

Characteristics of the Degradation and Improvement of the Thermal Stability of Poly(siloxane urethane) Copolymers

Jeh-Taut Yeh,¹ Yao-Chi Shu²

¹Graduate School of Polymer Engineering, National Taiwan University of Science and Technology, Taipei, Taiwan, Republic of China

²Department of Polymer Materials, Vanung University, Chung-Li, Tao-Yuan 320, Taiwan, Republic of China

Received 26 August 2007; accepted 27 June 2008

DOI 10.1002/app.29023

Published online 26 October 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: This work investigates the characteristics of the thermal degradation of poly(ether urethane) (E-PU) and poly(siloxane urethane) (S-PU) copolymers by thermogravimetric analysis (TGA) and thermogravimetric analysis/Fourier transform infrared spectroscopy (TG-FTIR). The stage of initial degradation for E-PU was demonstrated as a urethane-B segment consisting of 4,4'-diphenylmethane diisocyanate (MDI) and 1,4-butanediol. Moreover, the urethane-B segment in the copolymers had the lowest temperature of degradation (ca. 200°C). The degradation of E-PU was determined by TGA and TG-FTIR analyses and had three stages including seven steps. Although the soft segment of S-PU possessed the thermal stability of polydimethylsiloxane (PDMS), the unstable urethane-B segment existed in S-PU. Therefore, the initial degradation of S-PU appeared around 210°C. The four stages of degradation of S-PU involved eight steps, as

revealed by TG-FTIR, which identified the main decomposition products: CO₂, tetrahydrofuran, and siloxane decomposition products. The imide group with high thermal stability was to replace the urethane-B segment of S-PU, which had the lowest thermal stability herein. The poly(siloxane urethane imide) (I-PU) copolymer around 285°C exhibited a high initial temperature of degradation, and the initial degradation occurred at the urethane-S segment consisting of MDI and PDMS. The degradation of I-PU was similar to that of S-PU and had four stages including six steps. Moreover, the degradation region of the imide group between 468 and 625°C was merged into the degradation stage of the siloxane decomposed products. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 2616–2628, 2010

Key words: degradation; polysiloxanes; polyurethanes

INTRODUCTION

Silicone rubber based on polydimethylsiloxane (PDMS) has been used in various fields, such as the automobile and machinery industries. The PDMS backbone consists of alternating silicon and oxygen atoms with two methyl groups attached to each Si atom. The chemical bonds of the PDMS backbone have Si–O, Si–C, and a few C–C bonds. The siloxane bond (Si–O) brings many special properties because of its high bond angle and flexible bond around the oxygen atom, which make the methyl side group easy to rotate around the backbone axis. The 50% ionic characteristics from the siloxane backbone cause the high stability PDMS. The oxygen atom acts as an electron drain, increasing the stability even in the Si–CH₃ bonds, and makes the methyl group slightly polarized. The partly ionic siloxane is

also susceptible to electrophilic or nucleophilic attacks, and this is further enhanced by the high bond angle at the oxygen atom, which leads to little steric hindrance.^{1–4} The bond energy of the side group becomes smaller as the size of the side group increases (e.g., Si–CH₃, 79 kcal/mol; Si–C₂H₆, 51 kcal/mol). The high bond energy of the CH₃ side group makes a contribution to the thermal stability of PDMS.^{5,6}

Several scholars have investigated the thermal degradation of PDMS. Lewis⁷ studied the deleterious effect of a residual basic catalyst on the thermal stability of PDMS and found that the existence of active chain ends induced an ionic breakdown mechanism at temperatures below the depolymerization temperature. Wright et al.⁸ indicated that the amounts of impurities caused the difference in the thermal stability of two fluorinated siloxane polymers. Murphy et al.⁹ examined the degradation products of PDMS by isothermal measurement. Thomas and Kendrick¹⁰ were concerned about the thermal degradation and activation energy of catalyst-free PDMS in controlled atmospheres. However, the characteristic study of the thermal degradation and thermal stability of poly(siloxane urethane) (S-PU) copolymer is now deficient. Furthermore, the thermal degradation of

Correspondence to: J.-T. Yeh (jyeh@tx.ntust.edu.tw).

Contract grant sponsor: Department of Industrial Technology, Ministry of Economic Affairs, Republic of China, Taiwan; contract grant number: 95-EC-17-A-11-S1-057.

ether-type polyurethane has been reported in several studies,^{11–15} but its initial degradation is unclear because of the unknown behavior of degradation on the shoulder peak of thermogravimetric analysis (TGA).

Although a TGA instrument is suitable for the investigation of the degradation characteristics, it is not enough to analyze the degradation mechanism of materials. Thermogravimetric analysis/Fourier transform infrared spectroscopy (TG–FTIR) is a powerful device for identifying the volatile products of degradation. Thus, it can help us to study the process of pyrolysis. TG–FTIR simultaneously provides thermogravimetry/differential thermogravimetry (TG–DTG) curves and the Fourier transform infrared (FTIR) spectrum of the gas. The FTIR spectrum, coupled with the TG–DTG curves, can be used to examine the scission of segments in the polymer chains and simulate the thermal degradation steps. The TG–DTG and TG–FTIR analyses herein were employed to determine the thermal stability and degradation steps of poly(ether urethane) (E-PU) and S-PU copolymers. Furthermore, the imide group was incorporated into the main chain of S-PU in an attempt to increase the thermal stability of S-PU. The characteristics and steps of degradation for the copolymer poly(siloxane urethane imide) (I-PU) were investigated with TG–DTG and TG–FTIR analyses.

EXPERIMENTAL

Materials

The monomers, 4,4'-diphenylmethane diisocyanate [MDI; weight-average molecular weight (M_w) = 250; Aldrich, USA], 1,4-butanediol (1,4-BD; M_w = 90; TCI, Tokyo, Japan), OH-terminated PDMS (M_w = 1800; Shin-Etsu, Tokyo, Japan), and poly(tetramethylene glycol) (PTMG; M_w = 2000; Aldrich), were used to synthesize E-PU and S-PU copolymers. 3,3',4,4'-Sulfonyldiphthalic anhydride (DSDA; M_w = 358; TCI) reacted with the isocyanate group to form the I-PU copolymer. Solvents, including *N,N*-dimethylformamide (DMF; Tedia) and tetrahydrofuran (THF; Fisher, Fair Lawn, NJ), were employed in these systems. Furthermore, di-*n*-butyltin dilaurate (T-12; TCI) and triethylene amine (TEA; TCI) were used as catalysts in the syntheses of the S-PU and I-PU copolymers, respectively.

Preparation

E-PU was synthesized by a one-step method in the solvent DMF. A 250-mL reaction flask, equipped with a stirrer, a dropping funnel, and a four-way cock, was used for the polymerization. The monomers, MDI, PTMG, and 1,4-BD, and the solvent

DMF were put into the flask at 75°C with stirring for 2–3 h. As the viscosity increased gradually, the solvent DMF was put into the flask to adjust the viscosity for a sample with a solid content of 30 wt %.

S-PU was also carried out by a one-step method in a mixed solvent (DMF/THF). The S-PU monomers, consisting of MDI, PDMS, and 1,4-BD, in the mixed solvent were put into the flask at 55°C to react for 1.5–2 h. Subsequently, the T-12 catalyst (0.1 wt % of the net weight of the monomer) was placed in the solution with stirring for 2–3 h. When the viscosity gradually increased, the solvent DMF was added to the flask stepwise to adjust the viscosity for a sample with a solid content of 30 wt %. I-PU is similar to S-PU; the monomers, however, are composed of MDI, PDMS, and DSDA. Furthermore, the reaction adopted 0.2 wt % triethylene amine as the catalyst. The compositions and structures for the S-PU and I-PU copolymers are presented in Figure 1 and Table I.

Measurement: TGA and TG–FTIR

TGA (Pyris 1, PerkinElmer, USA) was employed to analyze the thermal degradation of the copolymers. Each sample weighed about 5 mg. The TG–DTG curves were obtained from 50 to 700°C at a heating rate of 10°C/min in a nitrogen atmosphere. TGA was coupled with a Pike 6141 spectrometer to perform the TG–FTIR analysis. Samples were put into the TGA apparatus, and the emitted gases were led to the FTIR spectrometer for identification of the gaseous products in the process of degradation. The scan rate of the FTIR spectrometer was 1 scan per 6 s at 500–4000 cm^{-1} with a resolution of 2 cm^{-1} .

