

Preparation, Morphology, and Properties of Polyurethane–Urea Elastomers Derived from Sulphone-Containing Aromatic Diamine

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ABSTRACT: An aromatic diamine containing both sulfone and diphenyl ether groups, bis[4-(4-aminophenoxy)phenyl]sulfone, was synthesized in a two-step way, whose structure was confirmed through Fourier transform infrared spectrometry, nuclear magnetic resonance, and elemental analysis. Then, the obtained BAPS was used as the chain-extender to prepare a polyurethane–urea elastomer, whose morphology, thermal stability and mechanical properties were examined by means of attenuated total reflection,

DSC, thermogravimetric analysis, dynamic mechanical thermal analysis, and stress–strain measurements. The results showed that the PUU elastomer based on BAPS showed good heat-resistance and mechanical properties. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3554–3561, 2007

Key words: polyurethanes; elastomer; synthesis; modification; thermal stability

INTRODUCTION

Polyurethane–urea (PUU) and polyurethane (PU) elastomers are multiblock copolymers with an [A-B]_n-type structure, where A and B represents the soft and hard segments, respectively, which are chemically dissimilar. In general, the soft segment is polyether or polyester macroglycol, while the hard segment forms through extending a diisocyanate with a low molecular weight diamine or diol. Generally, PUU and PU elastomers exhibit a two-phase morphology due to thermodynamic incompatibility between soft and hard segments. It is just the microphase separation that endows them with excellent properties, such as high tensile strength, high flexibility, and toughness. PUU elastomers have relatively higher cohesive urea linkages in the hard segment, and the degree of microphase separation is superior to that of the corresponding PU elastomers. Therefore, thermal and mechanical properties of PUU elastomers are better than those of the conventional PU elastomers.^{1–6} However, PU and PUU materials are generally known to exhibit poor resistance to heat. Their mechanical properties tend to disappear from about 80–90°C, which greatly limits their application in many fields.

Polymers containing both aryl sulfone and aryl ether linkages are generally amorphous and thermoplastic, which have high thermooxidative stability,

and chemical resistance, because of the strong resonant aryl sulfone groups and the hexavalent sulfur.^{7–10} Furthermore, they can maintain excellent physical, mechanical, and electrical properties over a wide temperature range.^{11–14} In recent years, there is much literature about polyamide or polyimide containing sulfone groups,^{15–23} whereas the studies on the modification of PUU or PU with sulfone have been less reported. Filip blended poly(ether sulfone) with PU elastomers.⁸ In Lin's work, a sulfone-containing polyamide (PSA) was synthesized to prepare PU-PSA block copolymers.²⁴

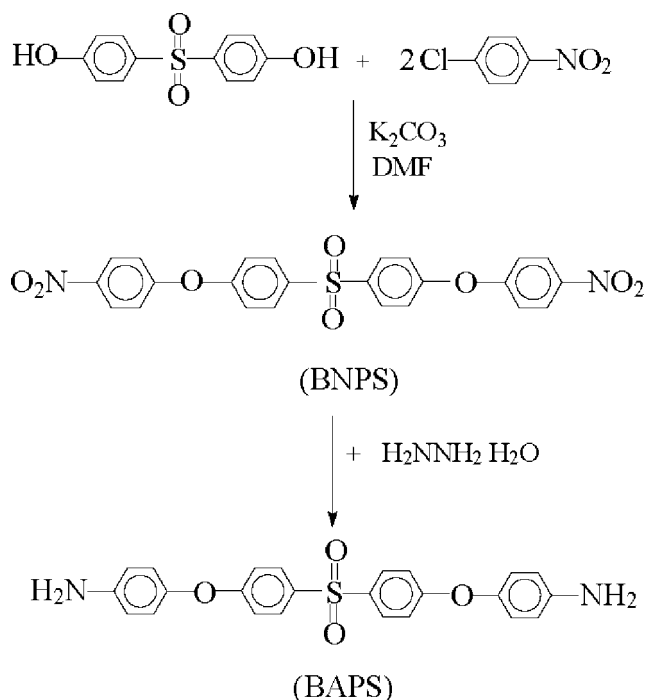
It is well-known that the structure of chain-extender has a significant effect on PUUs or PUs, and some researchers have examined the effects of a chain-extender on the structure, morphology, and properties of PUUs by solution, prepolymer, or model polymer synthesis.^{1,25–33} In this work, a sulfone-containing aryl diamine (BAPS) chain-extender was synthesized to prepare PUUs containing sulfone groups. The obtained PUU elastomers were examined by means of ATR-FTIR, DSC, TGA, tensile testing, and WAXD and their preparation, morphology, and properties were discussed at length.

