1} (C–O stretch) and the very strong bands around 1734 cm^{-1} (free urethane C=O) are assigned in the structural unit. Moreover, –OH of 3450 cm^{-1} and –BH of 2600 cm^{-1} demonstrate that hydroxyl-terminated carborane-containing polyarylester is obtained. Figure 3 shows ^1H NMR spectrum of P1. The aromatic protons from 4,4'-oxydiphenol appear at $\delta = 7.14$ and 7.33 ppm, respectively. The aromatic protons from 1,7-carboxyphenyl-carborane are observed at $\delta = 8.12$ and 7.80 ppm, respectively. The carborane protons from 1,7-carboxyphenyl-carborane are assigned at $\delta = 1.90$ – 2.90 ppm. The hydroxyl protons from polyarylate are observed at $\delta = 8.68$ ppm. The assignment of the chemical shifts in ^1H NMR verifies the molecular structure and confirms polyarylate formation.

Characterization of Carborane-Containing Hydroxyl-Terminated Prepolymer (P3)

Carborane-containing hydroxyl-end polyarylate was designed and synthesized in order to further react with PBA and MDI to prepare carborane-containing hydroxyl-terminated prepolymer. Thus, the molar ratio of bisphenol and dicarboxylic acid was determined to be 1.1 : 1, and three carborane-containing

Table II. Mechanical Properties and Hardness of PUR 2 with Different Ratios of P3 and P5

PUR 2	Weight ratio of P3 to P5	Hardness, Shore A	Tensile Strength (T_s) (MPa)	Elongation at break (E_b) (%)
1#	100 : 20	34	16	1026
2#	100 : 30	54	24	730
3#	100 : 50	73	25	199
4#	0 : 100	86	30	52

polyarylates (P1, P7, and P8) were synthesized. As can be seen in Table I, the molecular weight of P1 ($M_w=7500$) is much higher than that of P7 ($M_w=2400$), which could be explained by the different steric effect of 4,4'-oxydiphenol and bisphenol. The molecular weight of P8 is the lowest among synthesized polyarylates for the same reason. The polydiversity index of P1 is less than 2, which is the best to prepare the following prepolymer. As an oligomeric diol, PBA shows rather low molecular weight (2000 g/mol). The polyarylates with high molecular weight ($M_w > 20 \times 10^3$) are difficult to react with MDI and PBA to form copolymer as a result of poor reactivity caused by long chains and their strong steric effect. On the other hand, if the molecular weight of polyarylates is lower than 5.0×10^3 , it will deteriorate the mechanical properties of the following resultants.^{14,25} Considering the above requirements, P1 is designated to be the most appropriate choice among the three obtained carborane-containing polyarylates because its molecular weight (M_w) is between 20×10^3 and 5.0×10^3 .

P3 was prepared from the condensation of MDI, PBA, and P1 at the molar ratio of NCO/OH = 1:1.5. PBA was one of the most important soft segments used for the preparation of dif-

ferent polyurethane products. PBA with molecular weight of 2000 g/mol and carborane-containing P1 were as soft segments of carborane-containing PURs. For the purpose of synthesizing hydroxyl-terminated prepolymer, PBA reacted with MDI at the molar ratio of NCO/OH = 1 : 1.5 and P1 was used as a modifier. PBA, P1, and MDI formed copolymers via the urethane linkages which were bonding with -NCO in MDI and -OH in PBA and P1.²⁵ The obtained prepolymer (P3) was characterized with spectroscopic method, and giving satisfactory analysis data corresponding to its expected molecular structures. FTIR spectrum of P3 is shown in Figure 4. The spectra of its reactants, MDI, PBA, and P1, are also given in the figure for comparison. MDI exhibits absorption bands at 2273 cm^{-1} , which is ascribed to -NCO stretching vibrations. The bands completely disappear in the spectrum of P3, indicating that the -NCO bonds of MDI have been fully consumed by the condensation polymerization. The absorption bands around 3342 cm^{-1} (urethane N-H stretch), the bands at 1261 cm^{-1} corresponding to -C-O-C and the very strong bands around 1734 cm^{-1} (free urethane C=O) are assigned in the urethane linkage, which prove the existence of -NHCOO-. Moreover, -OH of 3521 cm^{-1} and -