RESULTS AND DISCUSSION

TGA

Degradation of the E-PU polymer

In the preceding works,^{11–15} the degradation of a typical polyurethane consisting of MDI, PTMG, and 1,4-BD has been considered a two-stage degradation on TGA. The first stage of degradation between 200 and 370°C is depolycondensation resulting from the urethane hard segments. The second stage of degradation between 370 and 500°C is the decomposition of the PTMG soft segment. Although the thermogravimetry (TG) and differential thermogravimetry (DTG) curves on TGA present two peaks of the maximum rate and two distinct weight-loss areas, the DTG curve in the first stage always displays a split peak or a shoulder peak. The split peak on the DTG curve has been interpreted as follows: a typical polyurethane undergoes a complex process of degradation¹⁴ or the formation and bursting of CO₂ bubbles

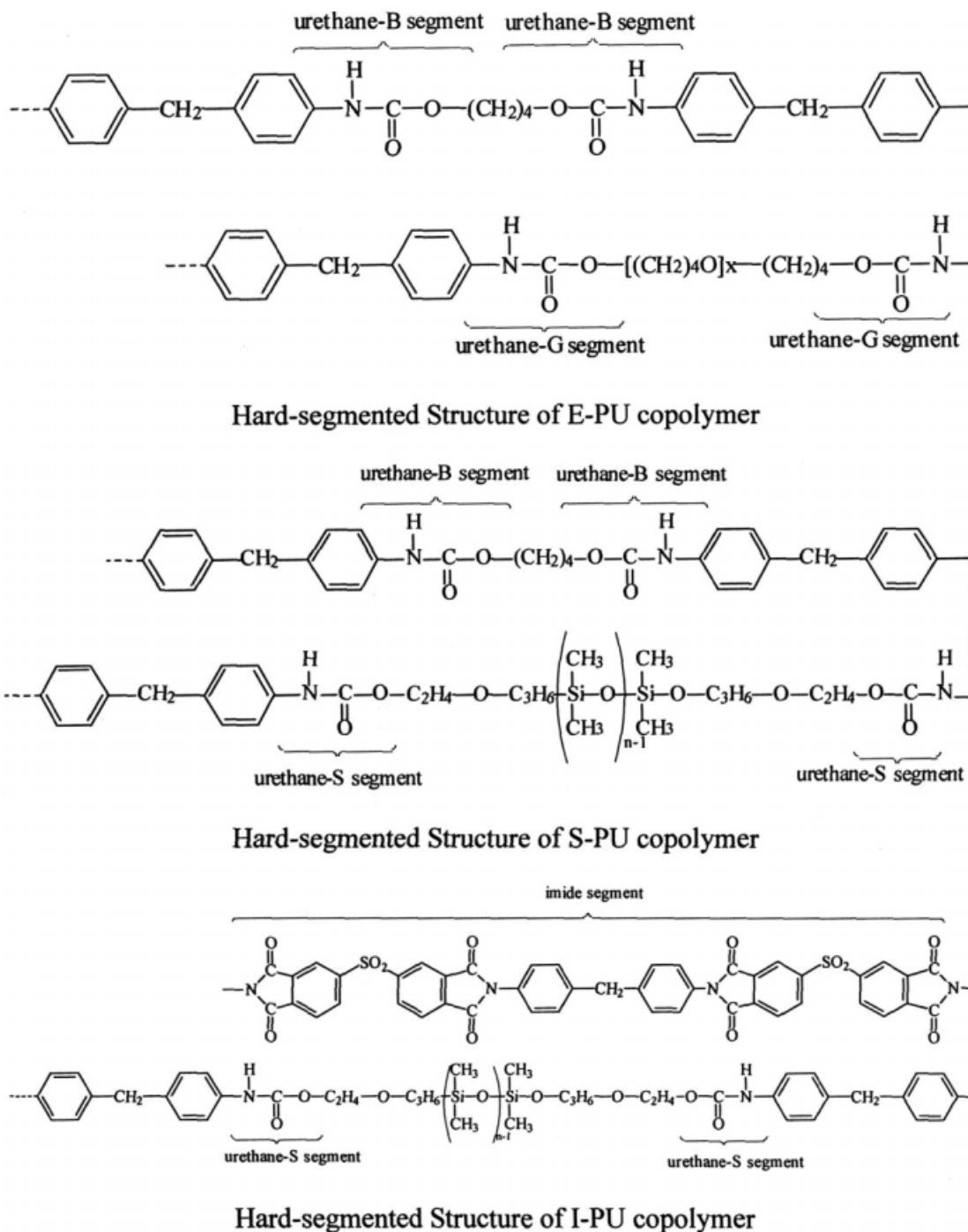


Figure 1 Hard-segment structure of polyurethane copolymers.

during degradation.^{14,15} However, the shoulder in the DTG curve of the polyurethane is unclear.

The TG curve of E-PU exhibits two distinct weight-loss ranges, which reflect two peaks of the maximum rate on the DTG curve, as shown in Figure 2. The first and second stages of degradation of E-PU appear at 200–370 and 370–500°C, respectively. The degradation of E-PU is similar to that of a typical polyurethane because E-PU has the same composition as a typical polyurethane. Notably, the DTG

curve of E-PU in the first stage appears as a shoulder peak at 200–280°C, and then the DTG curve at 280–370°C exhibits the maximum rate peak in the first stage, as shown in Figure 2. The temperatures of the shoulder peak and the maximum rate peak appear at 250 and 330°C. For a typical polyurethane between 200 and 370°C, one stage of degradation resulting from the decomposition of the urethane segment has been reported.^{13,15} Therefore, the degradations of E-PU in the temperature ranges

TABLE I
Chemical Compositions of the Copolymers

Code	Component molar ratio	Hard-segment content (%)	Soft-segment content (%) ^f
E-PU	2/1/1 MDI/1,4-BD/PTMG	22.8 ^a	77.2
S-PU	2/1/1 MDI/1,4-BD/PDMS	24.9 ^b	75.1
Soft-EPU	1/1 MDI/PTMG	11.1 ^c	88.9
Soft-SPU	1/1 MDI/PDMS	12.2 ^d	88.8
I-PU	2/1/1 MDI/DSDA/PDMS	32.3 ^e	67.7

$$^a \text{ E-PU hard-segment content (wt \%)} = \frac{\text{MDI}+1,4\text{-BD}}{\text{MDI}+1,4\text{-BD}+\text{PTMG}} \times 100\%$$

$$^b \text{ S-PU hard-segment content (wt \%)} = \frac{\text{MDI}+1,4\text{-BD}}{\text{MDI}+1,4\text{-BD}+\text{PDMS}} \times 100\%$$

$$^c \text{ Soft-EPU hard-segment content (wt \%)} = \frac{\text{MDI}}{\text{MDI}+\text{PTMG}} \times 100\%$$

$$^d \text{ Soft-SPU hard-segment content (wt \%)} = \frac{\text{MDI}}{\text{MDI}+\text{PDMS}} \times 100\%$$

$$^e \text{ I-PU hard-segment content (wt \%)} = \frac{\text{MDI}+\text{DSDA}}{\text{MDI}+\text{DSDA}+\text{PDMS}} \times 100\%$$

$$^f \text{ Soft-segment content (wt \%)} = 100\% - \text{Hard-segment content (wt \%)}$$

are possibly caused by the dissociation of the urethane-B and urethane-G segments. The urethane-B and urethane-G segments consist of 1,4-BD and MDI and PTMG and MDI, respectively, as shown in Figure 1. However, both of the urethane segments in the regions of the degradation temperature are undecided.

Soft-EPU was prepared from MDI and PTMG to investigate further the degradation temperature of the urethane segments because soft-EPU contains only the urethane-G hard segment. The TG and DTG curves for soft-EPU also display two-stage degradation, as displayed in Figure 3. The first stage of degradation between 280 and 370°C involves an 11% weight loss, which corresponds to the urethane-G content. The second stage of degradation between 370 and 510°C has an 86% weight loss, which corresponds to the content of the PTMG soft segment. Comparing E-PU with soft-EPU in the ranges of the degradation temperature, we have found that the degradation of E-PU at 200–280°C can be attributed

to the degradation of the urethane-B segment, and that at 280–370°C can be assigned to the degradation of the urethane-G segment. Beyond 370°C, degradations of E-PU and typical polyurethane have the same characteristic temperature of degradation, so the degradation is the decomposition of the PTMG soft segment according to their characteristic temperatures, as shown in Table II. Accordingly, the shoulder peak between 200 and 280°C is the first stage of degradation (stage E1), resulting from the urethane-B segments; the second stage (stage E2), the maximum rate peak at 330°C, is the degradation of the urethane-G segments; and between 370 and 500°C is the third stage (stage E3). The characteristic temperatures for the three-stage degradation are shown in Table II. The same segment has a closely characteristic temperature of degradation; that is, the temperatures of the maximum rate peak for E-PU and soft-EPU appear around 330 and 420°C, belonging to the degradation of the urethane-G and PTMG soft segments, respectively.