EXPERIMENTAL

Materials

Bis(4-hydroxyphenyl)sulfone, 4-chloralnitrobenzene, ethylene glycol monomethyl ether, H₂NNH₂ · H₂O(85%), 1,4-dioxane, anhydrous potassium carbonate (K₂CO₃), methanol, and ethanol were all used as received from

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Scheme 1 Synthesis of bis[4-(4-aminophenoxy)phenyl]sulfone.

Shanghai Chemical Reagent. Polytetramethylene glycol (PTMG, DuPont) with molecular weight 1000 was dried thoroughly under vacuum over 100°C for at least 2 h before synthesis. Toluene diisocyanate (TDI, Mitsui Takeda Chemical) was used as received. *N,N*-dimethylformamide (DMF, Shanghai Chemical Reagent) was distilled under vacuum after being stirred in anhydrous magnesium sulfate for a week. Methylene-bisortho-chloroaniline (MOCA) was used as received.

Synthesis

Synthesis of bis[4-(4-aminophenoxy)phenyl]sulfone

BAPS was synthesized with reference to Liaw's work (as shown in Scheme 1),²⁰ and yet there were some differences between the synthesis procedures of two sulfone monomers due to the differences of their structure. The yield of BAPS was 71.7%, and its melting point is 186.5°C .

Step 1. Synthesis of bis[4-(4-nitrophenoxy)phenyl]sulfone. 2,2-Bis(4-hydroxyphenyl)sulfone (100 g, 0.4 mol), 4-chloronitrobenzene (126 g, 0.8 mol), K_2CO_3 (120 g, 1.21 mol), and DMF (700 mL) were taken into 1000-mL round-bottom flask equipped with a mechanical stirrer, a thermometer, and a condenser. After being kept at $140\text{--}150^\circ\text{C}$ for 10 h, the reaction system was cooled to room temperature and then the mixture was poured into methanol under stirring. One hour later, the crude product was filtered under reduced pressure, washed several times by distilled water, and put

in vacuum oven at 50°C for at least 24 h to provide yellowish powder, bis[4-(4-nitrophenoxy)phenyl]sulfone (BNPS). The productivity was about 84.3%.

Step 2. Synthesis of bis[4-(4-aminophenoxy)phenyl]sulfone. BNPS (98.4 g, 0.2 mol), active carbon (10 g), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1 g), and ethylene glycol monomethyl ether (about 300 mL) were put into three-necked flask with a thermometer, a mechanical stirrer, and a condenser. The system was held at 100°C under stirring for 0.5 h and then $\text{H}_2\text{NNH}_2 \cdot \text{H}_2\text{O}$ (85%, 1 mol) was added through a dropping funnel. After the addition was finished, the reaction was maintained at 105°C for another 8 h. To prevent the product from separating out, the mixture was heat filtered, and then washed by hot ethylene glycol monomethyl ether. The filtrate was neutralized by hydrochloric acid (20%, 300 mL). When white precipitate emerged, ammonia was added to neutralize the excessive hydrochloric acid until the PH value became 11–12. The precipitate was washed with distilled water several times, recrystallized from anhydrous ethanol, and then put into 60°C vacuum oven to constant weight.