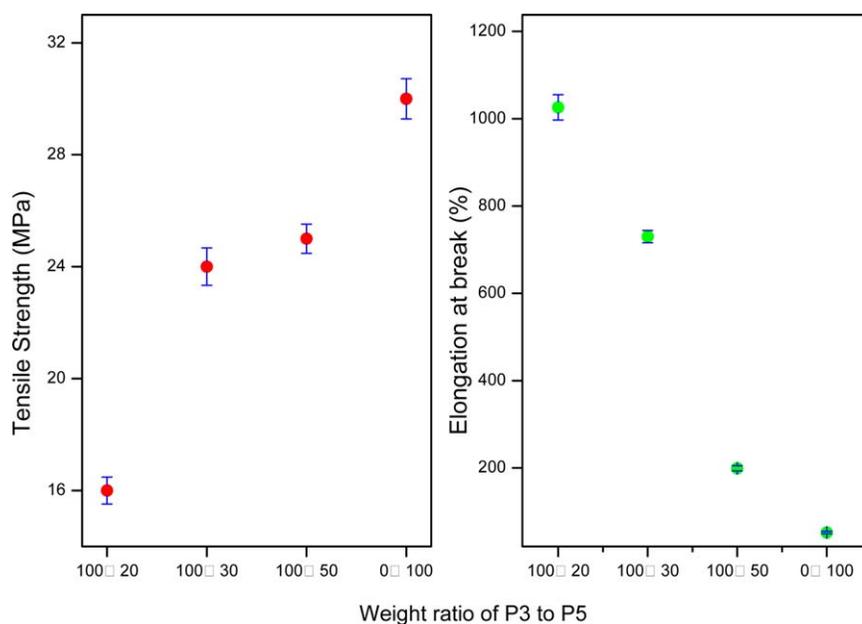
**Figure 7.** Mechanical properties of PURs. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Mechanical Properties of PURs with Different Carborane Biphenol Dosage

PURs	PUA	PUB	Carborane-biphenol (wt %)	Tensile strength (T_s) (MPa)	Elongation at break (E_b) (%)
PUR 1	P4	P6	0	9	73
1#	P3	P5 ₀ *	5	24	730
2#	P3	P5 ₁ *	10	22	428
3#	P3	P5 ₂ *	15	14	284
4#	P3	P5 ₃ *	20	6	146

BH of 2580 cm^{-1} demonstrate that hydroxyl-terminated prepolymer P3 is prepared as previously expected.

Characterization of Isocyanate-Terminated Carborane-Containing Prepolymer (P5)

The isocyanate-terminated carborane-containing prepolymer (P5) was prepared employing MDI, TMP, and 1,2-carborane bisphenol. TMP is one of the most universal chain extenders for PURs. It is a triol with active chemical properties, which shows high reactivity with MDI at a lower temperature and forms a great degree of branching chemical substances. In order to synthesize isocyanate-terminated prepolymer, TMP reacted with MDI at the ratio of MDI/TMP = 3.2 : 1, and 1,2-carborane bisphenol was used as a modifier with the amount of 5% of the mass of reactants. At this molar ratio, MDI and TMP could form a great degree of branching chemical substances since TMP was an active hydrogen compound with three functions. If added too much 1,2-carborane bisphenol, there would be a certain damage on the crosslinked structure, and lead to the cross-linking density of resultants decreased, because 1,2-carborane bisphenol was an active hydrogen compound with two functions while TMP was a triol. The obtained P5 was characterized and satisfactory results were obtained. FTIR spectrum of P5 is