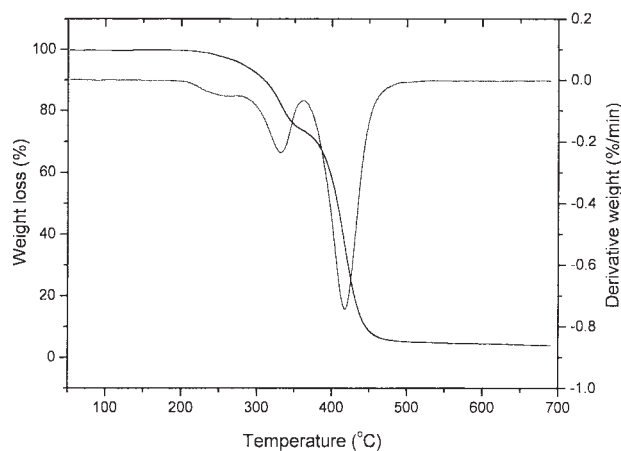


Figure 2 TG and DTG curves of the E-PU copolymer.

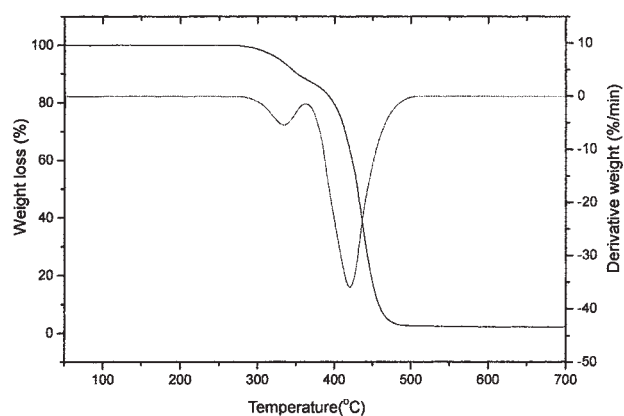


Figure 3 TG and DTG curves of the soft-EPU copolymer.

TABLE II
Characteristic Degradation Temperatures of the Copolymers (All Values in Degrees Celsius)

Code	T_{1i}^a	T_{1s}^b	T_{1m}^c	T_{2i}^a	T_{2m}^c	T_{2s}^b	T_{3i}^a	T_{3m}^c	T_{3s}^b	T_{4i}^a	T_{4s}^b	T_{mw}^d
E-PU	200	250	—	280	330	—	370	420	—	—	—	500
Soft-EPU	280	—	330	370	420	—	—	—	—	—	—	510
S-PU	210	258	—	282	330	—	380	450	—	525	550	650
Soft-SPU	282	350	—	382	436	—	525	—	541	—	—	650
I-PU	285	370	—	385	440	—	468	—	480	530	568	650

^a T_{1i} , T_{2i} , T_{3i} , and T_{4i} are the initial temperatures of the first, second, third, and fourth stages of degradation, respectively.

^b T_{1s} , T_{2s} , T_{3s} , and T_{4s} are the shoulder peak temperatures of the first, second, third, and fourth stages of degradation, respectively.

^c T_{1m} , T_{2m} , and T_{3m} are the maximum rate temperatures of the first, second, and third stages of degradation, respectively.

^d T_{mw} is the temperature of the maximum weight loss.

Degradation of the S-PU polymer

S-PU on the TG curve also exhibits two stages of degradation; the first and second stages of degradation appear at 210–380 and 380–650°C, as shown in Figure 4. The DTG curve initially exhibits a shoulder peak at 210–282°C, and then the maximum rate peak appears at 282–380°C. Figure 1 displays the S-PU hard-segment structure, which is composed of the urethane-B and urethane-S segments. The urethane-S segment is obtained from MDI and PDMS, and the urethane-B segment has the same composition as E-PU. S-PU between 210 and 380°C is related to the degradation of E-PU according to the results of the Degradation of the E-PU Polymer section, the hard-segment structures, and the characteristic temperature of degradation. Thus, S-PU is considered to have a two-stage degradation consisting of stages S1 and S2, respectively, in the region. The first stage at 210–282°C is regarded as the shoulder peak resulting from the urethane-B segment degradation, and the second stage between 282 and 380°C corresponds to the decomposition of the urethane-S segment. The shoulder peak temperature of the first stage of degradation and maximum rate temperature of the second stage of degradation of S-PU appear around 258 and 330°C and are similar to those of E-PU, as shown in Table II.

Above 380°C, S-PU exhibits a two-stage degradation consisting of stages S3 and S4 according to the DTG curve, and the third and fourth stages of degradation appear at 380–525 and 525–650°C, respectively. Stage S3 displays the degradation temperature of the maximum rate peak around 450°C, and stage S4 presents a small shoulder peak around 550°C, as shown in Figure 4. Several works^{11–15} have determined that the soft-segment degradation of polyurethane copolymers is followed by the hard segments. Therefore, the degradation of S-PU at 380–650°C in this study is likely to be

the process of the degradation of the PDMS soft segment.

Soft-SPU, consisting of MDI and PDMS, was prepared from a composition similar to that used for the preparation of S-PU to verify the degradation temperatures of S-PU. Thus, soft-SPU involves only the urethane-S hard segment and PDMS soft segment. Soft-SPU in TGA was heated from 50 to 700°C at a heating rate of 10°C/min, as shown in Figure 5. The TG and DTG curves display a three-stage degradation at 280–375 (a shoulder peak), 375–525 (the maximum rate peak), and 525–650°C (a shoulder peak). According to the previous discussion, the degradation of the urethane-S segment has been determined to occur at 282–380°C, which almost corresponds to the first stage of soft-SPU degradation. Moreover, soft-SPU in the second and third regions of degradation, respectively, corresponds to the degradation of S-PU in the region of 380–650°C. Thus, the degradation of the PDMS soft segment in S-PU is perhaps beyond 380°C.

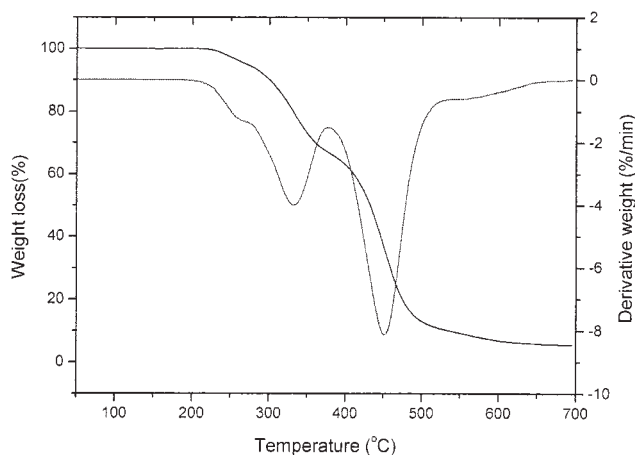


Figure 4 TG and DTG curves of the S-PU copolymer.

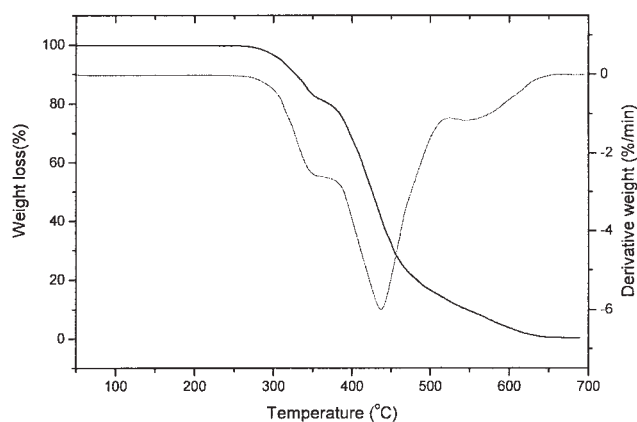


Figure 5 TG and DTG curves of the soft-SPU copolymer.

Several studies^{16,17} have indicated that the PDMS OH-terminated degradation occurs at the OH end group. The instability of the end groups is due to the back-biting of the terminated silicon in PDMS by the primary hydroxyl oxygen, which leads to stable heterocyclic compounds. The principal product of degradation is cyclosiloxane. The cyclosiloxane-forming reaction is strongly accelerated by KOH or methane because of the driving force provided by the negatively charged hydroxyl ions. Cyclosiloxane is formed by the interchange reaction of the siloxane bonds, which involves the formation of a cyclic four-center transition state when PDMS is heated. Furthermore, cyclosiloxane products and linear PDMS are expected to undergo a similar interchange reaction. Hence, cyclic PDMS and linear PDMS under heating are predicted to be macrocyclic siloxanes with a much higher molecular weight than those of the starting materials.^{10,18}

Accordingly, the soft-SPU degradation stages are predicted as follows. The first stage at 282–382°C is the degradation of the urethane-S segment; the second stage at 382–525°C is the degradation of the PDMS monomers, which are decomposed into cyclosiloxane and low-molecular-weight siloxane; and the third stage at 525–650°C is the degradation of macrocyclic siloxanes. As for the degradation of S-PU, the first stage between 210 and 282°C is the decomposition of the urethane-B segment; stages S2, S3, and S4 are similar to those of the degradation of soft-SPU in the region of 282–650°C.