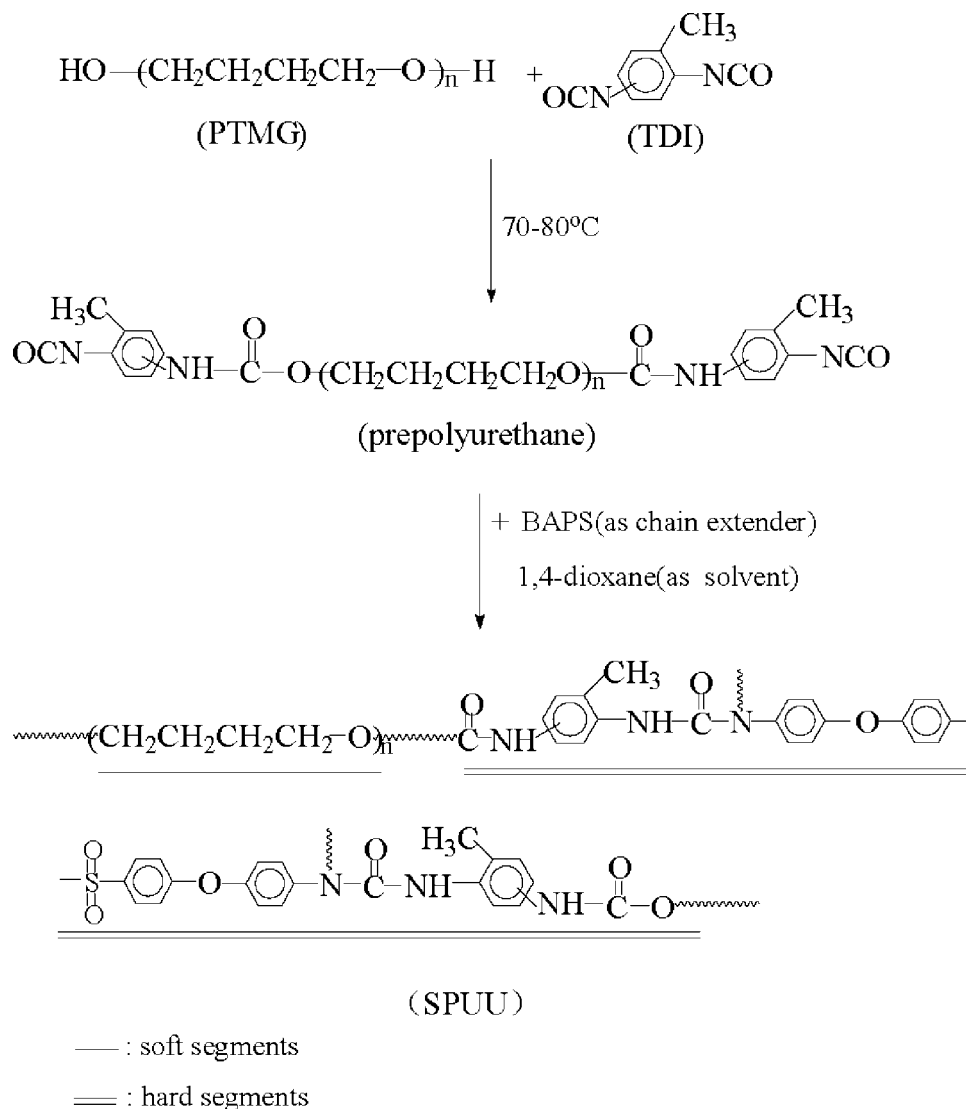
Preparation of PUU elastomers

PUU elastomers were prepared according to Scheme 2.

Step 1. Synthesis of NCO-capped PU prepolymer. TDI (17.4 g, 0.1 mol) was weighed into a 250-mL three-necked round-bottom flask equipped with mechanical stirrer, dropping funnel, and nitrogen inlet. The flask was then placed in water bath at 70°C . The pre-dried PTMG (50 g, 0.05 mol) was added from a constant-pressure dropping funnel into TDI while stirring over a period of 30 min. After completing the addition, the mixture was maintained at $70\text{--}80^\circ\text{C}$ for 2 h with stirring under nitrogen to obtain NCO-capped PU prepolymer.

Step 2: Preparation of PUU. The $-\text{NCO}$ content of PU prepolymer was determined by dibutylamine titration, according to which the exact amount of BAPS as the chain extender was calculated on the basis of $[-\text{NCO}]/[-\text{H}] \approx 1.05 (\text{mol/mol})$. BAPS was dissolved in 1,4-dioxane and was poured into PU prepolymer; at the same time, more 1,4-dioxane was added into the mixture to obtain a 30% (wt %, solid content) solution. Subsequently, the mixture was intensively stirred for several minutes and was vacuum degassed 10 min. Afterwards, the degassed product was poured onto Teflon molds and kept under room temperature for 24 h to produce flexible PUU films. Finally, the films were held in 110°C oven for 3 h and taken into 60°C vacuum oven at least 48 h.

PUU films based on MOCA were prepared in a polymerizing process similar with those derived from BAPS.



Scheme 2 Preparation of sulfone-containing polyurethane-urea elastomer.

Measurements

Fourier transform infrared spectrometry

The Fourier transform infrared spectrometry (FTIR) spectra were recorded on a Paragon 1000 instrument (Perkin-Elmer) over the range 4400–450 cm^{-1} . BAPS powder was ground with KBr and pressed into tablet for transition-FTIR measurements. PUU films were measured by means of attenuated total reflection-FTIR.

Nuclear magnetic resonance spectroscopy

^1H -NMR spectrum of BAPS was recorded on Varian DRX 500 NMR spectrometer with the operating frequency at 400 MHz. The solvent was deuterated dimethyl sulfoxide ($\text{DMSO-}d_6$).

Elements analysis

Elements analysis (EA) of BAPS was performed on 2400 series II CHNS/O Analyzer (Perkin-Elmer).

