Study on Synthesis and Thermal Properties of Polyurethane–Imide Copolymers with Multiple Hard Segments

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ABSTRACT: Different multiple hard segment polyurethane–imide copolymers (MHPUI) were synthesized and characterized. FTIR spectroscopy confirmed the characteristic absorption of the MHPUI copolymer. The difference in the imide group FTIR absorption bands in different MH segment PUI copolymers was found in this study and was explained by the different MH segment types, hard segment contents, and hard segment rigidity with different interactions of the molecular chains. The hard segment interaction in MHPUI with an increase of the structure rigidity of the short hard segments is strengthening. The DSC analysis revealed that the glass-transition temperature of the soft segment of PUI rose in value from -42 to -3.4°C with the introduction of MH and different MH segments. The DSC results suggest that the soft segment is more compatible with the hard segment rigidity increase. The TGA results showed the hard segment structure symmetry has a more important role in the MHPUI thermal stability. Every sample containing symmetrical structure short hard groups (4,4′-diphenylmethane diisocyanate or 4,4′-diaminodiphenylmethane) is more thermally stable than that with worse symmetry structure groups (2,4-toluene diisocyanate or 3,3′-dichloro-4,4′-diamino-diphenylmethane). The three-step mechanism of PUI thermal degradation was further verified by the TGA study. The thermally unstable group was confirmed as urethane or a urea–urethane segment. The TGA results showed that MHPUI copolymers with higher separation of the soft–hard phase have higher thermal stability. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2206–2215, 2002

Key words: multiple hard segment polyurethane–imide; polyurethanes; polyimide synthesis; properties

INTRODUCTION

Polyurethane (PU) has gained considerable attention because of its applications in membrane ma-

terials.[1–4] However, PU is well known to exhibit poor heat resistance that largely limits its use as engineering materials.[5] The thermal stability of PU is very dependent on the chemical structure of its backbone, which consists of various hard segments and soft segments; for example, PUs produced from monomers with different diisocyanate structures present different thermal stabilities. There have been extensive research efforts on improving the thermal stability of PU that led to

great progress on its processing and application.[6,7] A very effective way to improve the thermal stability of PUs is the chemical modification of their structures by blending or copolymerizing with more thermally stable polymers, and poly(urethane–urea), poly(urethane–epoxy), and PU–diacetylene are good examples. Polyimides are a class of aromatic heterocyclic polymers with excellent heat resistance and mechanical properties, and they can retain their applicability even after exposure at 500°C or above for several minutes or at 300°C for a couple of months.[8] However, there are some disadvantages for polyimide applications in terms of their brittleness and low processibility.[9] The incorporation of a polyimide or oligoimide unit into PU has been attempted. The synthesis of imide-modified PU by a one-shot technique or via a sequential method to inject an imide group in the PU backbone and the consequent improvements in thermomechanical properties has been reported.[10–13]

In addition, the thermal degradation of PU is a complicated process. Several groups[14–16] have shown that the thermal degradation initiates at the hard segments of urethane groups, which decomposes and forms isocyanate and alcohol, primary or secondary amine and olefin, and carbon dioxide. However, to date, the mechanism of PU degradation remains somewhat unclear.

We recently studied the synthesis and properties of PU–imide (PUI) with different soft segments.[17] In order to improve and elevate the properties for the application of PUI, a polyether–urethane–imide with different MH segments was synthesized (MHPUI). The properties of the MHPUI with different MH segments were explored by using FTIR, DSC, and TGA.

EXPERIMENTAL

Materials

Poly(ethylene glycol) (PEG, M_n = 1031, First Reagent Factory of Shanghai), Its molecular weights was checked using a terminal group titration method.[18] 4,4′-Diphenylmethane diisocyanate (MDI) was supplied as Desmodur 44MS by Bayer AG. Pyromellitic dianhydride (PMDA, First Reagent Factory of Shanghai) was purified by sublimation under a vacuum before use. Dimethylformamide (DMF) was dried over 4-Å; molecular sieves for 24 h followed by distillation prior to use. 2,4-Toluene diisocyanate (TDI) was supplied by

the Factory Shanghai Chemical Agent and distilled before use. 3,3′-Dichloro-4,4′-diamino-diphenylmethane (MOCA) was produced by Qian Jin Chemistry Industry in Suzhou and recrystalized before use in the synthesis of MHPUI. 2,2-Bis(4-hydroxyphenyl) propane (BPP), 4,4′-diaminodiphenylmethane (DDM), and 4,4′-dihydroxydiphenylsulfone (DDS) were purchased from First Reagent Factory of Shanghai and were recrystalized before use in our experiments.

Instruments

The FTIR spectra of the MHPUI copolymers were recorded at a resolution of 1 cm^{-1} with a WQF-300 spectrometer (Second Optical Instrument Factory, Beijing). All samples were prepared on KBr crystal flakes by coating the MHPUI sample solution.