TG-FTIR analysis

The TGA section elucidates the degradation stages of E-PU and S-PU according to the TG and DTG analyses. TG-FTIR is a useful device for investigating the gaseous products in the process of degradation. Therefore, the steps of these copolymers can be predicted by the TG-FTIR analysis. The gaseous products at each degradation temperature are dis-

played in the FTIR spectra, as shown in Figure 6 and later in Figure 8.

Steps of degradation of E-PU

Figure 6 displays the spectra of the decomposition products at several specific temperatures for E-PU heated under an N₂ atmosphere. The FTIR spectra below 200°C are almost unchanged, indicating that none of the volatile products in the degradation region are detected, as shown in Figure 6(a). The absorption peaks, including 2990 cm⁻¹ assigned to C–H stretching in –CH₂–, 2350–2310 cm⁻¹ corresponding to carbon dioxide, and 1080–900 cm⁻¹ assigned to –C–O–C– stretching in aliphatic ether, initially appear around 200°C, as shown in Figure 6(b). The asymmetrical and symmetrical stretching vibrations for –C–O–C– absorption peaks, which correspond to THF, appear around 1080 and 900 cm⁻¹. According to the E-PU volatile products between 200 and 280°C, the degradation stage at least includes the decomposition products of THF and CO₂, which correspond to the decomposition mechanism of pure polyurethane, which consists of 1,4-BD and MDI.¹² Accordingly, the degradation of E-PU between 200 and 280°C is associated with the dissociation of the urethane-B segment and includes three steps, which are given in Scheme 1 (steps 1–3). Subsequently, the absorption region of THF disappears around 280°C, whereas the CO₂ absorption peak almost remains until 370°C, as shown in Figure 6(d). Thus, the degradation at 280–370°C suggests that the urethane-G segment is decomposed to form PTMG and MDI, as shown in Scheme 1 (step 4). MDI is decomposed to form carbodiimide and CO₂, as shown in Scheme 1 (step 5). Between 280 and 370°C, the ethylene oxide absorption peak is detected at 1270 cm⁻¹, as shown in Figure 6(c,d),

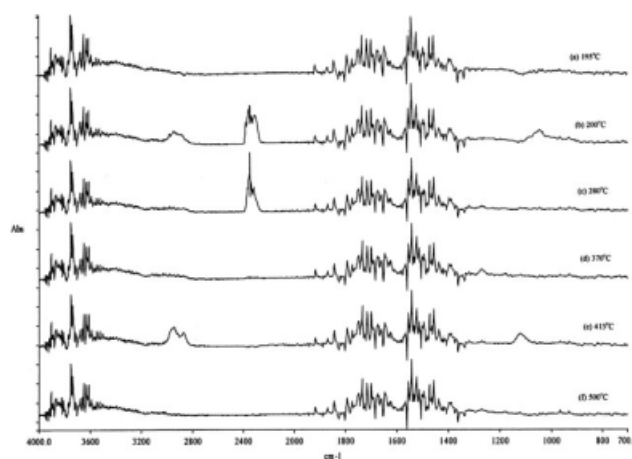
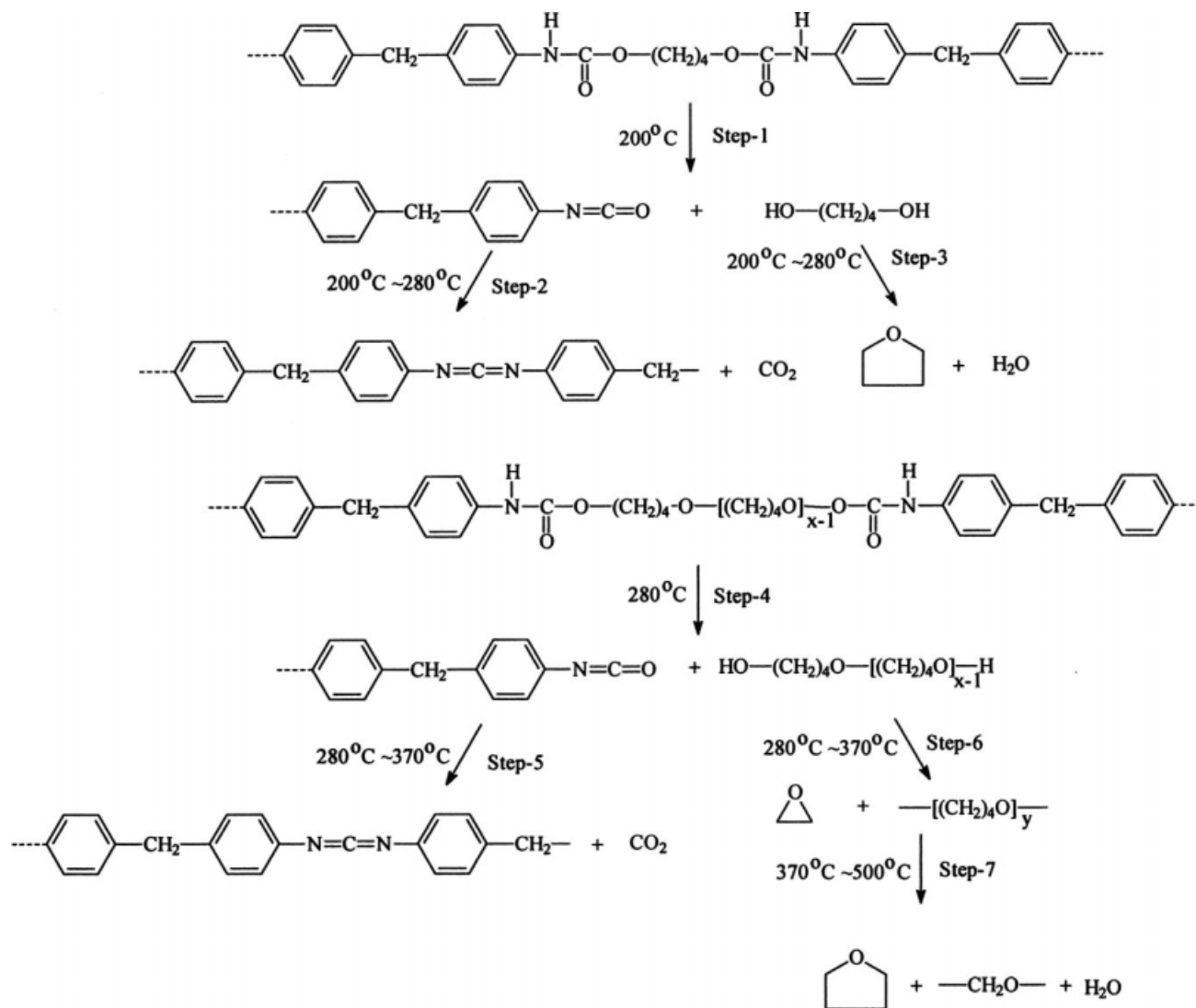


Figure 6 Spectra of the E-PU copolymer heated at several specific temperatures under an N₂ atmosphere.



Scheme 1 Steps of degradation for E-PU.

indicating that PTMG also yields decomposition resulting from the hydroxyl end group of PTMG, as presented in Scheme 1 (step 6). Between 370 and 500°C, the spectra around 2990 and 1100 cm^{-1} exhibit the absorption peaks corresponding to the stretching vibration of ether, and they disappear around 500°C, as shown in Figure 6(e,f). Accordingly, the region of 370–500°C is caused by the PTMG main chains decomposing to form cyclic ether and aliphatic ether, as shown in Scheme 1 (step 7). Combining the TG–FTIR results with the TG and DTG analyses reveals that the degradation of E-PU has at least three stages of degradation that include seven steps of degradation. Notably, the degradation of the PTMG soft segment for E-PU occurs around 280°C, not above 370°C. Figure 7 shows that the TG and DTG curves for the PTMG monomers start around 200°C. Therefore, the PTMG soft segment should be degraded after the degrada-

tion of the urethane-G segment; that is, the PTMG soft segment in E-PU occurs around 280°C.