shown in Figure 5. The spectra of its reactants, MDI, TMP, and 1,2-carborane bisphenol, are also given in the same figure for comparison. TMP and 1,2-carborane bisphenol exhibit absorption bands at 3335 cm^{-1} and 3402 cm^{-1} , which are ascribed to $-\text{OH}$ stretching vibrations. The bands completely disappear in the spectrum of P5, indicating that the $-\text{OH}$ bonds have been fully consumed by the reaction owing to the ratio of reactants. The absorption bands around 3324 cm^{-1} (urethane N-H stretch), the bands at 1218 cm^{-1} corresponding to $-\text{C}-\text{O}-\text{C}$ and the very strong bands around 1723 cm^{-1} (free urethane C=O) are assigned in the urethane linkages, which prove the existence of $-\text{NHCOO}-$. Moreover, $-\text{NCO}$ of 2272 cm^{-1} and $-\text{BH}$ of 2593 cm^{-1} demonstrate that isocyanate-terminated prepolymer P5 is prepared as previously expected.

Characterization of PUR Containing Carborane (PUR 2)

The PUR chains, in general, have a special architecture. They might be linear, branched, or network. PURs display stereo microstructure and could exist as homopolymers and copolymers. Copolymers might be random, alternating, segmented, block, or graft types. PURs could be crystalline solids, segmented solids, amorphous glasses, or viscoelastic solids.²⁹ The main purpose of this work was to prepare carborane-containing

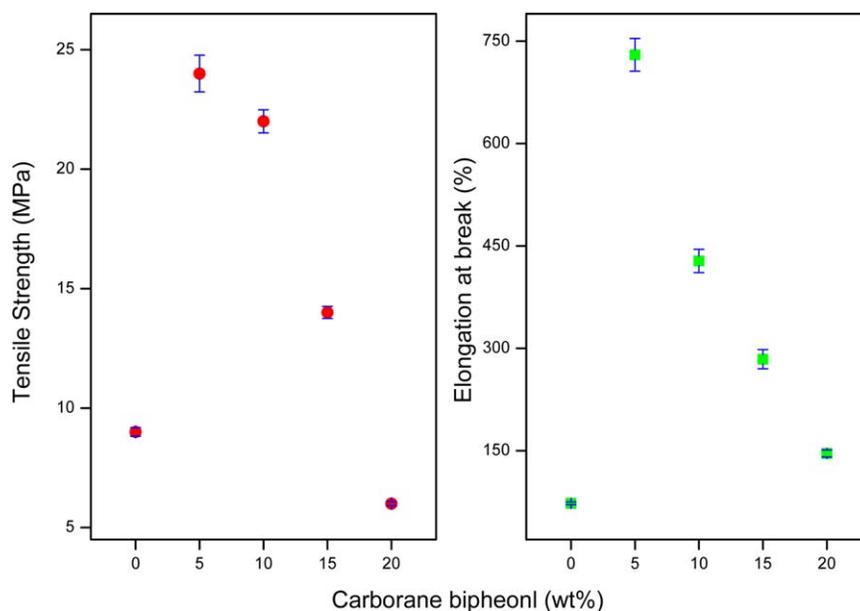


Figure 8. Mechanical properties of PUR 2s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