A Perkin–Elmer Pyris 1 DSC instrument was used to analyze the thermal properties of MHPUI. All samples were measured at a heating rate of 20°C min^{-1} in a temperature range of −100 to 270°C in a helium atmosphere. The samples were first scanned above 200°C and then rapidly quenched to −100°C at a rate of 100°C min^{-1}, and a second scan was used to measure the sample's glass-transition temperature (T_g).
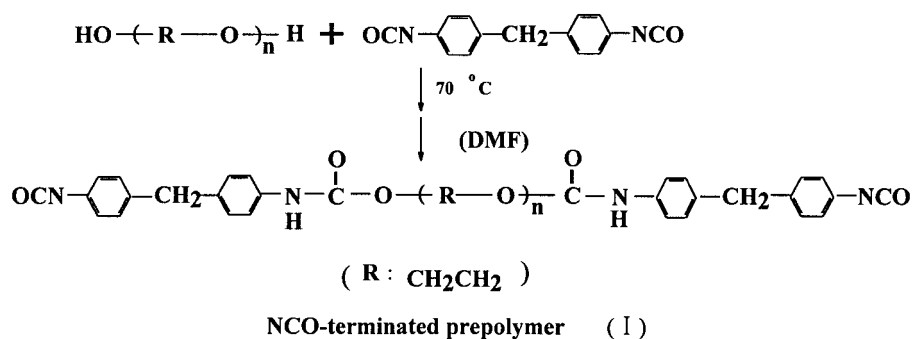
A Smarzer TGA-50H TGA apparatus was used to study the thermal degradation properties of MHPUIs. All samples were measured from room temperature to 800°C at a heating rate of 10°C min^{-1} under a nitrogen atmosphere with a flow rate of 100 mL min^{-1}.

The inherent viscosities of all soluble PUIs were measured in DMF at 30°C using an Ubbelohde viscometer.
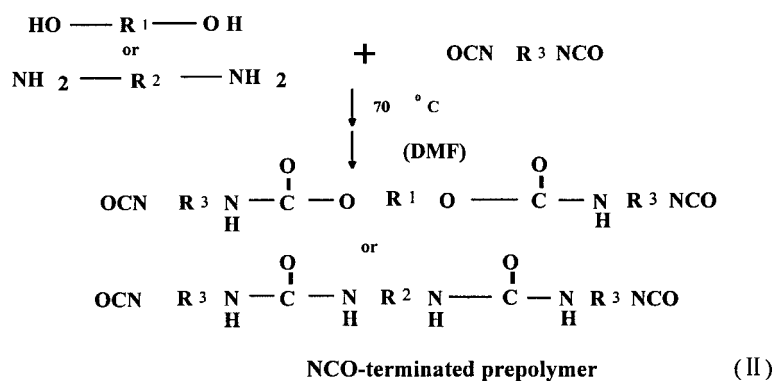
Synthesis of MHPUI Segment Copolymers

The synthesis flowchart of the MHPUI block copolymers is shown in Scheme 1. The prepolymers for the MHPUI copolymers were prepared in a three-step process. In the first step an HO-terminated soft segment PEG was degased and dried in a round flask under a high vacuum (20 Pa) at 105°C for 1.5 h. After the temperature was cooled to about 70°C, MDI was added into the above system at a NCO/OH molar ratio of 2/1, and the reaction was conducted at 70°C for 1 h followed by adding DMF. Subsequently, the reaction system was kept at 70°C for 2 h under stirring, and then 20 wt % of NCO-terminated prepolymer (I) was obtained. The second step was begun by selecting
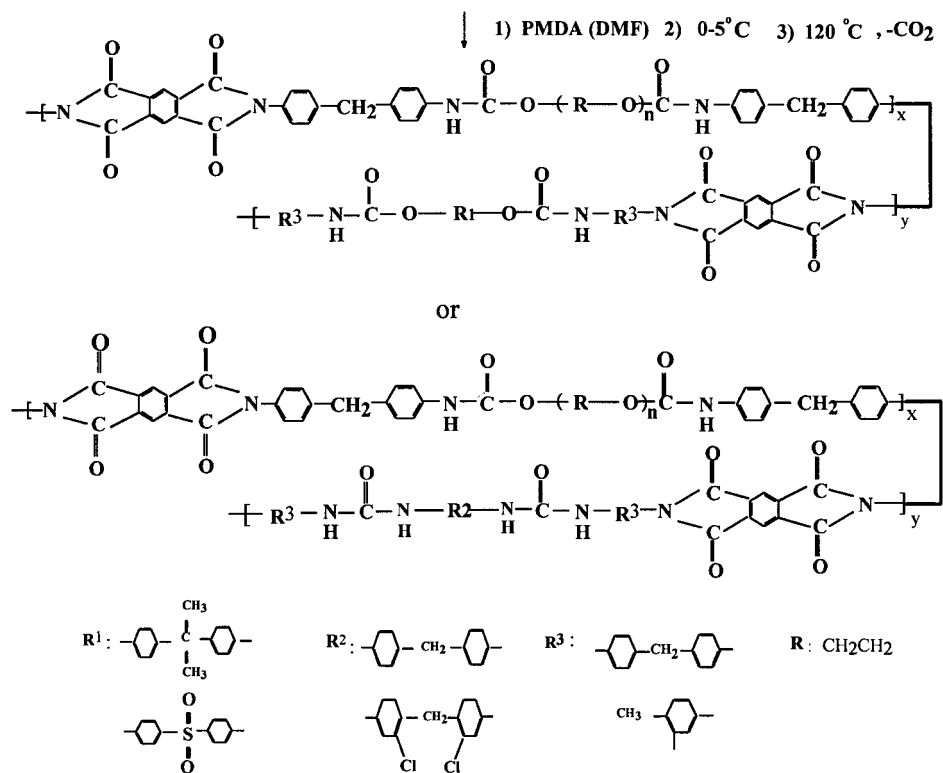
First step:

