

Structure and Thermal Properties of Polyether Polyurethaneurea Elastomers

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SYNOPSIS

Three series of polyether polyurethaneurea (PEUU) elastomers based on poly(tetramethylene glycol) (PTMG, MW = 1000 or 2000), 4,4'-diphenylmethane diisocyanate (MDI), and three kinds of diamine chain extenders, i.e., 4,4'-diaminodiphenylmethane (DAM), *m*-phenylenediamine (MPD), and *p*-phenylenediamine (PPD) were synthesized in dimethylformamide or DMF-LiCl solvent by the prepolymer method. The degree of phase separation was higher in the samples with PTMG-2000 than in those with PTMG-1000. Three-dimensional hydrogen bonding between hard segments led to strong hard-domain cohesion, but solubilized soft segment and the remaining LiCl within hard domains interfered with microstructural ordering of hard segments. According to the TG/DTA analyses, as-cast PEUU elastomers showed two-stage degradation behavior at a heating rate of 20°C/min in a nitrogen atmosphere. Initial degradation temperature was closely related with both hard-segment content and microstructural ordering, i.e., most of the hard segments were degraded in the first stage and samples with less ordered hard segments degraded at a lower temperatures. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Extensive studies on the unique morphology and properties of polyurethane (PU) elastomers have been reported recently.¹⁻³ These polymers are $A-B_n$ type linear multiblock copolymers, which consist of two chemically dissimilar alternating segments. In general, the soft segment (S/S) is polyether or polyester macroglycol and the hard segment (H/S) is formed by extending a diisocyanate with a low molecular weight diol. The two segments are thermodynamically incompatible, and there is a strong intermolecular interaction between urethane units, which is the primary driving force for domain formation of the H/S. The degree of phase separation of urethane H/S into microdomains is regarded as the decisive factor governing the end properties of polyurethane (PU) elastomers. More recently, morphology and properties of polyurethaneurea (PUU) elastomers from diamine chain extenders instead of diol chain extenders have been

studied extensively. This elastomer has highly cohesive urea linkages in the H/S and the degree of phase separation is better than that of the corresponding PU elastomers.⁴⁻⁷ Therefore, thermal and mechanical properties of PUU elastomers are known to be superior to those of the conventional PU elastomers.⁷⁻¹⁰ PUU elastomers have wide use as high-performance materials in the textile and other industrial fields through dry or wet processes.

Sung et al.^{5,6} studied the properties of segmented polyether polyurethaneurea (PEUU) based on 2,4-tolylene diisocyanate (2,4-TDI), ethylenediamine (ED), and poly(tetramethylene glycol) (PTMG). Microphase separation of PEUUs extended with ED was suggested to be better than that of PU chain-extended with 1,4-butane diol. This was interpreted to be due to the presence of three-dimensional hydrogen bonding between the H/S, i.e., two urea N—H groups are bonded to one urea carbonyl in a nonplanar three-dimensional configuration, which was also tentatively suggested by Bonart et al.¹¹

Wang and Cooper¹² studied 4,4'-diphenylmethane diisocyanate (MDI)-based PEUUs, i.e., composed of PTMG/MDI/ED. The effect of the H/S content and block length on the morphology and properties of PEUUs were studied systematically. The me-

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chanical properties depended primarily on the H/S content and the strong hard-domain cohesion due to the interurea hydrogen bonding that resulted in semicrystalline behavior as observed in thermal analyzes.

There are many earlier studies concerning the hydrogen bonding and morphology of PEUU elastomers, including those of Ishihara et al.,¹³ Kimura et al.,¹⁴ and Chang and Wilkes,¹⁵ but their studies were mostly limited to the molar ratio of 1/2/1 (PTMG/MDI/aromatic diamine). Therefore, in this study, we systematically investigated the effect of the H/S content, MW of the S/S, and the kind of diamine chain extender on the morphology and properties of these materials.

The thermal stability of PU elastomers has not been studied extensively. Grassie et al.¹⁶ studied the thermal degradation behavior of polyester-type PU having the H/S of MDI/BD by thermogravimetry. Recently, Lee et al.¹⁷ synthesized PUU through an unconventional synthetic method and elucidated that the thermal degradation temperature of PUU is higher than that of PU by thermogravimetric measurements. This article also focuses on the relationship between microstructural ordering of the H/S and the thermal stability of the synthesized PEUU series.