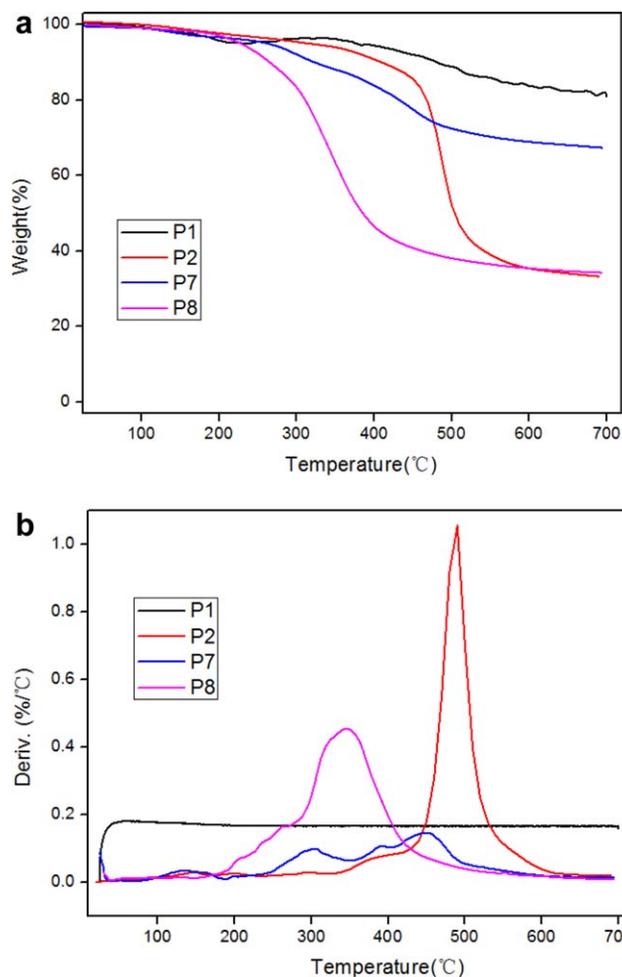


Figure 9. (a) TGA and (b) DTG curves of P1, P7, P8, and P2 in N_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

PURs, which were considered to have excellent high temperature properties. As shown in Figure 1, novel polyurethane (PUR 2) was prepared by P3 and P5, then the crosslink density was improved a lot and formed a great amount of three-dimensional network structures. Carborane-free PUR 1 was also prepared from P4 and P6 in order to compare with PUR 2. FTIR spectra of PUR 1 and PUR 2 are shown in Figure 6. The existence of bands for N–H (3342 cm^{-1}), C=O (1725 cm^{-1}), –C–O–C (1528 cm^{-1}) of the urethane, –BH (2593 cm^{-1}), and the disappearance of –NCO and –OH indicate the formation of PUR 2.

Mechanical Properties

By changing the weight ratio of PUA (P3) and PUB (P5), different properties can be realized. Four kinds of weight ratio of P3 and P5 were chosen to prepare PUR 2 (1#, 2#, 3#, and 4#) and the results of mechanical properties are shown in Table II and Figure 7. It indicates that as the weight ratio of P3 and P5 decreases, namely with the increasing mass of the isocyanate-terminated prepolymer, hardness and tensile strength of PURs will show a trend of increasing, while elongation at break will