Differential scanning calorimetry analysis

Differential scanning calorimetry analysis (DSC) analysis was carried out on a PYRIS DSC analyzer (Perkin-Elmer) under a dry nitrogen purge. The PUU samples were first heated from room temperature to 250°C to counteract the thermal history. Three minutes later, the temperature was reduced to -70°C, and then improved to 250°C at the heating rate of 10°C/min. Sample weights were 10–15 mg.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the PUU elastomers were performed on a TGA 7 instrument (Perkin-Elmer) at the heating rate of 20°C/min in nitrogen atmosphere.

Mechanical properties

Tensile properties of PUU films were investigated with an Instron Model 4465 Universal Testing instru-

ment. The crosshead speed was 500 mm/min with a full load of 10 kg. The specimens were $20 \times 4 \times 0.5\text{--}1\text{ mm}^3$. The results reported were the mean values for five replicates. Hardness measurement was carried out with a calibrated Shore A Durometer at 23°C . All samples were stored in desiccator under room temperature for at least 2 weeks before tensile tests and hardness measurements were performed.

Wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WAXD) was taken on a XRD-6000 X-ray diffractometer (SHIMADZU) with Cu target (40 kV, 15 mA), and the scanning rate was $8^\circ/\text{min}$.

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) of PUU elastomers was carried out on a PIRIS series instrument (Perkin-Elmer) with the operating frequency of 1 Hz, and the heating rate of $3^\circ\text{C}/\text{min}$. The operating temperature range was from -100 to 160°C . The PUU specimens were $20 \times 10 \times 0.7\text{--}1\text{ mm}^3$.

RESULTS AND DISCUSSION

Structure of bis[4-(4-aminophenoxy)phenyl]sulfone

The transmission FTIR spectrum of BAPS was presented with that of BNPS as the contrast in Figure 1. In the spectrum of BNPS, there were two strong absorption peaks at about 1583 cm^{-1} (asymmetrical $-\text{NO}_2$ stretch) and 1345 cm^{-1} (symmetrical $-\text{NO}_2$ stretch), which denoted the existence of $-\text{NO}_2$ function. In that of BAPS, however, the two absorption bands disappeared and another two sharp strong peaks at about 3458 , 3369 (aromatic N-H stretch),

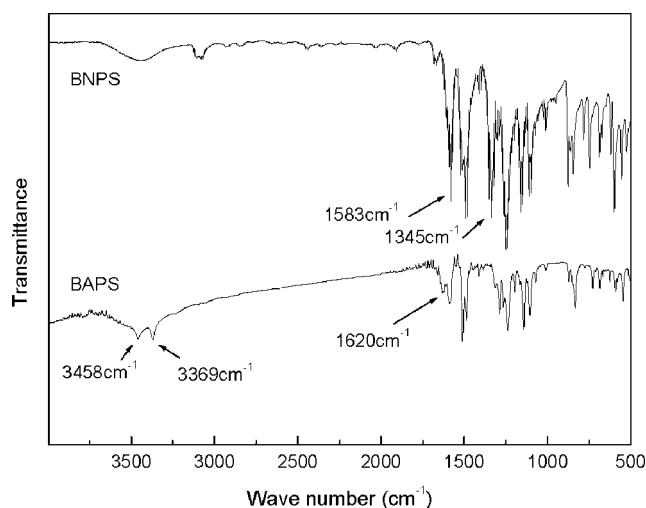


Figure 1 Infrared spectra of bis[4-(4-nitrophenoxy)phenyl]sulfone and bis[4-(4-aminophenoxy)phenyl]sulfone.

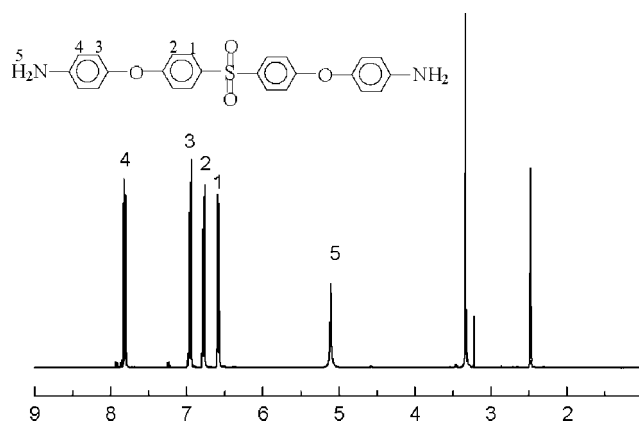


Figure 2 $^1\text{H-NMR}$ spectrum of bis[4-(4-aminophenoxy)phenyl]sulfone.

and 1620 cm^{-1} (N-H bond) appeared. This indicated that the $-\text{NO}_2$ in BNPS had been deoxidized into $-\text{NH}_2$.