EXPERIMENTAL

Materials

Reagent-grade PTMG of molecular weight 1000 and 2000 (Aldrich Chemical Co.), 4,4'-diaminodiphe-

nylmethane (DAM, Fluka Chemie AG), *m*-phenylenediamine (MPD, Fluka Chemie AG), and *p*-phenylenediamine (PPD, Fluka Chemie AG) were dehydrated under vacuum at 60°C before use. Spectrophotometric grade *N,N'*-dimethylformamide (DMF, 99.9%, 0.004% moisture content, J. T. Baker Chemical Co.) was dehydrated with molecular sieves. Anhydrous lithium chloride (LiCl, Yakuri Pure Chemicals Co.) was dehydrated under vacuum at 100°C for 12 h. All other reagents were used as received.

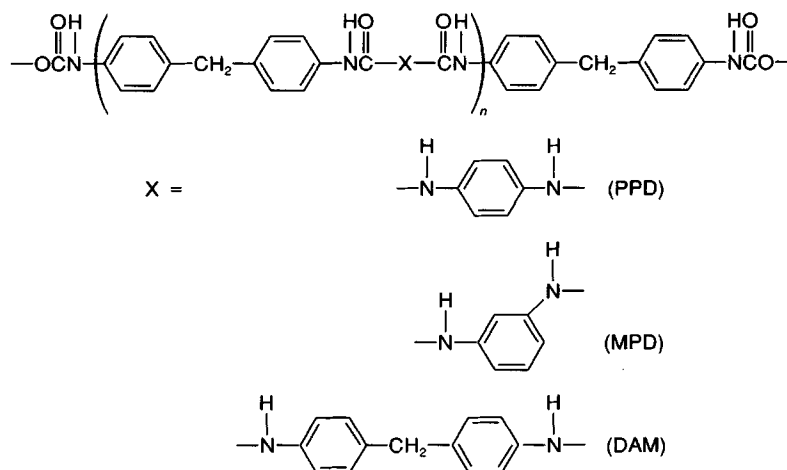
Polymer Synthesis

Segmented PEUUs were synthesized by a modified solution polymerization method in a dry N₂ atmosphere.¹⁸ The calculated amount of 40% solution of dehydrated MDI in DMF was prepared in a four-neck reactor. A 40% solution of PTMG in DMF was added to the stirred MDI solution at 30°C. After reacting at 30°C for 30 min and at 60°C for 1.5 h, NCO-capped prepolymer was identified by the ASTM D 2572 method. In the second step, a dilute solution (10%) of diamine chain extender in DMF was added slowly through a dropping funnel to the well-stirred solution of prepolymer and unreacted MDI cooled to 35°C. The reaction was performed for 30 min at 35°C and continued for 3 h at 40–45°C. In the course of the reaction, DMF solvent was added when the viscosity of the solution increased and the final solid content of the system was controlled to 12–20%. The molar ratio of reactants was altered to produce samples with systematically varied H/S content (26, 36, and 44%). In Table I,

Table I Feed Composition of Various PEUU Series

Sample Code	Molar Ratio PTMG/MDI/Diamine	No. Functional Groups per Repeat Unit		
		—NH	—C=O (Urethane)	—C=O (Urea)
DAM-26-2	1/2/1	6.0	2	2.0
DAM-36-2	1/3/2	10.0	2	4.0
DAM-44-2	1/4/3	14.0	2	6.0
MPD-26-2	1/2.3/1.3	7.2	2	2.6
MPD-36-2	1/3.5/2.5	12.0	2	5.0
MPD-44-2	1/4.7/3.7	16.8	2	7.4
PPD-26-2	1/2.3/1.3	7.2	2	2.6
PPD-36-2	1/3.5/2.5	12.0	2	5.0
PPD-44-2	1/4.7/3.7	16.8	2	7.4
DAM-36-1	1/1.7/0.7	4.8	2	1.4
MPD-36-1	1/1.9/0.9	5.6	2	1.8
PPD-36-1	1/1.9/0.9	5.6	2	1.8

Soft segment: polytetramethylene glycol (MW = 1000 or 2000)
 $H-(OCH_2CH_2CH_2CH_2)_m-OH$, where $m = 14$ or 28
 Hard segment: MDI/aromatic diamine



Scheme 1 Chemical structures of soft segment and hard segment.

the sample code DAM-26-2 designates a sample whose chain extender is DAM, content of H/S is 26%, and molecular weight of PTMG is 2000. Even though the molar ratio of reactants is higher than 1 : 2 : 1 (PTMG : MDI : diamine), side reactions including the formation of homopolymer have not essentially occurred, which could be understood by taking into account the reactivity of isocyanate compounds, although the sequence length of the hard segment illustrated in Scheme 1 may have a distribution in "n."^{19,20} A small amount of LiCl was added when the solubility of reaction mixture decreased in some PEUU series during the chain-extension step. Synthesized PEUU solution was diluted to 10–15%, cast on a glass plate, and dried under vacuum at 60–70°C for 3 days. The dried films were immersed in purified water overnight to remove remaining chain extenders and LiCl.