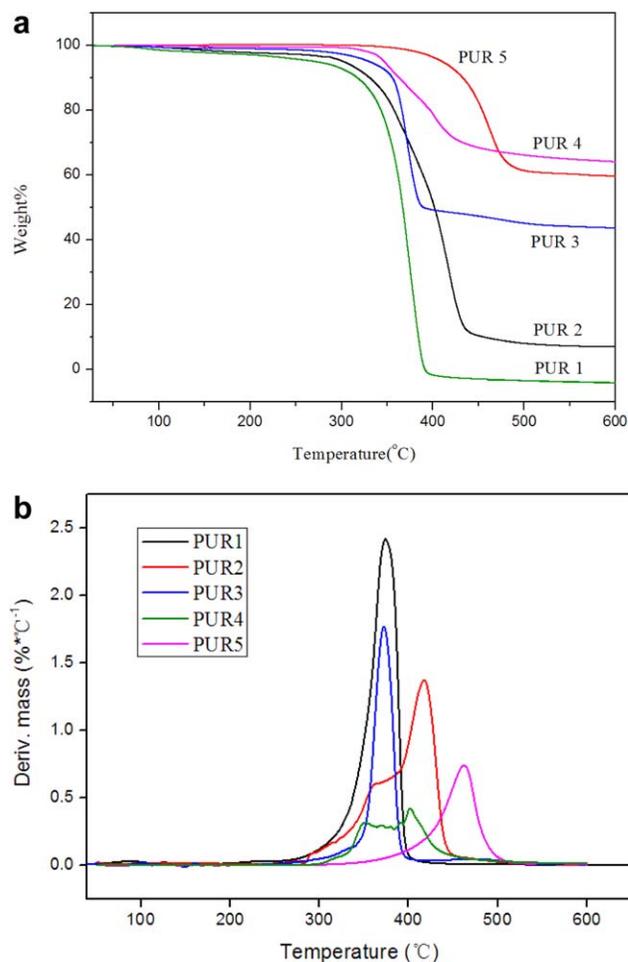


Figure 10. (a) TGA and (b) DTG curves of PURs in N_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

decrease continuously. The standard deviations for mechanical tests are less than 5%.

As more PUB (P5) added, there are more NCO groups in the mixtures, then the crosslink density increases. Due to the cohesion enhanced, the tensile strength is improved obviously. If there is too much PUB, curing reaction cannot be taken completely, and the concentration of –NHCOO– and –NHCONH– boosts, then the resin becomes hard. As hard segment content increases, soft segment content may have smaller proportion and elongation at break will decrease obviously.

Although the weight ratio of P3 and P5 is fixed, in order to obtain the PUR 2 with satisfied mechanical properties, P5₀, P5₁, P5₂, and P5₃ were synthesized with different carborane biphenol dosage. Afterwards, 1#–4# were prepared by P3 and P5₀, P5₁, P5₂, and P5₃, respectively. As a carborane-free PUR, PUR 1 is used for comparing. The results of mechanical properties are shown in Table III and Figure 8. It is seen that as the dosage of carborane biphenol increasing, tensile strength will increase first, and then decrease gradually. The standard deviations for mechanical properties are less than 5%. While using 20 wt % carborane biphenol, the tensile strength of PUR 5 is even lower

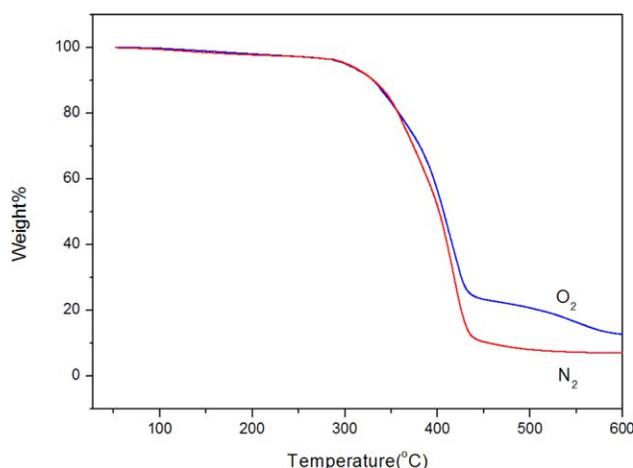
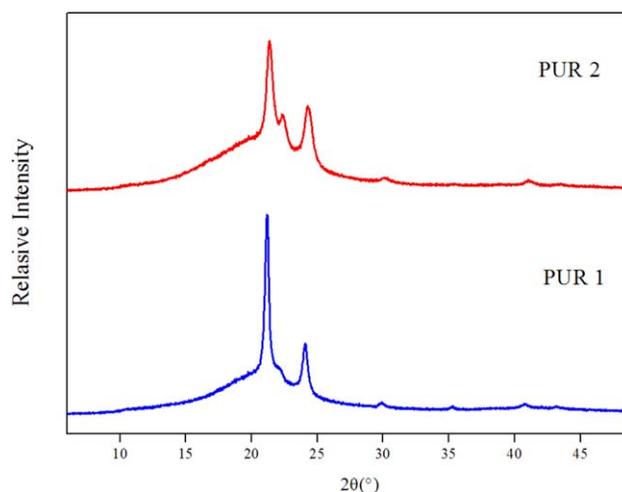
Table IV. Thermal Analysis of Polyarylates and PURs