$$\text{HO}-\!\!\left(\!R\!-\!O\!\right)_{\!\overline{n}}\!H \;+\; \text{OCN}-\!\!\bigcirc\!\!-\!CH_2\!-\!\bigcirc\!\!-\!NCO$$

70 °C

(DMF)

$$\text{OCN}-\!\!\bigcirc\!\!-\!CH_2\!-\!\bigcirc\!\!-\!\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O\!-\!\!\left(\!R\!-\!O\!\right)_{\!\overline{n}}\!\overset{O}{\overset{\|}{C}}-\underset{H}{N}-\!\!\bigcirc\!\!-\!CH_2\!-\!\bigcirc\!\!-\!NCO$$

(R : CH_2CH_2)

NCO-terminated prepolymer (I)

Second step:

$$\text{HO}-\!R^1\!-\!\text{OH}$$
or
$$\text{NH}_2-\!R^2\!-\!\text{NH}_2 \qquad + \qquad \text{OCN}\;\;R^3\;\;\text{NCO}$$

70 °C

(DMF)

$$\text{OCN}\;\;R^3\;\underset{H}{N}-\overset{O}{\overset{\|}{C}}-O\;\;R^1\;\;O-\!\!\!-\overset{O}{\overset{\|}{C}}-\underset{H}{N}\;\;R^3\;\;\text{NCO}$$

or

$$\text{OCN}\;\;R^3\;\underset{H}{N}-\overset{O}{\overset{\|}{C}}-\underset{H}{N}\;\;R^2\;\underset{H}{N}-\!\!-\overset{O}{\overset{\|}{C}}-\underset{H}{N}\;\;R^3\;\;\text{NCO}$$

NCO-terminated prepolymer (II)

Third step:

NCO-terminated prepolymer (I) and NCO-terminated prepolymer(II)

1) PMDA (DMF) 2) 0-5°C 3) 120 °C , $-CO_2$

R^1 : $-\bigcirc\!-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}\!-\bigcirc-$ R^2 : $-\bigcirc\!-CH_2\!-\bigcirc-$ R^3 : $-\bigcirc\!-CH_2\!-\bigcirc-$ R : CH_2CH_2

$-\bigcirc\!-\underset{O}{\overset{O}{\underset{\|}{\overset{\|}{S}}}}\!-\bigcirc-$ $-\bigcirc\!-CH_2\!-\bigcirc-$ $CH_3-\bigcirc-$
                                   Cl   Cl

MHPUI copolymer

Scheme 1 The synthesis of MHPUI block copolymers.

Table I Thermophysical Properties of MHPUI Copolymers

Samples	η_{inh} (dL/g)	Soft Content (wt %)	T_{gs} (°C)
PUI-1	0.52	58.9	−42.0
MHPUI-2	0.38	44.7	−26.6
MHPUI-3	0.34	44.1	−3.4
MHPUI-4	0.34	42.3	−27.9
MHPUI-6	0.63	43.8	−26.9
MHPUI-7	0.41	44.1	−8.0
MHPUI-8	0.34	44.1	−24.8

T_{gs}, The glass-transition temperature of the soft segment rich phase of PUI.

one of the NH_2^- or OH-terminated small diamino or dihydroxy moleculars (such as MOCA, DDM, DDS, or BPP), dissolving it in DMF, and stirring it under a N_2 atmosphere. After the temperature reached about 40°C, MDI (or TDI) was added to the solution at a NCO/OH(NH_2^-) molar ratio of 2/1; then the reaction was conducted at 70°C for 2 h with stirring, followed by the addition of DMF. Subsequently, the reaction system was kept at 70°C for 2 h under stirring, and then 20 wt % of NCO-terminated prepolymer (II) was obtained. In the third step 20 wt % NCO-terminated prepolymer (I) and 20 wt % NCO-terminated prepolymer (II) were mixed at a weight ratio of 4:1 [(I)/(II)]. Then the 50% PMDA in DMF was added into the above mixture system at a molar ratio of 2:1 (NCO/PMDA), and the reaction mixture was vigorously stirred in an ice-water bath for 8 h under a N_2 atmosphere. The MHPUI copolymer precursor solution as synthesized was a viscous yellow (or incarnadine) liquid. For preparing the MHPUI copolymer, the precursor solution was placed into a Teflon pan maintained at 120°C for 24 h in a dried box, and the final MHPUI cellular sample was obtained. For the purpose of further analysis, the cellular MHPUI samples were dissolved in DMF again to obtain a 20 wt % MHPUI solution and cast into a Teflon mold. The DMF solvent was allowed to evaporate at 60°C for 24 h, and the resulting films were kept under reduced pressure at 80°C for 2 weeks to remove residual solvent. The film samples were postcured for 10 h at 110°C. The synthesis method for PUI-1 without a MH segment sample is the same as our previous study.[17]

The inherent viscosities of MHPUI with different MH segments are in range of 0.34–0.63 dL/g as listed in Table I. This result implied all sam-

ples of MHPUI had a higher molecular weight. The values of the inherent viscosity demonstrated the MHPUI sample was synthesized successfully, as anticipated.