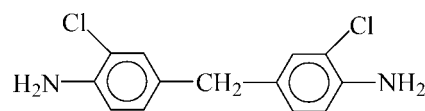
$^1\text{H-NMR}$ spectrum of BAPS (Fig. 2) showed aromatic protons at $\delta = 6.573$ and 6.594 ppm (d, 4H), 6.768 and 6.792 ppm (d, 4H), 6.944 and 6.968 ppm (d, 4H), 7.805 and 7.828 ppm (d, 4H), respectively. The peak at 5.110 ppm (s, 4H) was assigned to the protons of $-\text{NH}_2$.

Moreover, EA of BAPS showed good agreement with the theoretical values (Table I). Therefore, it can be concluded from the results of FTIR, $^1\text{H-NMR}$, and EA that the chemical structure of the obtained BAPS conformed to the expectation.

Preparation of PUU elastomers

PUU elastomers were prepared in a two-step polymerization procedure without catalyst, that is, NCO-capped PU prepolymer was synthesized at first and then was chain-extended by BAPS or MOCA. In this work, MOCA was selected as the contrast with BAPS since it is a typical chain extender and most used in the preparation of PUU elastomers.

In the following text, PUUs based on BAPS and MOCA are designated as SPUU and MPUU, respectively, unless noted especially.



It took about 3 h for SPUU films to cast from the polymer solution while for MPUU films it spent at least 5 h, which showed that the reactivity of BAPS with PU polymer was higher than that of MOCA. In MOCA molecules (as shown in above figure), there are chlorine atoms adjacent to $-\text{NH}_2$ groups. The electrophilic

TABLE I
Elemental Analysis Results of 2,2-Bis[4-(4-aminophenoxy)phenyl]sulphone

C (wt %)		H (wt %)		N (wt %)		O (wt %)		S (wt %)	
Theo. ^a	Test. ^b	Theo.	Test.	Theo.	Test.	Theo.	Test.	Theo.	Test.
66.67	66.46	4.63	4.81	6.48	6.29	14.81	14.98	7.41	7.12

^a The theoretical value.

^b The tested value.

effect and steric hindrance effect of chlorine atoms weakened the reactivity of hydrogen atoms in $-\text{NH}_2$ groups, while in BAPS molecule, there were not such effects, so the reactivity of MOCA with the NCO-capped PU is lower than that of BAPS.

In addition, in the preparation of PUU films a solvent was added to obtain a polymer solution to cast smooth films, because films cast from bulk polymer tend to be rough as a result of the formation of some air bubbles.

The PUU films were hold in 110°C oven for 3 h in order that excessive $-\text{NCO}$ would react with urethane or urea groups to produce some chemical cross-linked bonds and then gain better mechanical properties.

FTIR spectrometry of PUUs

Figure 3 displayed the FTIR spectra of PUUs. Both of them showed intense absorption bands of urethane carbonyl at 1720 cm^{-1} ($\text{C}=\text{O}$) and bands at $3400\text{--}3300\text{ cm}^{-1}$ ($\text{N}-\text{H}$ stretch). In addition, the bands at 2940 and 2856 cm^{-1} were ascribed to aliphatic groups ($\text{C}-\text{H}$ stretch), while the bands of ether was found in the range of $1100\text{--}1300\text{ cm}^{-1}$. All above the absorption bands indicated the typical characteristics of PUU. For SPUU, specific vibrations of the sulfone group should have appeared in the range of $1350\text{--}1300\text{ cm}^{-1}$ and $1160\text{--}1120\text{ cm}^{-1}$. In the spectrum of SPUU, the

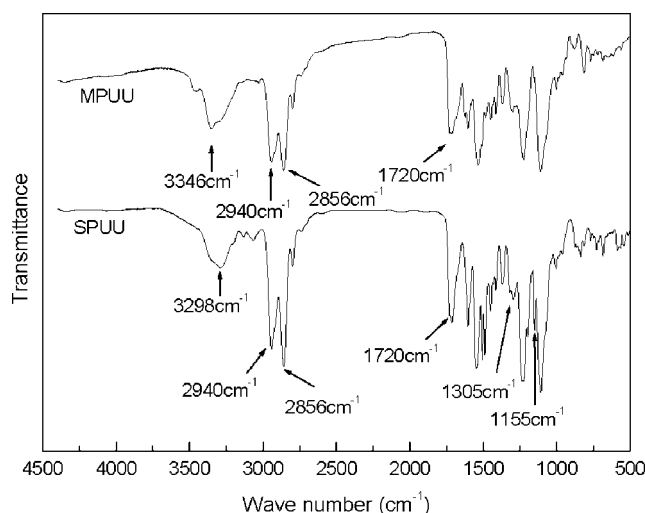


Figure 3 Infrared spectra of polyurethane-ureas.

absorption band at 1305 and 1155 cm^{-1} appeared, which indicated that SO_2 groups have been introduced into the backbone of PUUs.