Steps of S-PU degradation

No products of degradation can be found in the S-PU spectra below 210°C, as shown in Figure 8(a). The S-PU spectrum at 210°C initially shows the characteristic absorption of the CO_2 and THF volatile products, which are similar to E-PU, as shown in Figure 8(b). The absorption peaks of THF and CO_2 around 285°C are almost unchanged. Therefore, the S-PU degradation steps below 285°C correspond to the degradation of the urethane-B segment, as shown in Scheme 2 (steps 1–3). Between 285 and 370°C, there are two large absorption peaks at 1255 and 810 cm^{-1} assigned to $\text{---Si(CH}_3\text{)}_2\text{---O---}$; a twin peak appears at 1010–1125 cm^{-1} , corresponding to ---Si---O---Si--- , except for the characteristic absorption

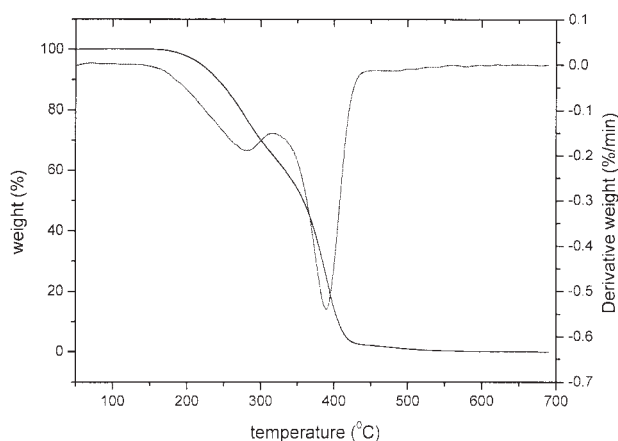


Figure 7 TG and DTG curves of the PTMG monomer.

peaks of $-\text{CH}_3$ (2990 cm^{-1}) and CO_2 (2350 cm^{-1}), as shown in Figure 8(c). The CO_2 absorption peak disappears around 370°C , as shown in Figure 8(d). According to the characteristic absorption between 285 and 370°C , the S-PU degradation region possibly starts at the urethane-S segments. The urethane-S segments under depolymerization produce the MDI and PDMS monomers, as presented in Scheme 2 (step 4). Subsequently, MDI is decomposed to form carbodiimide and CO_2 (step 5); the PDMS monomers under the interchange reaction of the siloxane bond decompose to form cyclosiloxane and low-molecular-weight linear siloxanes,¹⁸ as shown in Schemes 2 (step 6) and 3. Therefore, the degradation stage between 285 and 370°C includes the degradation of the PDMS mono-

mers. Notably, the TG-FTIR results differ from the TGA results in the degradation region of 282 – 380°C . The TGA results in the Degradation of the S-PU Polymer section show that the degradation stage at 282 – 380°C is the degradation of the urethane-S segment decomposed into the MDI and PDMS monomers, and then the PDMS monomers are further degraded above 380°C . However, the TG-IR spectra at 285 – 370°C show the decomposition products of siloxane, so the degradation of the PDMS monomers should be carried out above 280°C .

The PDMS monomer was measured by TGA to determine the degradation temperatures of the PDMS soft segment. The DTG curve displays a three-stage degradation, as shown in Figure 9. The first stage presents a shoulder peak at 245 – 370°C , the second stage is the maximum rate peak between 370 and 525°C , and the third stage appears as a shoulder peak at 525 – 650°C . Considering the TGA results of soft-SPU (Fig. 5) and the PDMS monomers and reviewing the PDMS degradation,^{19–21} we find that the decomposition of the PDMS monomers initially occurs at their hydroxyl end groups, and then the chains of the PDMS monomers are further decomposed to form low-molecular-weight siloxane segments. According to the results of Figures 8(c,d) and 4, the degradation of the PDMS soft segment should be included in the second stage of the S-PU degradation at 285 – 380°C . This stage involves a three-step degradation, as shown in Scheme 2 (steps 4–6); these are the degradation of the urethane-S segment and the MDI and PDMS monomers. The

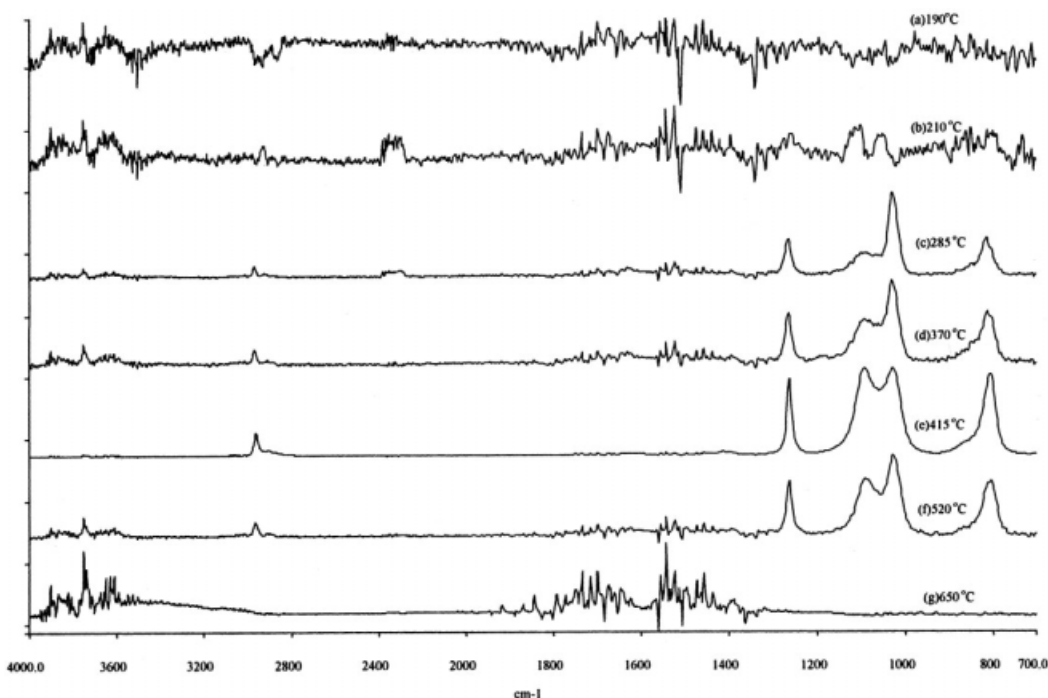
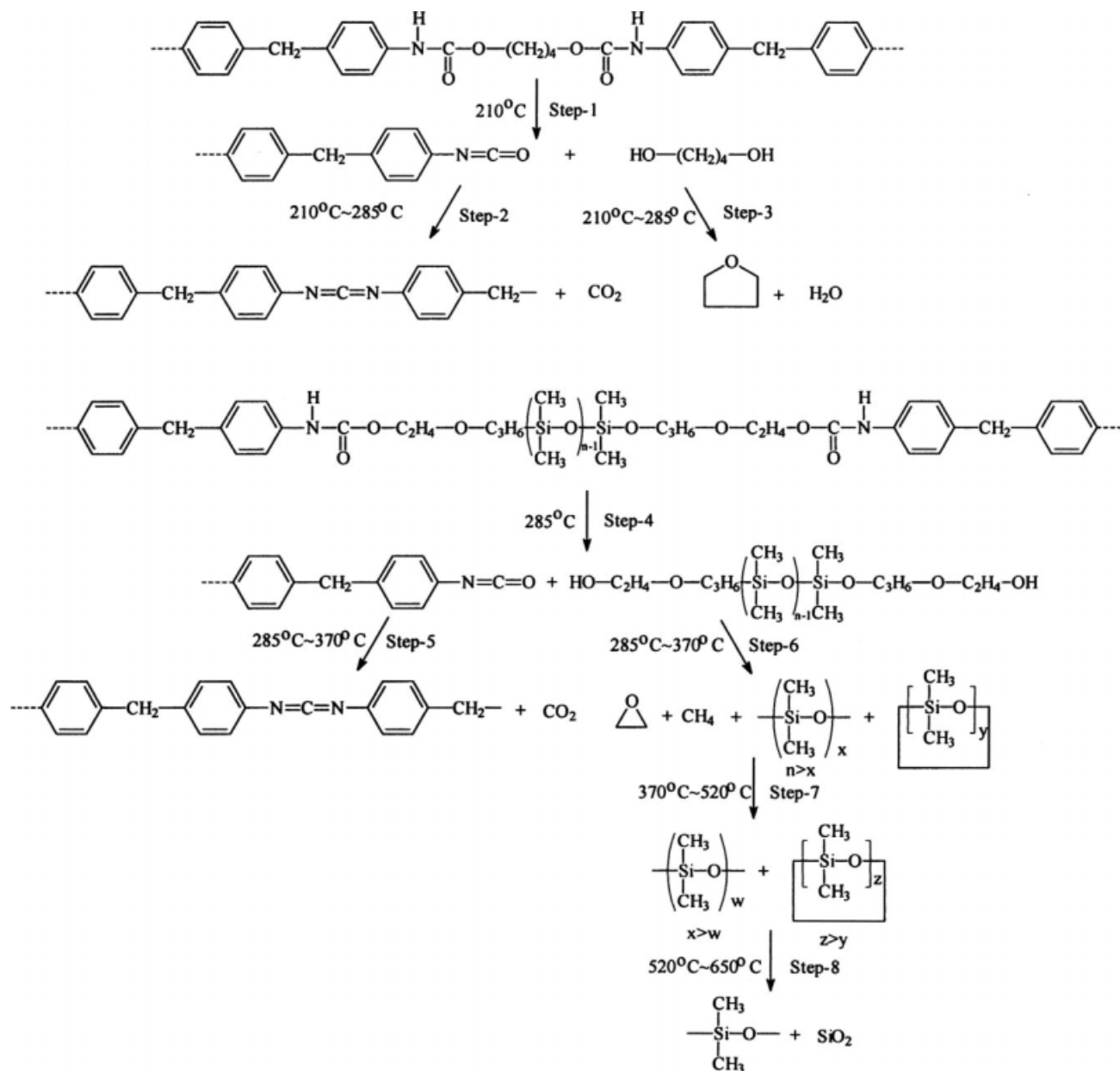


Figure 8 Spectra of the S-PU copolymer heated at several specific temperatures under an N_2 atmosphere.