An H/S analogous polymer, i.e., MDI/DAM (1 : 1, molar ratio) copolymer, was prepared in DMF/LiCl solution. MDI, 0.032 mol (5% excess), was added to 110 g of DMF solution containing 0.5% LiCl at 30°C; then 0.03 mol of diamine compound (ex.: DAM) solubilized in 25 g of DMF was added and reacted for 30 min and for an additional 3 h at 45°C. The polymer was precipitated in methanol, washed, and vacuum-dried for 5 days at 60°C to ensure complete removal of the solvent.

Polymer Characterization

Intrinsic Viscosity Measurements

The intrinsic viscosity of PEUU was measured in DMF or DMF/LiCl solvent at 25°C using a Ubbelohde capillary viscometer.

Gel Permeation Chromatography (GPC)

GPC analyses of the PEUUs were carried out using a Ultrastaygel column (Waters Associates). The concentration of specimens was 0.25% in DMF or DMF/LiCl. The data, calibrated with standard polystyrene, are summarized in Table II.

Dynamic Mechanical Property Measurements

The dynamic mechanical properties were measured on a Rheovibron DDV-II-EP (Orientec Corp.) using PEUU films in a nitrogen atmosphere at frequency of 110 Hz. The sample size was 30 (length) × 5.0 (width) × 0.1–0.15 mm (thickness) and the heating rate was 3°C/min.

IR Studies

The IR spectra of thin polymer films (5 μm in thickness) were obtained with a Fourier transform IR spectrophotometer (Digilab Division, FTS-20/80) at a resolution of 4 cm⁻¹. For analysis of the peak positions of the specific functional groups, spectra were obtained at a resolution of 1 cm⁻¹. The H/S copolymer (MDI/DAM) was analyzed by the KBr pellet method.

Differential Scanning Calorimetry (DSC)

DSC thermograms in the temperature range -120 to 200°C were obtained by using a Stanton Redcroft differential scanning calorimeter with a liquid nitrogen coolant under a nitrogen purge. The first heating curve was obtained by heating at 20°C/min to 200°C after cooling the specimen from room tem-

Table II Solubility and MW of Synthesized PEUU Elastomers

Sample Code	DMF Solution (10%, 50°C)	[η], (dL/g)	GPC Results ^a		
			$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	MWD
DAM-26-2 ^b	Clear ^c	0.46	84	159	1.89
-36-2 ^d	Clear	0.73	126	176	1.39
-44-2 ^d	Opaque ^e	0.75	114	201	1.77
MPD-26-2 ^b	Clear	0.42	80	154	1.93
-36-2 ^b	Clear	0.40	75	304	4.40
-44-2 ^b	Clear	0.63	125	264	2.11
PPD-26-2 ^d	Clear	0.53	123	163	1.33
-36-2 ^d	Opaque	0.51	101	128	1.28
-44-2 ^d	Opaque	0.59	87	132	1.52
DAM-36-1 ^b	Clear	0.80	151	684	4.52
MPD-36-1 ^b	Clear	0.50	110	303	2.76
PPD-36-1 ^d	Opaque	0.61	146	210	1.44

^a Polystyrene equivalent MW.

^b DMF solvent in [η] and GPC measurement.

^c Clear: transparent, absolutely solubilized in the above condition.

^d DMF/LiCl solvent in [η] and GPC measurement.

^e Opaque: hazy, poorly solubilized in the above condition.

perature to -130°C at $-10^\circ\text{C}/\text{min}$. The second heating curve was obtained by heating at $20^\circ\text{C}/\text{min}$, after rapidly cooling the specimen from 200°C to r.t. and from r.t. to -130°C at $-10^\circ\text{C}/\text{min}$. Sample weights were 10–20 mg and the data were normalized to an equivalent sample weight.