RESULTS AND DISCUSSION

FTIR Analysis

The MHPUI structures were determined by FTIR analysis. Figure 1 represents the IR spectra of the as-synthesized MHPUI. In general, the chain-extension reaction was characterized by absorption bands of about 1780 and 1720 (imide I), 1380–1370 (imide II), 1120 (imide III), and 720 cm^{-1} (imide IV). The stretching vibration of two carbonyls that are weakly coupled was present in the FTIR spectra of all MHPUI samples. The absorption bands at about 1780 and 725 cm^{-1} are char-
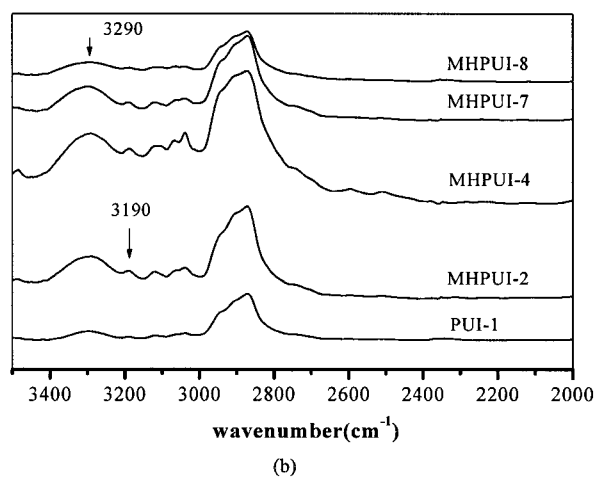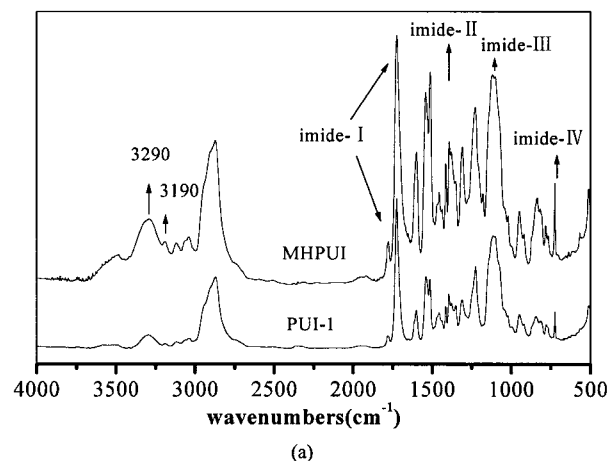

Figure 1 FTIR spectra of the as-synthesized PUI-1 and MHPUI.

Table II   Wavenumbers of N—H Stretching Vibration Bands for Different MHPUIs

Samples	N—H Stretching Vibration Bands (cm^{-1})	
PUI-1	3296	3190
MHPUI-2	3290	3190
MHPUI-3	3292	3190
MHPUI-4	3290	3188
MHPUI-6	3296	3190
MHPUI-7	3290	3190
MHPUI-8	3290	3192

acteristic bands of imide bonds, confirming the imide group was introduced to polyether–urethane backbone. Imides II, III, and IV are assigned to the axial, transverse, and out of plane vibrations, respectively, of the cyclic imide structure.[19]

It is noted that the imide I and imide II absorption bands vary with different kinds of hard blocks. The main changes of the IR absorption bands are summarized in Table II. Table II clearly shows that the imide I (1780 cm^{-1}) characteristic bands for MHPUI samples with different hard segment contents have the same variety of trends (except for the MHPUI-4 sample). The change is from 1782 to 1776 cm^{-1}. The band at 1780 cm^{-1} is assigned to the asymmetric stretching vibration of the carbonyl of the imide groups. The absorption band shifted to lower frequency (from 1782 to 1776 cm^{-1}) because of the introduction of the MH segments to the PUI system. Obviously, the MH segments are composed of hard segments with urethane or urea linkages that contain the proton donor N—H group for forming a hydrogen bond. The hydrogen bond acceptor may be the carbonyl of the imide groups in the hard segments (or the ether oxygen in the PEG soft segments). Therefore, the hydrogen bond is more easily formed between the N—H in the MH segment and the carbonyl of the imides in the PUI or MHPUI. As a result, the interaction of hard–hard segments in the intermolecular chains of MHPUI should increase because of strong hydrogen bonding. Thus, the absorption band of imide I changes to a lower frequency because of the increase of the interaction between the hard–hard segments. The hydrogen bonding will make the carbonyl bond length elongated, leading to the reduction of the stretching vibration frequency. Certainly the absorption band changed to lower

frequency, and the wavenumbers shifted to lower values.[20]

Of course, some of the ether oxygen in the PEG soft segments might also act as an acceptor in the formation of the hydrogen bonds (i.e., the bands at 3290 cm^{-1} should be assigned to N—H bonds mainly with ether oxygen). Therefore, the interaction between the soft and hard segments would increase to a certain degree. As a result, the intermolecular interaction of MHPUI should increase, which is due to strong hydrogen bonding.