Scheme 2 Steps of degradation for S-PU.

ethylene oxide and methane are produced at step 6, resulting from the decomposition of the hydroxyl end groups of the PDMS monomers, and the broad molecular weight distributions of the linear PDMS and cyclic oligomer in this stage are produced by the interchange reaction of siloxane bonds,²⁰ as shown in Schemes 3 and 2 (step 6).

After the degradation of the urethane-S segment, the siloxane products resulting from the degradation of PDMS monomers are further decomposed to form linear siloxane segments and macrocyclic siloxanes between 370 and 520°C, as shown in Schemes 3 and 2 (step 7); meanwhile, the degradation of siloxane chains is accelerated by methane.^{16,17} Therefore, the maximum absorption peaks for $\text{---Si(CH}_3\text{)}_2\text{---O---}$ and

---Si---O---Si--- are detected around 415°C, as shown in Figure 8(e). The temperature is close to the degradation temperature of the maximum rate peak (ca. 450°C) in the process of the degradation of S-PU, as shown in Figure 4. This result demonstrates that the maximum rate of S-PU degradation is caused by the methane hastening the degradation rate of siloxane chains. Moreover, the interchange reaction of siloxane bonds in cyclic PDMS carries out the intermolecular reaction resulting in macrocyclic and cyclic oligomer siloxanes, as shown in Scheme 4. Therefore, the S-PU degradation products at 370–520°C at least include the macrocyclic, cyclic oligomer, and low-molecular-weight linear siloxanes. Figure 8(f) demonstrates that the absorption peaks for the

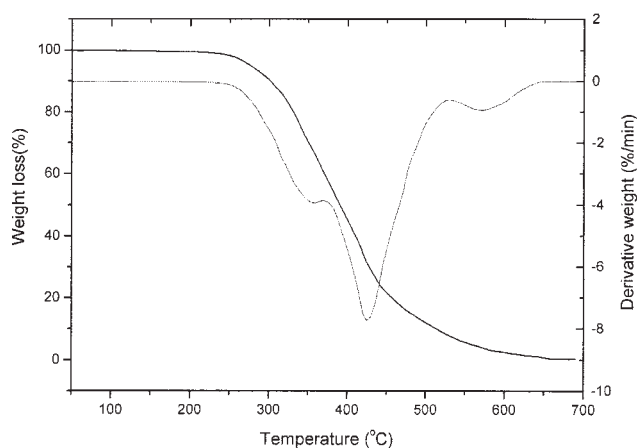


Figure 9 TG and DTG curves of the PDMS monomer.

compound products of siloxane and methyl exist above 520°C. Accordingly, in the degradation above 520°C, the macrocyclic, cyclic oligomer, and small siloxane segments are dissociated to form volatile siloxane SiO_2 and char, as shown in Scheme 2 (step 8). Finally, the absorption peaks disappear around 650°C, as shown in Figures 8(g) and 9.

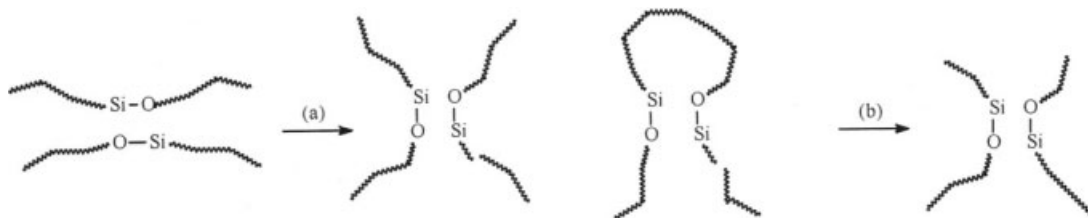
According to the TGA and TG-FTIR results, the S-PU degradation behaviors can be summarized as follows. The first stage between 210 and 280°C includes three steps: the urethane-B segment under depolymerization is decomposed to form MDI and 1,4-BD (step 1), and then the MDI and 1,4-BD monomers are dissociated to form carbodiimide and CO_2 (step 2) and THF (step 3), respectively. The second stage between 285 and 370°C includes three steps: the urethane-S segment is decomposed into MDI and PDMS monomers (step 4), MDI is decomposed to form the carbodiimide and CO_2 (step 5), and the PDMS monomers are dissociated to form cyclosiloxane (cyclic oligomers) and nonuniform linear PDMS with a low molecular weight (step 6). Moreover, the low-molecular-weight linear PDMS in the degradation region is carried out in an interchange reaction of siloxane bonds in linear PDMS, which results in the cyclic oligomer (Scheme 3) and the broader molecular weight distributions of nonuniform linear PDMS segments. The third stage at 370–520°C includes a degradation step (step 7) and an inter-

change reaction; that is, the nonuniform siloxane segments suffer sustained degradation, and the cyclic siloxane also suffers an interchange of siloxane bonds to form macrocyclic and cyclic oligomer siloxanes (Scheme 4). The fourth stage at 520–650°C involves the macrocyclic, cyclic oligomer, and short-chain siloxanes, which are decomposed to form the volatile composition, SiO_2 and char (step 8).

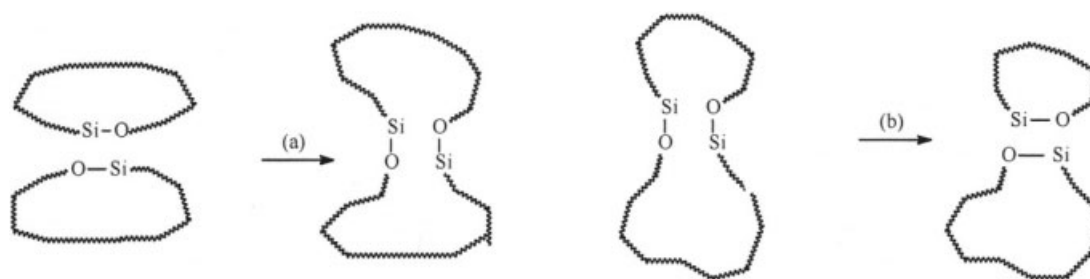
Improvement of the thermal stability

As mentioned in the TGA and TG-FTIR Analysis sections, the initial degradation for E-PU and S-PU around 200°C has been considered to involve the urethane-B segment consisting of MDI and 1,4-BD. Several works have attempted to improve the thermal stability of typical polyurethane (E-PU) by the incorporation of aromatic amide and aromatic imide groups.^{22–24} Aromatic imide groups, which can be formed by the aromatic diisocyanate and aromatic dianhydride, possess high thermal stability; the polyimide would not be degraded under heating at 400°C for several months.²⁴ Therefore, imide groups have been incorporated into the main chain of polyurethane for the thermal stability of E-PU.²⁴ The low-thermal-stability urethane-B segment was replaced with aromatic imide groups to improve the thermal stability of S-PU in this study. The I-PU copolymer is the S-PU hard segment incorporated into aromatic imide groups; therefore, I-PU involves the PDMS soft segments, urethane-S segments, and imide hard segments, as shown in Figure 1. Figure 10 shows that I-PU on TGA involves four stages of degradation at 285–385 (stage I1), 385–468 (stage I2), 468–530 (stage I3), and 530–650°C (stage I4). Comparing the region of the degradation temperature with the structures of I-PU, S-PU, and E-PU, we find that stages I1 and I2 of I-PU include the degradations of urethane-S and PDMS, which are similar to stages S2 and S3 of S-PU. Because the degradation region of the polyimide is between 450 and 700°C,²⁵ stages I3 and I4 of I-PU involve the degradation of the aromatic imide segment and the degradations of the linear siloxane chain and cyclic siloxane.