Products	T_5 (°C)	T_{10} (°C)	T_d (°C)	Y_c at 600°C (%)
P1	376	481	–	81 ^a
P7	269	312	447	68 ^a
P8	231	259	338	34 ^a
P2	308	407	487	33 ^a
PUR 1	180	295	367	0.0
PUR 2	300	331	394	7.4
PUR 3	330	355	373	43
PUR 4	347	363	398	62
PUR 5	410	432	456	59

^aChar yield at 700°C. T_5 : Initial decomposition temperature. T_{10} : Temperature for 10% weight loss. T_d : Maximum decomposition temperature. Y_c : Char yield; weight of polymer remained.

than that of carborane-free resin PUR 1. For elongation at break, as the dosage of carborane biphenol increasing, it may show a trend of decreasing, but is still higher than PUR 1.

Carborane-containing PURs are modified by introducing carborane into the main chains with carborane-containing polyarylate and carborane biphenol. The soft segments in PURs form by long-chain polyesters control the flexibility and softness. Since P1 has a higher molecular weight than PBA, so introducing P1 into P3, it is beneficial to improve flexibility of soft segments for its high molecular weight. Plus, elongation at break is dependent on flexibility of polyurethane chains. As a result, carborane-containing PURs possess higher elongation at break than that of PUR 1. However, as the dosage of carborane biphenol increasing, namely with the increase of rigid groups in polyurethane chains, it can lead to increase of the proportion of hard segment, then elongation at break of PURs will reduce. But comparing with PUR 1, flexibility of PURs is improved by the addition of P1, so elongation at break of carborane-containing PURs is still higher than that of PUR 1.

**Figure 11.** TGA curves of PUR 2 in air and N_2 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 12.** X-ray diffraction patterns of PUR 1 and PUR 2. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The hard segments (composed of diisocyanates and short-chain diols) particularly affect the modulus, hardness, tear strength, and high-temperature resistance. Due to the addition of carborane biphenol into P5, a large amount of rigid groups in hard segment make tensile strength of PURs highly effective. Nevertheless, when the dosage of carborane biphenol exceeds 15 wt %, tensile strength will begin to decrease and the tensile strength is even lower than that of PUR 1. This is because carborane-bisphenol was bifunctional hydroxyl compound while TMP is trifunctional hydroxyl compound, if too much carborane-biphenol is added, there will be a certain damage on the crosslinked structure formed by MDI and TMP, and lead to decreasing the degree of crosslinking, thereby reducing the tensile strength. Consequently, using 5–10 wt % carborane biphenol is the best choice to obtain PURs with high tensile strength and elongation at break.

Thermal Stability

The TGA and DTG traces under nitrogen atmosphere of both carborane-containing polyarylates (P1, P7, and P8) and carborane-free polyarylate (P2) are shown in Figure 9. There is a peak at the temperature of 45°C on the DTG curve of P1, that is because there some residual solvent (ethanol) used to prepare P1 exists. It is seen that the ultimate char yield of P1 at 700°C is 81% under N_2 , which is much higher than those of P2 (33%), P7 (68%), and P8 (34%). Besides, P1 shows slow weight loss until 700°C, while P2 exhibits obvious degradation temperature at 480°C (T_d). Plus, the 5% and 10% weight-loss temperatures of P1 are 376°C and 481°C, respectively. Both T_5 and T_{10} of P1 are approximately 70°C higher than those of P2. However, T_5 , T_{10} , and T_d of P7 and P8 are both lower than those of P1 and P2, which are attributed to very low molecular weight (Table I). It demonstrates that carborane groups significantly improve thermal stability of polyarylates. If molecular weight of polyarylate is also high, it could be better. Therefore, the thermal stability of P1 which possessed both carborane group and aromatic rings is far more excellent compared to P2, P7 and P8.