This result elucidated that adding a hard segment to the PUI main chains caused the interaction of intersegments to become stronger. Therefore, those hard segment polar groups could make the polymeric chain close together because of this stronger molecular force resulting from the formation of a hydrogen bond. Hence, it may make a lot of soft segments restricted by hard segments and give rise to some soft segment parts in the hard segment rich phase. The compatibility between the soft and hard segments will thereby be improved. The imide I (1780 cm^{-1}) band of the MHPUI-4 sample with the DDS structure has any different for that of the PUI-1 sample, but its imide I (1720 cm^{-1}) band shifts to lower wavenumbers (1724 to 1720 cm^{-1}). This result also showed that the above interaction occurred in other MHPUI samples in the polymeric interchain. Comparing sample MHPUI-4 and MHPUI-7, the imide I (1780 cm^{-1}) band showed an obvious change; it may indicate that the sample MHPUI-7 intermolecular or intramolecular chain interaction force is stronger than that of sample MHPUI-4. This force should include the hard segment impact to the soft segment.

A comparison of the imide II band (1380 cm^{-1}) or imide III band (1120 cm^{-1}) data of sample MHPUI-2 and MHPUI-8 clearly showed that the bands shift to lower wavenumbers with TDI instead of MDI with the short hard segment chain-terminated group. The imide II and imide III bands belong to the C—N stretching vibration absorption peak in the imide group. In Table II the shift of the IR imide bands implies that the intermolecular combining force was strengthened when TDI instead of MDI was used in the above MHPUI system.[21] In samples PUI-1, MHPUI-3, and MHPUI-6 we observed the difference of the imide II and III bands from 1380 and 1120, to 1376 and 1116, to 1375 and 1113 cm^{-1}, respectively. However, the difference between the PUI-1 and all MHPUI samples is the MHPUI sample structure with the MH segment versus the PUI-1

Table III   FTIR Data of Imide Absorption Band

Sample	Segment Construction (Molar Ratio)	Multiple-Hard Type	Hard Content (wt %)	Imide I Band (cm^{-1})	Imide II Band (cm^{-1})	Imide III Band (cm^{-1})	Imide IV Band (cm^{-1})
PUI-1	MDI/PEG/PMDA (2/1/1)		41.1	1782,1724	1379	1117	725
MHPUI-2	MDI/PEG/PMDA/MDI/BPP (3.4/1.7/2.7/2/1)	MDI-BPP	54.3	1776,1724	1379	1119	725
MHPUI-3	MDI/PEG/PMDA/TDI/MOCA (2.8/1.4/2.4/2/1)	TDI-MOCA	55.9	1776,1726	1375	1113	725
MHPUI-4	MDI/PEG/PMDA/MDI/DDS (2/1/2.2/2.4/1.2)	MDI-DDS	57.7	1782,1720	1378	1103	725
MHPUI-6	MDI/PEG/PMDA/TDI/DDM (2.5/1.25/2.25/2/1)	TDI-DDM	56.2	1776,1726	1376	1115	725
MHPUI-7	MDI/PEG/PMDA/TDI/DDS (2.8/1.4/2.4/2/1)	TDI-DDS	56.0	1776,1726	1375	1105	725
MHPUI-8	MDI/PEG/PMDA/TDI/BPP (2.8/1.4/2.4/2/1)	TDI-BPP	56.0	1776,1726	1375	1113	725

without the MH segment, and the difference between the MHPUI-3 and MHPUI-6 samples is the different MH segments of the DDM linkage in the former and the MOCA linkage in the latter. This phenomenon tells us MHPUI-3 has a stronger interchain force than MHPUI-6. According to the FTIR experimental results, in considering the hard group of MDI to TDI and DDM to MOCA, the latter (TDI and MOCA) has a more rigid structure than the former (MDI and DDM).

On the other hand, the N—H stretching vibration bands also gave us some important evidence. The corresponding wavenumbers of the N—H band are listed in Table II. The absorption bands at about 3290 and 3190 cm^{-1} are assigned to the N—H stretching vibration. Several groups[22–24] proved that the splitting of the bonded N—H band was related to different acceptors with which the N—H groups were hydrogen bonded, and the bands at 3325 and 3260 cm^{-1} were assigned to N—H groups bonded with carbonyl (in hard segments) and ether oxygen (in polyether soft segments) in the PU system, respectively. Here the bands at 3290 cm^{-1} should be assigned to N—H bonds, mainly with ether oxygen (in PEG soft segments). This hydrogen bonding implied the intensity of the hard–soft segment interaction force. We obtained the following results from the Table II data: from the PUI-1 to MHPUI, the N—H stretching vibration bands (about 3290 cm^{-1}) that were assigned to the N—H groups bond with the ether oxygen (in PEG soft segments), which indicated the intensity of the hydrogen bonding of the hard and soft segments in PUI shift from 3296 to 3290 cm^{-1}.