Table II lists the characteristic temperatures for each stage of the polyurethane copolymers. I-PU at



Scheme 3 Interchange reaction of the siloxane bond in linear PDMS: (a) intermolecular reaction resulting in broader molecular weight distributions and (b) intramolecular reaction resulting in a cyclic oligomer.²⁰



Scheme 4 Interchange reaction of the siloxane bond in cyclic PDMS: (a) intermolecular reaction resulting in higher molecular weight macrocyclics and (b) intramolecular reaction resulting in a cyclic oligomer.²⁰

the first degradation has the highest temperature, around 285°C, which is close to the degradation temperature of the urethane-S segment, and at 380–468°C (stage I2), I-PU has lower weight loss than S-PU, as shown in Figure 11. The TGA results demonstrate that the thermal stability of S-PU has been successfully improved by the stable aromatic imide groups substituting for the urethane-B segments of S-PU. However, in terms of stages I3 and I4 between 468 and 650°C, the I-PU degradation stages are similar to those of S-PU because the degradation of the urethane-S and PDMS segments is largely degraded in the region, and the imide groups begin to be decomposed around 450°C, as shown in Figure 11. Although the degradation of I-PU between 468 and 650°C shows no further improvement, its initial temperature of degradation is higher than that of E-PU and S-PU. The initial temperature of degradation is more significant for the practical application of elastomers than other degradation temperatures because the processed temperature is always below the initial temperature, such as that of melt spinning or the process of extrusion.

Steps of the degradation of the I-PU copolymer

The I-PU volatile products were also detected by TG-FTIR to identify the degradation steps of I-PU.

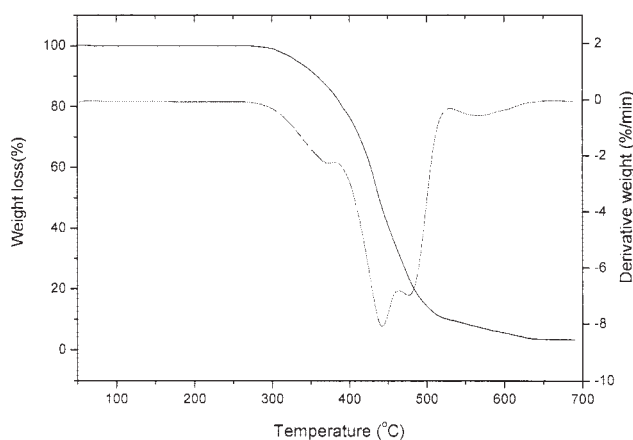


Figure 10 TG and DTG curves of the I-PU copolymer.

The FTIR spectra in Figure 12(a–h) display the I-PU decomposition products at different temperatures. Below 280°C, there are no volatile products detected on the FTIR spectra, as shown in Figure 12(a). At 280°C, the CO₂ and aliphatic ether absorption peaks initially appear on the FTIR spectra, as shown in Figure 12(b), indicating that the initial degradation of I-PU results from the urethane-S segment. Moreover, the aliphatic ether absorption peaks are for the degradation of the PDMS end group. Subsequently, the absorption peaks for the siloxane chain between 280 and 440°C are detected around 810, 1125–1010 (twin peaks), 1250, and 2965 cm⁻¹, which are similar to those for the degradation of S-PU, and the CO₂ absorption peak appears around 380°C, as shown in Figure 12(c). Otherwise, a lot of nitric oxides for N₂O₄ around 1750 cm⁻¹ [Fig. 12(d)], carbon bisulfonic (CS₂) around 2050 cm⁻¹ [twin peak; Fig. 12(e)], and carbon monoxide [Fig. 12(f)] around 2350 cm⁻¹ (twin peak) are detected between 440 and 625°C, except for the characteristic absorption of the decomposition products of siloxane chains, as shown in Figure 12(d–f). The volatile products, including CH₄, N₂O₄, CS₂, and CO, correspond to the imide segment degradation. Because the imide segment degradation above 440°C is merged into the degradation

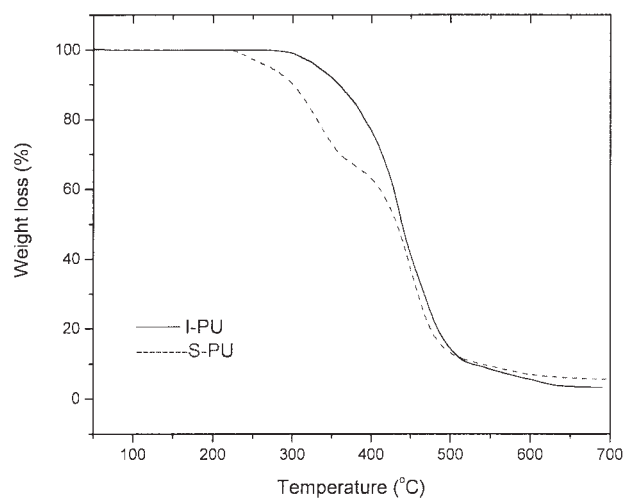


Figure 11 TG curves of the I-PU and S-PU copolymers.

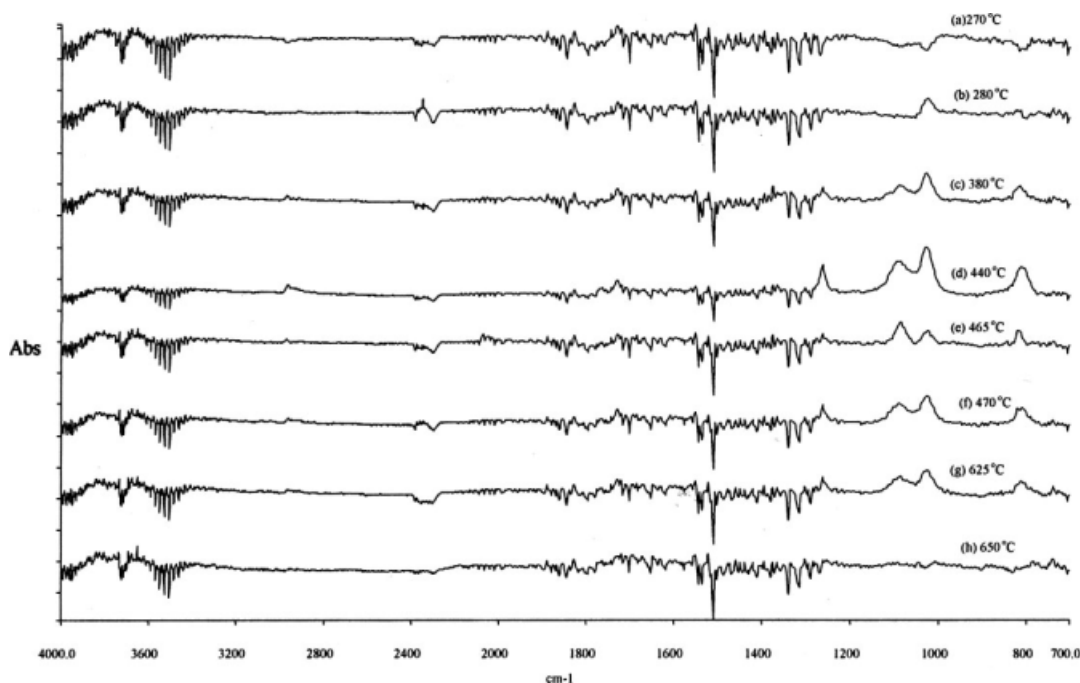
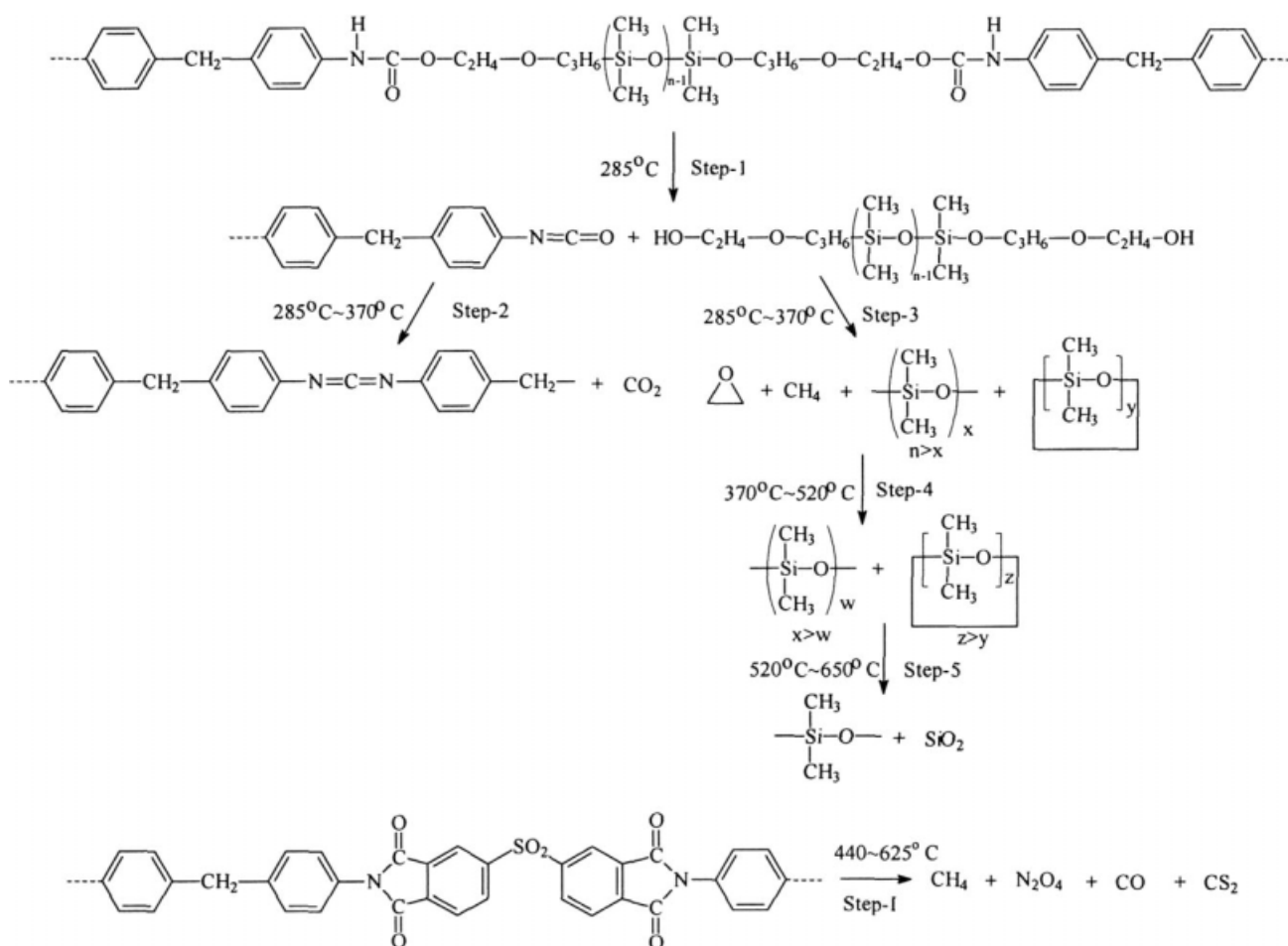