Thermogravimetry (TG)

A TG/DTA analyzer (Seiko Instruments Inc., SSC/5200) was used to obtain TG, DTA, and differential thermogravimetry (DTA) curves simultaneously. Samples were heated from r.t. to 50°C and held for 5 min and then heated to 650°C at a heating rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere.

Wide-angle X-ray Diffraction Studies (WAXD)

Wide-angle X-ray diffraction scans were made on a Rigaku Denki diffractometer (Ru 200B, 12 kW) with $\text{CuK}\alpha$ radiation. The thickness of film specimens was about 1 mm.

RESULTS AND DISCUSSION

Characterization of PEUU Series

Generally, PUUs composed of aromatic monomers have poor solubility in organic solvents. The PEUU series synthesized in this paper exhibited different

solubilities according to the chain extenders and H/S content, i.e., the solubilities in DMF decreased with increasing H/S content. PEUUs that have the same H/S content showed solubility in the order of the MPD \gg DAM $>$ PPD series, which reflects the poorer intersegmental hydrogen bonding due to the steric effect of the *meta*-extended MPD extender relatively to the other two extenders. The presence of side branches or cross-linking formed during syntheses affects solubility. Table III shows the results of solubility tests in various solvent systems. Synthesized PPD-36-1, e.g., was easily soluble in DMF/LiCl, which means that PPD-36-1 is almost linear without cross-linking. All the other polymers

Table III Solubility^a of PPD-36-1

Solvent ^b	Wt % of Sample in Solvent			
	0.1	1	5	20
DMF	Δ	–	–	–
DMSO/MIBK (w/w, 1/1)	Δ	–	–	–
DMAc	+	Δ	–	–
DMF (LiCl 0.5 wt %)	++	++	++	++

^a –, insoluble; Δ , slightly soluble; +, soluble; ++, very soluble.

^b DMSO: dimethylsulfoxide, DMAc: dimethylacetamide; MIBK: methyl isobutyl ketone.

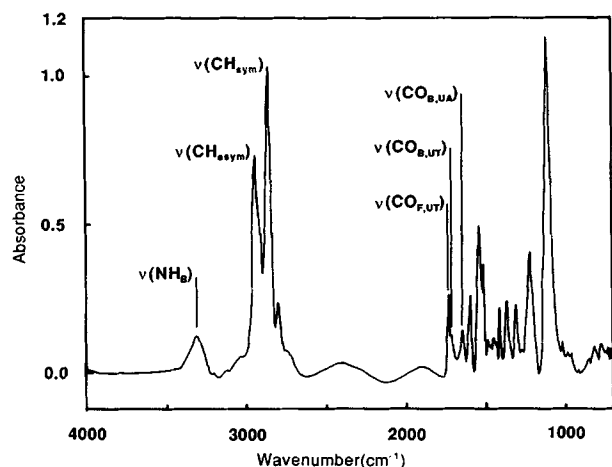


Figure 1 Infrared spectrum of DAM-26-2.

were soluble in DMF/LiCl, although the amount of LiCl required was different. The PEUUs may have become soluble because of the disruption of hydrogen bonding between H/S by the added LiCl. Table II shows the solubility of each PEUU in a 10% DMF solution at 50°C; for example, DAM-44-2 was almost nonsoluble in DMF alone at 50°C, but when 5% of LiCl based on the weight of polymer was added to DMF, the polymer became soluble. PPD-36-2, PPD-44-2, and PPD-36-1 became soluble with the aid of 5.5, 7, and 1% of LiCl, respectively. According to Table II, all PEUUs have MW's above 70,000, which should be large enough to exhibit useful mechanical properties.²¹

Figure 1 shows the IR spectrum of DAM-26-2 film. The hydrogen-bonded —NH stretching peak

(NH_B) appeared at 3310 cm⁻¹, the —CH_{asym} and —CH_{sym} stretching vibration peaks of soft-segment PTMG were located at 2941 and 2857 cm⁻¹, respectively. In the carbonyl region, the —C=O stretching peaks of the urethane group appeared at 1732 and 1713 cm⁻¹; the former is a non-hydrogen-bonded peak (CO_{F,UT}) and the latter shoulder is a hydrogen-bonded peak (CO_{B,UT}).¹³ At 1643 cm⁻¹, a hydrogen-bonded urea carbonyl peak (CO_{B,UA}) appeared. A free urea carbonyl around 1695 cm⁻¹ was not detected. The IR peak positions of the other series are summarized in Table IV. Figure 2 is an IR spectrum of the MDI/DAM copolymer; the H-bonded —NH and —C=O peaks of urea linkage are located at 3308 and 1652 cm⁻¹, respectively, whereas non-hydrogen-bonded peaks cannot be discerned.