According to the conclusions of Bellamy[21] and Wei,[25] the bands at 3190 cm^{-1} will be assigned to N—H groups bonded with the carbonyl of urethane by forming a "dual-cis bond" in the following structure.

$$-O-\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}-\overset{\displaystyle H}{\overset{\displaystyle |}{N}}-$$
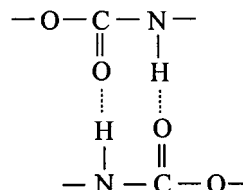
Therefore, the difference of the bands at 3190 cm^{-1} forming dual-cis bonds (in the hard segment) indicated the intensity of the interhard segments hydrogen bonding in the main chains of MHPUI. It showed that the bonded N—H (bonds at 3190 cm^{-1}) group in the PUI-1 system was less than in the MHPUI one [Fig. 1(a), (b)].

Comparing the N—H stretching vibration bands (about 3190 cm^{-1}) and the absorption intensity from Figure 1(b) for MHPUI-8 and MHPUI-2 or MHPUI-4 and MHPUI-7, the N—H band shifts to lower wavenumbers as listed in Table II. Moreover, comparing the N—H stretching vibration bands (about 3290 cm^{-1}) for MHPUI-6 and MHPUI-3, the N—H band shifts to lower wavenumbers. Such experimental results confirmed that the intensity of the hydrogen bonding of N—H with carbonyl in the hard segments of MHPUI is in the order MHPUI-2 > MHPUI-8 or MHPUI-4 > MHPUI-7 and the intensity of the hydrogen bonding of N—H with the ether

oxygen in the soft segments of MHPUI is in the order MHPUI-3 > MHPUI-6.

From the FTIR spectroscopy results it can be seen that MHPUIs with different MH segment types have different interactions of the molecular chains, and this force is stronger with a higher hard segment content in the PUI system. It can be concluded that MHPUI with different types of hard segment structures and hard segment contents have different interactions of the molecular chains, and the force of the soft–hard segment in MHPUI with the increasing of the structure rigidity of the short hard segment is particularly strengthening. This result suggests there is better compatibility between the hard segment and soft segment via the irregular distribution of the rigid short hard segment in the polymer main chain. Because of this the rigid short hard segment (TDI and MOCA) with greater space may lead the restricted soft segment into a hard segment rich phase.

Thermal Behavior of MHPUI Copolymers

The thermal behavior of the MHPUI copolymers was determined by DSC measurement. The results for different samples are listed in Table I and DSC plot shown in Figure 2. It can be seen that the T_g of the soft segment rich phase (T_{gs}) of different hard segment based MHPUIs with the same soft segment was very different. When introducing the short hard segment into the PUI backbone, the T_{gs} are very notably improved from -42 to $-3.4°$C. This phenomenon can account for the polymer hard molecular chain's rigid structure and interaction. When increasing the content
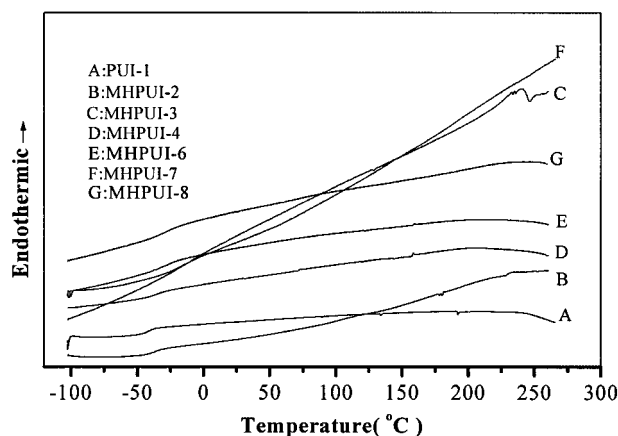
of hard segments and raising the cohesive energy density of PUI copolymers, the micro-Brownian motion of the soft segment chain was restricted and the T_{gs} increased.