Figure 12 Spectra of the I-PU copolymer heated at several specific temperatures under an N_2 atmosphere.



Scheme 5 Steps of degradation for I-PU.

products of siloxane, the steps of the imide segment are difficult to determine here from the TG-FTIR analysis. However, the imide group degradation of I-PU is proved at 440–625°C. In terms of the siloxane degradation products, the absorption peaks are still present at 625°C and nearly disappear around 650°C, as shown in Figure 12(g,h).

According to the TG-FTIR and TGA results, the degradation of I-PU possesses four stages of degradation containing six steps, as shown in Scheme 5. The degradation of I-PU around 285°C initially occurs at the urethane-S segment, which is depolymerized to form the MDI and PDMS monomers, as shown in Scheme 5 (step 1). Subsequently, the MDI monomers are decomposed to form the carbodiimide and CO₂ (step 2), and the PDMS monomers at 285–370°C are decomposed to form cyclosiloxane and low-molecular-weight linear siloxanes (step 3). Beyond 370°C, the degradation of I-PU is similar to that of S-PU, which includes a two-step degradation of the siloxane segments (steps 4 and 5), and the degradation of the imide segment is merged into the degradation of siloxane when the degradation temperature occurs at 440–625°C, as shown in Scheme 5(step I).

CONCLUSIONS

In previous studies, typical polyurethane degradation, consisting of MDI and PTMG, has been considered a two-stage degradation; the first and second stages originate from the urethane hard segment and soft segment. However, the degradation of the urethane hard segment is unclear because the degradation behavior on the shoulder peak of the DTG curve is unknown. The E-PU shoulder peak on the DTG curve and TGA and TG-FTIR analyses have demonstrated the degradation of the urethane-B segment. Therefore, E-PU in the analyses exhibits at least a three-stage degradation. That is, the degradation stages involve urethane-B at 200–280°C, urethane-G at 280–370°C, and the PTMG soft segment at 280–500°C; the stages in TG-FTIR exhibit a seven-step degradation.

The S-PU soft segment is composed of PDMS with high thermal stability, but the initial degradation temperature of S-PU, around 210°C, is close to that of E-PU. This is due to the low thermal stability of the urethane-B segment, which exists in E-PU and S-PU. S-PU in the TG-FTIR analysis exhibits a four-stage degradation, including the depolymerization of the urethane-B segments at 210–285°C (steps 1–3), the decomposition of the urethane-S segments and the PDMS monomers at 285–370°C (steps 4–6), the decomposed products of cyclosiloxane and low-molecular-weight linear PDMS at 370–520°C (step 7), and the macrocyclic PDMS, cyclic oligomer, and short-chain siloxanes at 520–650°C (step 8).

Although S-PU is incorporated with the thermal stability of PDMS, the initial degradation occurs around 210°C because of the urethane-B segments with their low thermal stability. Therefore, the imide group with high thermal stability is incorporated into S-PU through the reactivity between MDI and dianhydride. I-PU presents a higher initial degradation temperature around 285°C; however, the initial degradation is not the degradation of the imide group. The TGA and TG-FTIR results demonstrate that the initial degradation results from the urethane-S segment. The first stage of the I-PU degradation, including the urethane-S segment degradation and PDMS monomers, occurs between 285 and 370°C. Subsequently, a two-stage degradation, which is associated with the decomposition of the siloxane chains and imide groups, occurs at 370–650°C. The degradation stages of I-PU involve at least a six-step degradation.

References

- Kim, J.; Chaudhury, M. K.; Owen, M. J. *IEEE Trans Dielectr* 1999, 6, 695.
- Zeigler, J. M.; Gordon Fearon, F. W. *Silicon-Based Polymer Science*; American Chemical Society: Washington, DC, 1989.
- Clarson, S. J.; Semlyen, J. A. *Siloxane Polymers*; Prentice-Hall: New Jersey, 1993.
- Kricheldorf, H. R.; Burger, C.; Hertler, W. R.; Kochs, P.; Kreuzer, F. H.; Mulhaupt, R. *Silicone in Polymer Synthesis*, Springer: Berlin, 1996.
- Eaborn, C. *Organosilicone Compounds*; Academic Press: New York, 1960.
- Fried, J. R. *Polymer Science and Technology*; Prentice-Hall: New Jersey, 1995.
- Lewis, C. W. *J Polym Sci* 1958, 33, 153.
- Cox, J. M.; Wright, B. A.; Wright, W. W. *J Appl Polym Sci* 1964, 8, 2935.
- Murphy, C. M.; Ravner, H.; Kagarise, R. E. *Thermal Degradation Processes in Polysiloxanes and Thermal Stabilization by a Cerium Inhibitor*, Accession Number: AD0633068, Naval Research Laboratory: Washington, DC, 1966.
- Thomas, T. H.; Kendrick, T. C. *J Polym Sci Part A-2: Polym Phys* 1969, 7, 537.
- Ferguson, J.; Petrovic, Z. *Eur Polym J* 1973, 12, 177.
- Gassie, N.; Zulfiqar, M. *J Polym Sci Polym Chem Ed* 1978, 16, 1563.
- Petrovic, S.; Zavargo, Z.; Flynn, J. H.; Mackinght, W. J. *J Appl Polym Sci* 1994, 51, 1087.
- Lin, M. F.; Tsen, W. C.; Shu, Y. C.; Chuang, F. S. *J Appl Polym Sci* 2001, 79, 881.
- Chuang, F. S.; Tsen, W. C.; Shu, Y. C. *Polym Degrad Stab* 2004, 84, 66.
- Grassie, N.; Macfarlane, I. G. *Eur Polym J* 1978, 14, 875.
- Patnode, W.; Wilcock, D. F. *J Am Chem Soc* 1946, 68, 358.
- Bannister, D. J.; Semlyen, J. A. *Polymer* 1981, 22, 377.
- Yilgor, I.; Yilgor, E. *Polym Bull* 1998, 40, 525.
- Bannister, D. J.; Semlyen, J. A. *Polymer* 1981, 22, 377.
- Clarson, S. J.; Semlyen, J. A. *Polymer* 1986, 27, 91.
- Lin, M. F.; Wang, H. H.; Chuang, F. S.; Shu, Y. C.; Tsen, W. C. *J Polym Res* 1996, 3, 105.
- Masiulani, B.; Zielinski, R. *J Appl Polym Sci* 1985, 30, 2731.
- Lin, M. F.; Shu, Y. C.; Tsen, W. C.; Chuang, F. S. *Polym Int* 1999, 48, 433.
- Yang, H. H. *Aromatic High-Strength Fiber*; Wiley: New York, 1989.