Phase-separation Behavior

The glass transition temperature (T_g) of the S/S is usually utilized as a measure of phase separation in block copolymer elastomers. Typical DSC scans for the DAM series are illustrated in Figure 3. The T_g of the S/S phase appears in the region of -60 to -67°C for the samples whose PTMG MW is 2000 and appears at -41°C for the DAM-36-1 whose PTMG MW is 1000. Therefore, phase separation of the PTMG 2000 series is much better than that of the PTMG 1000 sample. But the S/S glass transition temperatures are nearly independent of the urea content or the H/S length for the PTMG 2000 series as summarized in Table V. Hu and Ward²² suggested that the relative crystallinity of the S/S of PUU

Table IV IR Peak Positions of Various Functional Groups for PEUU Series

Sample Code	NH _B	CH _{asy}	CH _{sym}	CO _{F,UT}	CO _{B,UT}	CO _{B,UA}
DAM-26-2	3310	2941 ± 1	2857 ± 1	1732 ± 1	1713	1643
-36-2	"	"	"	"	1709	1645
-44-2	3307	"	"	"	1707	1651
MPD-26-2	3306	"	"	"	1712	1641
-36-2	"	"	"	"	1712	1641
-44-2	"	"	"	"	1711	1641
PPD-26-2	3306	"	"	"	1710	1638
-36-2	"	"	"	"	1707	1641
-44-2	3308	"	"	"	1705	1643
DAM-36-1	3310	"	"	"	1711	1645
MPD-36-1	3307	"	"	"	1711	1641
PPD-36-1	3307	"	"	"	1707	1638
MDI/DAM	3308	—	—	—	—	1652

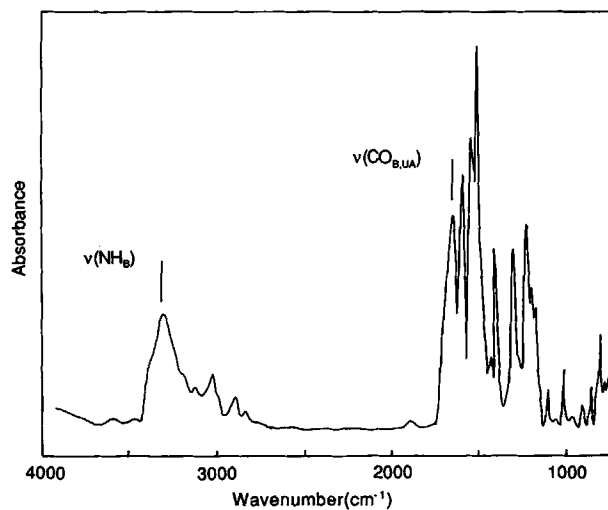


Figure 2 Infrared spectrum of H/S polymer (MDI/DAM).

could be used as a measure of phase separation more sensitively than could the conventional thermal transition temperature measurement. According to their test, increasing the H/S content in PUU decreased the crystallinity of the S/S for the same-type chain extenders. Also, in our test, as indicated in Figure 3 and Table V, DAM-26-2, which has the lowest H/S content, showed the highest S/S crystallinity, which suggests that this sample has the best phase-separated morphology. Figure 4 shows DSC scans of the PEUU-26-2 series (H/S 26%,

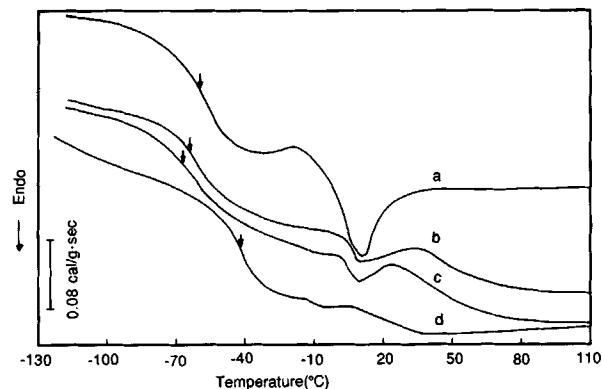


Figure 3 DSC thermograms (first heating) of DAM series: (a) DAM-26-2; (b) DAM-36-2; (c) DAM-44-2; (d) DAM-36-1.