Thermal stability of PUU elastomers

The thermal stability of PUUs was evaluated by TGA. Typical TG (thermogravimetry) and DTG (derivative thermogravimetry) curves of SPUU and MPUU were shown in Figures 4 and 5, respectively. Detailed results, such as $T_{d5\%}$ (the temperature corresponding to 5% weight loss), $T_{d50\%}$ (the temperature corresponding to 50% weight loss), $T_{\text{max}1}$ (the temperature of maximum weight loss percentage at the first stage), and $T_{\text{max}2}$ (the temperature of maximum weight loss percentage at the second stage), were shown in Table II.

The typical temperature values of SPUU were higher than those of MPUU (Table II). Moreover, the thermal degradation rate of SPUU is lower than that of MPUU (Fig. 4). Obviously, the introduction of sulfone linkages and more aryl rings into PUU backbone led to a higher thermal stability.

According to the DTG plots in Figure 5, SPUU and MPUU elastomers decomposed in a two-stage pattern, which agreed with previous work. Petrovic³³ indicated that PU materials have at least two stages of degradation and that the thermal degradation initiates from the urethane and urea groups of hard seg-

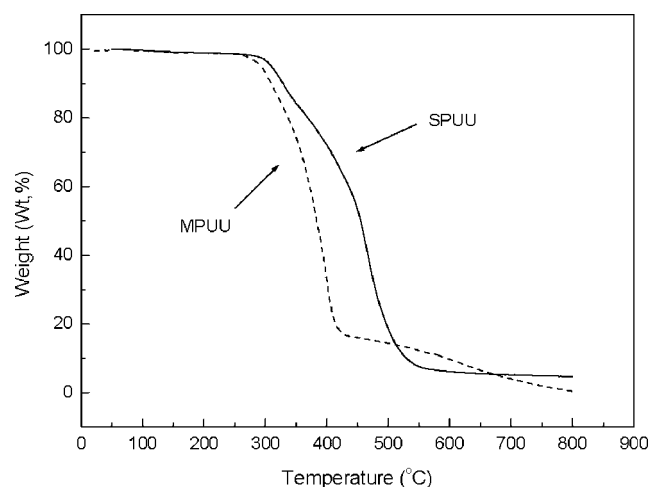


Figure 4 TG analysis of polyurethane-ureas.

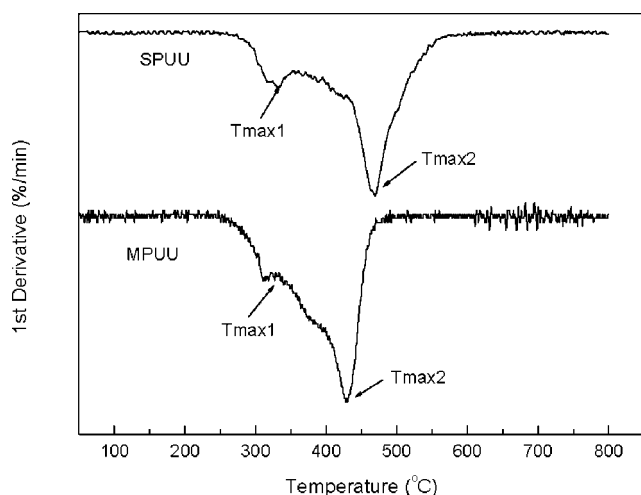


Figure 5 DTG curves of polyurethane-ureas.