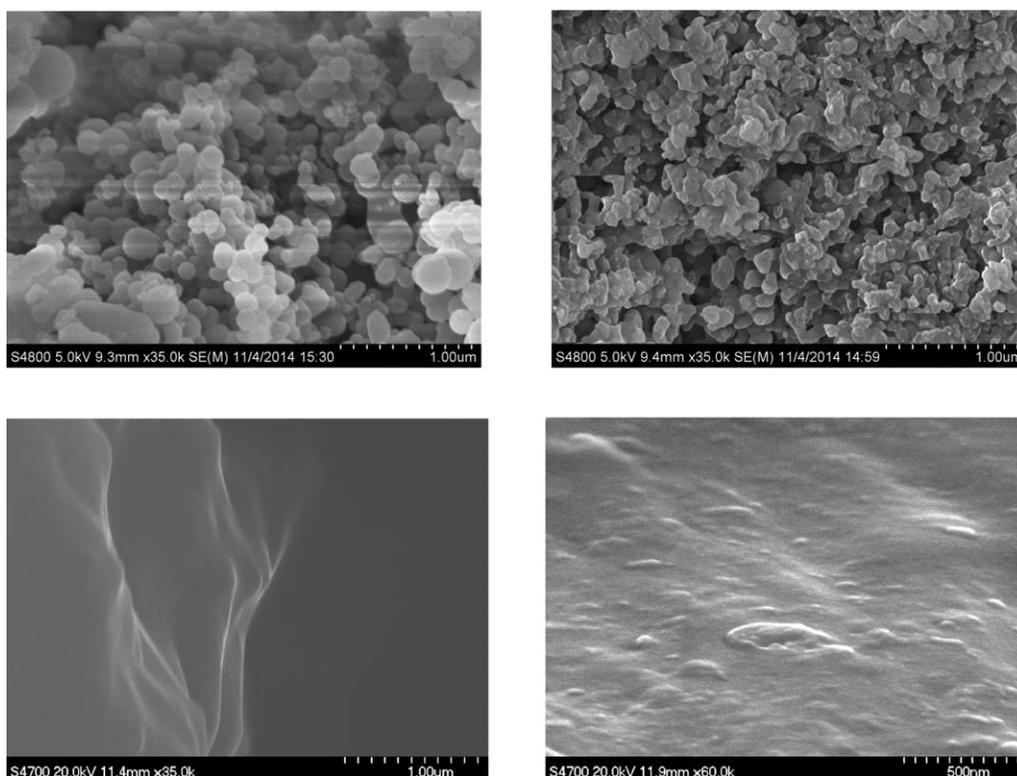


Figure 13. SEM images of (a) P1, (b) P2, (c) PUR 1, and (d) PUR 2.

Figure 10 shows the TGA and DTG traces of carborane-containing PURs prepared from P3 and P5 with different carborane biphenol dosage at the weight ratio of 100 : 30. The TGA trace of carborane-free PUR 1 is also given in the figure for comparison. From Table IV it can be seen that PUR 1 loses 5% weight at 180°C, while the lowest T_5 of carborane-containing PURs is 300°C. Moreover, T_{10} and T_d of carborane-containing PURs are all much higher than those of PUR 1. At 600°C, PUR 1 had a complete degradation while the char yield of PUR 4 was up to 62%, implying that the introduction of carborane into PUR dramatically increases the degradation temperature and the char yield. In addition, the more dosage of carborane biphenol, the more excellent thermal stability presented. Especially, as 20 wt % of carborane biphenol added, T_d was up to 456°C and the char yield was nearly 60%.