The other main factor affecting the T_{gs} is the various hard segment rigid structures in MHPUI. A comparison of the T_{gs} of MHPUI with different short hard segments is given in Table I. The more rigidity in the hard segments in the polymer chains, the higher the value of T_{gs}. The sequence of T_{gs} for different MHPUIs is as follows: (MHPUI-7) > (MHPUI-4) > (PUI-1), (MHPUI-8) > (MHPUI-2) > (PUI-1) and (MHPUI-3) > (MHPUI-6) > (PUI-1). The T_{gs} values of MHPUI-7 and MHPUI-8 with the same TDI terminate hard block group in the main chain are higher than that of MHPUI-4 and MHPUI-2 with the same MDI group. Moreover, when the DDM group replaces the MOCA group, the T_{gs} values of MHPUI decreased from -3.4 to $-26.9°$C. These results showed the hard block structural rigidity effects on the interaction force of the polymeric chain and the compatibility of the soft–hard segment in MHPUI. The DSC result suggests that the soft segment is more compatible with the hard segment when the hard segment rigidity is increased. However, some of the IR absorption frequencies of the N—H and T_{gs} change do not have the same trend, such as the order of compatibility: MHPUI-8 (3192 cm^{-1}, $-24.8°$C) > MHPUI-2 (3190 cm^{-1}, $-26.6°$C) and MHPUI-7 (3190 cm^{-1}, $-8°$C) > MHPUI-4 (3188 cm^{-1}, $-27.9°$C). This result can be explained by the symmetry and rigidity of the hard block. The bands at 3190 cm^{-1} assigned to dual-cis bonds of the N—H groups bond with the carbonyl of the urethane or urea groups. The symmetrical hard block structure (such as MDI) possibly forms a better hydrogen bonded complex structure of dual-cis bonds, and the hydrogen bonding of N—H with carbonyl may be strengthened. Therefore, the N—H bands (3190 cm^{-1}) shift to low frequency. This result also indicated that the governing factor of the compatibility of hard–soft segments in MHPUI should be the rigid structure of the hard segments (TDI and MOCA) with a greater space, leading to the restricted soft segments in the hard segment rich phase.

TGA Measurement of MHPUI Copolymers

We also investigated the thermal stability and thermal degradation of MHPUI copolymers as synthesized. The TG curves of different MHPUI
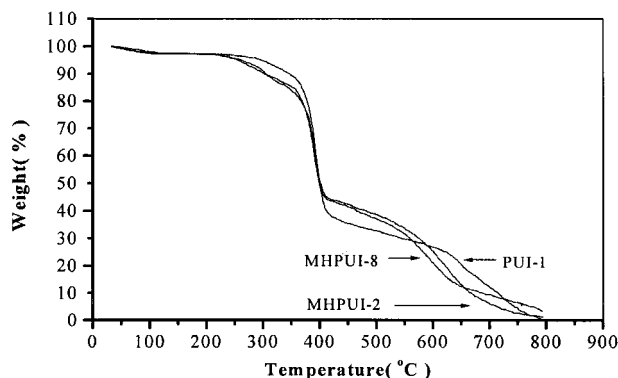

Figure 2 A DSC plot of the MHPUI samples with different multiple-hard segments.

Figure 3 A TGA plot of the MHPUI samples with different hard segments.

samples are represented in Figure 3, and representative temperatures of thermal degradation are listed in Table IV.

The characteristic thermal degradation temperatures of the first and last stage temperatures of degradation ($T_{di(1)}$ and $T_{di(2)}$) and the temperature of the first maximum rate of weight loss ($T_{\max(1)}$) indicated the thermal stability of MHPUI at different heating stages. The value of $T_{di(1)}$ originated from TGA is the representative temperature of the initial stage of thermal weight loss, which indicates the initial thermal stability of samples. The $T_{\max(1)}$ value obtained from DTG is the characteristic temperature of the first maximum rate of weight loss, and it represents the thermal stability of the soft segments in MHPUI. The $T_{di(2)}$ is the initial temperature of the second stage platform of thermal weight loss, and it depends on the stability of the imide segments in MHPUI. Table IV shows that by introducing the MH segment into the PUI, the $T_{di(1)}$ and $T_{di(2)}$ of the samples of MHPUI are all decreased. This result implied that the MH segment contains somewhat unstable groups. We consider that this unstable group in MHPUI is the urethane or urea groups. This degradation merely reflects the volatilization of the short chain of diamine and diols produced by decomposition of urethane groups.

A comparison of the stage degradation temperatures of the samples reveals that they are all different. The results showed that the thermal stability order is as follows: PUI-1 > MHPUI-4 > MHPUI-7, PUI-1 > MHPUI-2 > MHPUI-8, and PUI-1 > MHPUI-6 > MHPUI-3. Comparing the MHPUI-2, MHPUI-4, MHPUI-6, and MHPUI-8 chemical structures, there is only a difference with different diisocyanates (MDI vs. TDI). The MHPUI-2 and MHPUI-4 samples both with MDI

are different than the MHPUI-8 and MHPUI-7 samples with TDI. In addition, a comparison of the MHPUI-6 and MHPUI-3 samples reveals that the difference in their chain structure is with different diamines. The sample of MHPUI-6 with DDM is different than MHPUI-3 with MOCA. We know that the order of the molecular chain structure symmetry is MDI > TDI and DDM > MOCA.

The experimental results showed that every sample of MHPUI-2, MHPUI-4, and MHPUI-6 containing symmetry structure groups (MDI or DDM) is more stable than that without them. Comparing MHPUI to PUI-1, we consider that the hard segment structure symmetry has a more important role in the MHPUI thermal stability. We think that the hard segment with a clear and neat structure may produce the hard segment chain's aggregation. The soft and hard segments phase compatibility was decreased, and the soft–hard segment phase was more separable; at the same time, the soft or hard segments were close together. Therefore, the hard segments molecular interchains tend to combine and result in good thermal stability, as shown in Table IV and Figure 3.