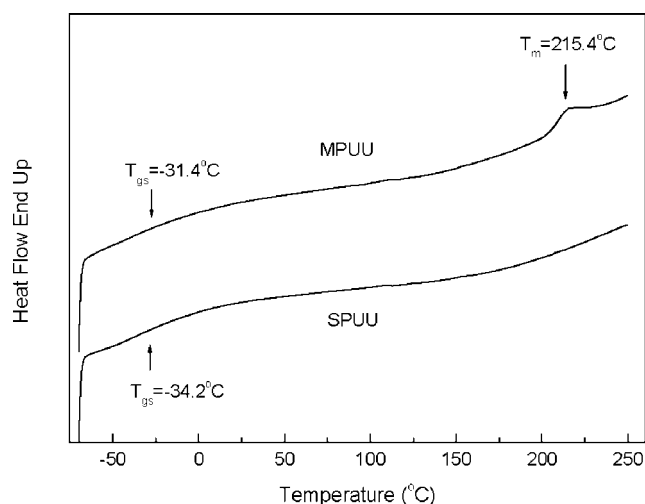


Figure 6 DSC curves of polyurethanes.

ments, followed by the degradation of the soft segments.

Since the hard segments decompose at first in the thermal degradation of PUU materials, the structure of hard segments has an important effect on their heat resistance. It is well-known that the hard segments of PUs are composed of diisocyanate and chain extender; therefore, the thermal stability is expected to improve by utilizing a chain extender containing groups with high heat resistance. In this work, after the chain extender containing aryl sulfone groups was introduced into hard segment, the thermal stability of PUUs had been exactly improved as expected.

Crystallizability of PUU elastomers

From DSC analysis (Fig. 6), an endothermic peak at 215.4°C was found in the DSC curve of MPUU, while in that of SPUU, no such endothermic peak appeared. This indicated that the crystalline of PUU elastomers had been destroyed due to the introduction of aryl sulfone and aryl ether linkages into the backbones.

In addition, the WAXD patterns of PUUs were measured, as shown in Figure 7. There was a peak at about $2\theta = 19.5^\circ$ in the diagram of MPUU but in that

of SPUU film only a small halo was found, which further indicated that there were some local order configuration or microcrystalline in MPUU while SPUU was almost amorphous.

According to previous studies, microcrystals can form in PU hard segments on the condition that films cast from polymer solution. In this work, it was probably due to the introduction of sulfone groups and more rigid benzene rings that weakened the flexibility of molecular chains and thereby disrupted the crystallization capacity of hard segments, which resulted in the amorphism of SPUU.

Tensile properties of PUU elastomers

The tensile curves of both SPUU and MPUU showed typical characters of elastomers (as shown in Fig. 8). The stress at 100% strain, ultimate strength, and hard-

TABLE II
TGA Results of Polyurethane-Urea Elastomers

Sample	$T_{d5\%}$ (°C) ^a	$T_{d50\%}$ (°C) ^b	T_{max1} (°C) ^c	T_{max2} (°C) ^d
MPUU	295	400	311	427
SPUU	310	455	332	469

^a The temperature corresponding to 5% weight loss.
^b The temperature corresponding to 50% weight loss.
^c The temperature of maximum weight loss percentage of the first stage.
^d The temperature of maximum weight loss percentage of the second stage.

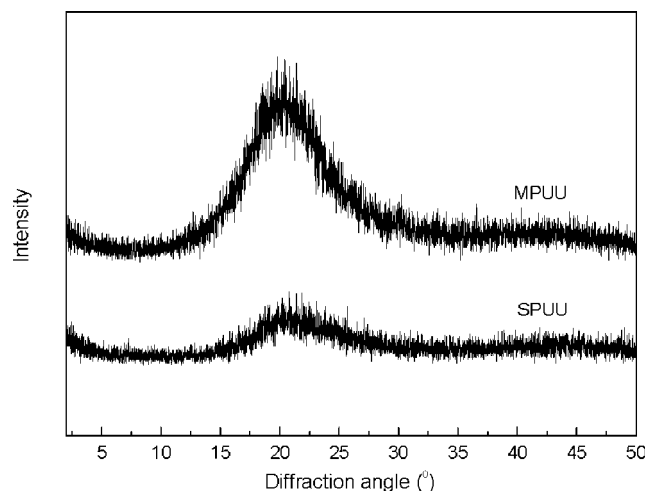


Figure 7 Stress-strain curves of polyurethane-urea elastomers.

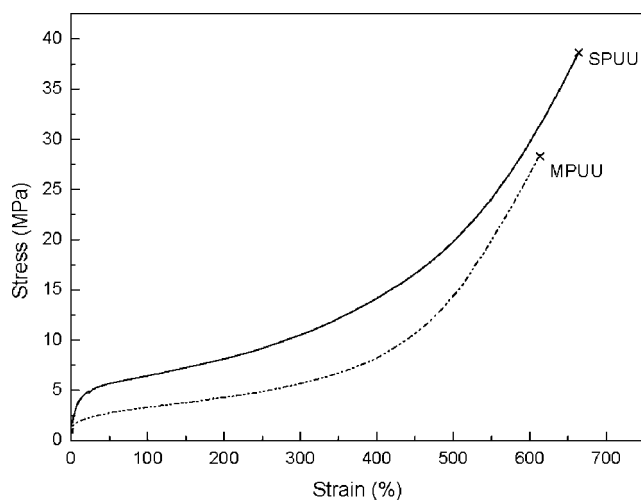


Figure 8 WAXD diagrams of polyurethane-ureas.