However, after analyzing the data of PUR 4 and PUR 5, founded that T_5 , T_{10} , and T_d of PUR 4 are less than PUR 5 while coke formation exceeds about 3%. It shows that at the temperature of below 450°C, PUR 5, which contains 20 wt % carborane biphenol, has a better thermal resistance than PUR 4. But at the temperature of above 450°C, with the temperature increasing, PUR 4 is better to form the coke. It supposes that more than 15 wt % carborane biphenol added, the polymerization could not react completely. A large amount of free carborane biphenol could not join in the PUR chain to guarantee and improve the thermal stability. Therefore, the amount of carborane biphenol cannot exceed 20 wt %.³⁰

From Figure 11, the weight loss of PUR 2 in air is higher than that in nitrogen. It is suggested that while B–H turns into B–O–B and B–B by the thermal oxidation, oxygen only comes from the oxygen-containing groups in the macromolecules under nitrogen; but under air, oxygen comes not only from the oxygen-containing groups in the macromolecules, but also comes from the air and moisture, so weight increment occurs under air.

XRD Analysis

X-ray diffraction measurement is an effective way to study the microstructure of crystalline substance. Figure 12 shows the XRD patterns of the synthesized carborane-containing PUR 2 and carborane-free PUR 1. The obtained XRD patterns demonstrate that the synthesized PURs have partially crystalline structures. Both of the PURs' patterns present three crystal peaks at $2\theta=20\sim 25^\circ$. Main peak is corresponded to hydrogen bonding between urethane linkages of PURs. The peaks of PUR 2 are smaller and wider than those of PUR 1. Carborane-containing PUR presents lower crystallinity compared to carborane-free PUR, because great steric hindrance of cage-like carborane structure in the main chain of PUR 2 reduces the degree of spatial ordering, and thus crystallization is hindered.

Fractured Surfaces Observation

Further evidence of the modification by carboranes in PARs and PURs was provided by SEM images. Figure 13 shows the SEM pictures of carborane-free polyarylate (P2) [Figure 13(a)], carborane-free polyurethane (PUR 1) [Figure 13(c)], carborane-containing polyarylate (P1) [Figure 13(b)], and carborane-

containing polyurethane (PUR 2) [Figure 13(d)]. The SEM images [Figure 13(a,b)] of polyarylates show that there is cluster structure in both P1 and P2. The cluster of P2 is composed of something like small balls, while the cluster of P1 consists of some flat balls. This is due to the fact that great steric hindrance of cage-like carborane structure in the main chain of P1 destroys the integrity of the original structure. The SEM images [Figure 13(c,d)] of polyurethane shows that there is some difference of structure between PUR 1 and PUR 2. The image of carborane-free PUR fracture surface was flat and glossy while the other was not smooth, there are some little papules that exists on the surface of PUR 2, but it is still with a certain planeness. The result is corresponding to the study of crystallization, that is to say, polyurethane remains its original structure, although carborane structure destroys the structure of polyurethane a little.

CONCLUSIONS

Novel segmented carborane-containing polyurethane (PUR 2) was obtained from P3 and P5 at the weight ratio of 100 : 30. Carborane-containing polyarylester (P1) was synthesized and well characterized, which was used to prepare hydroxyl-terminated polyurethane (P3). 1,2-carborane bisphenol was utilized to prepare isocyanate-terminated polyurethane (P5). The introduction of carborane cage into both soft and hard segments of polyurethane provides a novel method to prepare polyurethane resin which has extraordinary properties such as mechanical property, thermal stability, and crystallinity, etc. TGA study implies that carborane-containing polyurethane owns higher degradation temperature and char yield, and lower degradation rate due to the shielding effect, and great cohesive energy of carborane. The obtained polymer shows excellent mechanical property and thermal stability when 5–10 wt % of carborane is added. The obtained carborane-containing polymer still possesses good crystallinity although introduced large cage-like carborane which owns strong steric hindrance.

Consequently, carborane-containing polyurethane resin is successfully synthesized as a product with excellent thermal stability and mechanical properties. This kind of high-temperature polyurethane has enormous technical and economic value if used in the field of adhesive, especially mixing with different fillers. Under high environmental temperature, outstanding properties are capable of keeping polyurethane stable and expanding its service life.

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