The FTIR and T_{gs} data showed that the molecular interaction and miscibility between the hard and soft segments are in order of MHPUI-3 > MHPUI-6, MHPUI-8 > MHPUI-2, and MHPUI-7 > MHPUI-4. The FTIR results also showed that the intensity of the hydrogen bonding of N—H with carbonyl in the hard segments of MHPUI is in the order of MHPUI-2 > MHPUI-8 or MHPUI-4 > MHPUI-7 and the intensity of hydrogen bonding of N—H with soft segments in

Table IV   Thermal TG Data of Different Multiple-Hard Segment PUI Samples

Samples	Hard Segment Content (wt %)	$T_{di(1)}$ (°C)	$T_{\max(1)}$ (°C)	$T_{di(2)}$ (°C)
PUI-1	41.1	371.2	391.7	631.0
MHPUI-2	54.3	362.6	397.1	587.2
MHPUI-3	55.9	355.4	387.7	519.1
MHPUI-4	57.7	351.6	374.4	584.9
MHPUI-6	56.2	361.3	394.0	572.2
MHPUI-7	56.0	344.5	374.1	576.8
MHPUI-8	56.0	358.4	396.4	558.3

$T_{di(1)}$, The initial temperature of the first stage of thermal weight loss; $T_{\max(1)}$, the temperature of the first maximum rate of weight loss; $T_{di(2)}$, the initial temperature of the second stage of thermal weight loss.

MHPUI is in the order of MHPUI-3 > MHPUI-6. We consider that with the intensity of the hydrogen bonding of N—H with carbonyl (in interhard segments) in the MHPUI increasing, the soft–hard segment-rich phase was more separated. With the intensity of the hydrogen bonding of N—H with ether oxygen in the soft segments of MHPUI increasing, the soft–hard phase was more compatible.

Obviously, we may conclude that the better compatibility of the hard and soft segments gives worse thermal stability and leads to a lower weight loss degradation temperature. This conclusion can be easily understood by comparing the MHPUI-3 and PUI-1 samples. Their different thermal weight loss stage temperatures are listed in Table IV. The T_{gs} values of MHPUI-3 and PUI-1 are -3 and $-44°C$, respectively. This result implies that the miscibility of the soft and hard segments of MHPUI-3 is better than that of PUI-1. However, the $T_{di(1)}$, $T_{\max(1)}$, and $T_{di(2)}$ are all lower than those of PUI-1. This means that the thermal stability of MHPUI-3 is worse than that of PUI-1.

In summary, the TGA result implies that when the soft and hard phases are more separated, the MHPUI samples possess greater thermal stability. Meanwhile, this study investigated the different stages of temperature degradation of the MH segment PUI copolymer from the TGA curve. Figure 3 clearly demonstrates that PUI with different MH segment copolymers undergoes at least two stages of thermal degradation. Because the MH segment is introduced into the main chain of PUI, the initial thermal degradation temperature decreased from 371 to 344.5°C. As mentioned above, the initial degradation mechanism did not occur in the hard segments of the imide groups; instead it started in the hard segments of urethane because the MH segment contains a lot of urethane or urea groups. Nevertheless, we consider that the unstable hard segment in the PUI is the fatal factor for deciding the thermal degradation of PUI material. However, the change of $T_{\max}$ was not in evidence, because all MHPUI samples have the same soft segment, which is the PEG soft segment. This result further supports the three-step mechanism of thermal degradation of PUI that we proposed in our former work.[17]

CONCLUSIONS

We synthesized different MH segment PUI copolymers by a three-step process. The FTIR spectra confirmed the characteristic absorption bands of MHPUI copolymers. The shift of the absorption bands for the imide group can be explained by the different MH segment types and hard segment contents with different interaction forces of the molecular chains; especially the changes of the N—H stretching vibration bands showed the intensity of the hydrogen bonding of N—H with ether oxygen or carbonyl in the segments of MHPUI. This interaction force in MHPUI with the increasing of the structure rigidity of the short hard segment increases the strength.

The DSC analysis revealed that the T_{gs} of different MH segment based PUIs rise in value from -42 to $-3.4°C$. The DSC result suggests that the soft segment is more compatible with the hard segment when the hard segment rigidity is increased.

The TGA results showed the hard segment structure symmetry has an more important role in MHPUI thermal stability. Every sample containing symmetry structure groups (MDI or DDM) is more thermally stable than that with worse symmetry structure groups (TDI or MOCA). The three-step mechanism of PUI thermal degradation was further verified. The thermally unstable group was confirmed as the urethane or urea–urethane segment. From the FTIR results we conclude that with the intensity of hydrogen bonding of N—H with carbonyl in MHPUI increasing, the soft–hard phase was more separated; and with the intensity of hydrogen bonding of N—H with ether oxygen in MHPUI increasing, the soft–hard phase was more compatible.

We concluded that better compatibility of the hard and soft segments gives worse thermal stability and leads to a lower temperature of weight loss degradation. The TGA result showed that MHPUI copolymers with higher separation of the soft–hard phase have higher thermal stability.

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