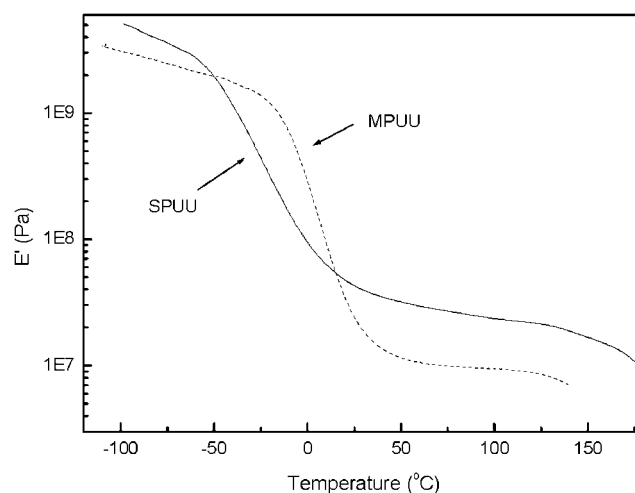


Figure 9 DMTA curves of polyurethane-urea elastomers.

ness of SPUU were superior to that of MPUU. Furthermore, SPUU elastomer also showed higher break elongation than MPUU, merely in a little degree (as listed in Table III).

The properties of PUU elastomers imparted by aromatic diamine chain extenders may be explained on the basis of groups present in the diamines. Compared with MOCA, there were sulfone linkages and more rigid benzene rings in the structure of BAPS. The improved ultimate strength and hardness of SPUU was probably attributed to the introduction of more rigid aromatic rings.

What's more, the improvement of ultimate strength and hardness may be also attributed to the difference between the molecular weight of BAPS and MOCA. The BAPS has higher molecular weight and more rigid benzene rings than MOCA, so if they were introduced at the same molar ratio, the hard segment content of PUU derived from BAPS would be higher than that of MPUU. It is known that the hard domains provided both physical crosslink sites and filler-like reinforcement to the soft segment matrix, so the ultimate strength and hardness generally were enhanced with the increase of hard segment.^{1,34-38}

In addition, the break elongation of SPUU was just a little higher than that of MPUU perhaps due to the little difference between their morphology; in other words, the introduction of BAPS increased the hard

segments length, thereby improving the microphase separation degree of PUU elastomer at some degree.

Consequently, the effect of hard segments on the flexibility of soft segments became weakened, that is, soft segments became more flexible. This result was consistent with the results of DSC analysis (as shown in Fig. 6), in which the glass transition temperature of soft segments (T_{gs}) of SPUU was a little lower than that of MPUU.

Viscoelastic properties of PUU elastomers

Viscoelastic properties of PUU films were determined by DMTA analysis. It has been observed from E' (storage modulus) curves that both samples showed dynamic mechanical behavior of typical elastomer, as shown in Figure 9. Both PUU films showed wide rubber plateau after soft segment glass transmission zone. However, the storage modulus of SPUU elastomer was higher than that of MPUU. Furthermore, SPUU elastomer could retain most strength over 150°C, but then the strength of MPUU began to become weak from about 120°C. This showed that the former exhibited better mechanical property at high temperature than the latter. In other words, the thermal stability of SPUU elastomer was higher than that of MPUU, due to the introduction of sulfone groups and more aromatic rings.

In addition, it has been found that the soft segment glass transition of SPUU was lower than that of MPUU, which agreed with the results of DSC analysis in previous section.

TABLE III
Mechanical Properties of Polyurethane-Urea Elastomers

Sample	Stress at 100% strain (MPa)	Ultimate strength (MPa)	Break elongation (%)	Hardness (Shore A)
MPUU	4.3	30.4	615	74
SPUU	6.8	38.5	660	85

CONCLUSIONS

BAPS has been successfully synthesized by a two-step method. The results of FTIR, ¹H-NMR, and ele-

mental analysis showed that its composition and structure agreed with the expectation.

The PUU elastomers derived from BAPS exhibited high heat resistance and mechanical properties probably due to the incorporation of aryl sulfone and aryl rings according to the results of TGA, DSC, DMA, and stress-strain measurements.

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