PTMG 2000). The T_g of the S/S were almost the same, but the MPD sample's S/S crystallinity is smaller than that of the other two samples.

Dynamic mechanical analysis can also be used to estimate the degree of phase separation, i.e., the low-temperature transition can be related to the glass transition of the amorphous S/S rich phase in segmented PUs. The dissipation factor ($\tan \delta$) of the DAM series is plotted as a function of temperature in Figure 5. Despite the variation in sample composition, two maxima in the $\tan \delta$ curve occur approximately at -120 and -50°C for the samples using PTMG-2000. The lower-temperature loss peak is related to the local mode motion of the $-\text{CH}_2-$

Table V DSC Results of PEUU Elastomers Measured with a Heating Rate of $20^\circ\text{C}/\text{Min}$ Under a Nitrogen Atmosphere

Sample Code	Thermal Condition	$T_{g,S/S}$ ($^\circ\text{C}$)	$T_{m,S/S}$ ($^\circ\text{C}$)	$\Delta H_{f,S/S}^a$
DAM-26-2	1st heating	-60	10	3.4
	2nd heating	-60	14	4.6
DAM-36-2	1st heating	-63	9	0.8
	2nd heating	-65	9	0.8
DAM-44-2	1st heating	-67	8	0.5
	2nd heating	-69	5	1.1
DAM-36-1	1st heating	-41	—	—
	2nd heating	-45	—	—
MPD-26-2	1st heating	-58	13	0.7
	2nd heating	-61	15	2.4
PPD-26-2	1st heating	-63	10	1.9
	2nd heating	-63	13	6.4

^a cal/g (wt normalized by unit gram of S/S).

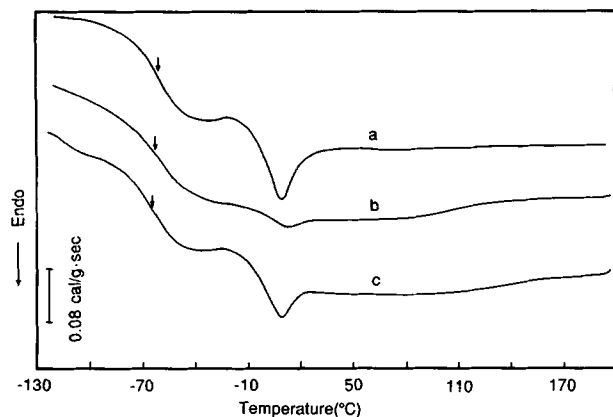


Figure 4 DSC thermograms (first heating) of PEUU elastomers having different chain extenders: (a) DAM-26-2; (b) MPD-26-2; (c) PPD-26-2.

O group, whereas the higher-temperature loss peak is attributed to the S/S glass transition.²³ On the other hand, for the DAM-36-1 using PTMG-1000, the glass transition of the S/S occurs at -22°C . Peak positions in the $\tan \delta$ and E'' curves (the loss modulus curves, not shown) are summarized in Table VI. The results indicate that the glass transition temperature of the S/S is closely related to the S/S molecular weight, but the effects of the H/S content or chain extenders on the phase behavior were

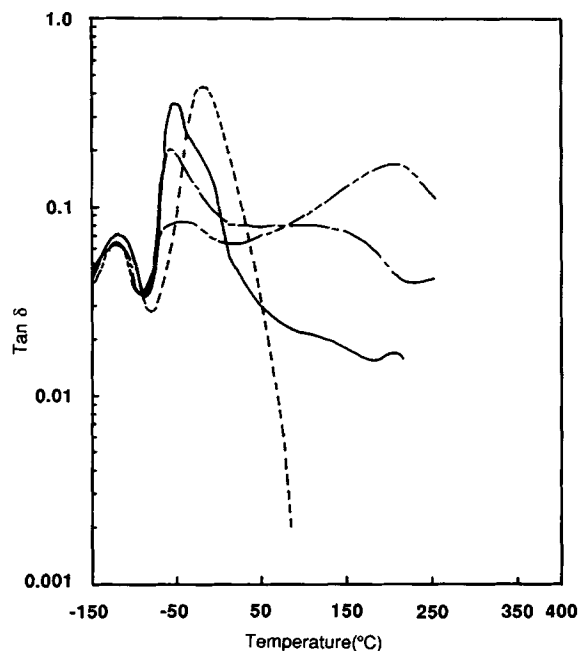


Figure 5 $\tan \delta$ curves of the DAM series: (—) DAM-26-2; (---) DAM-36-2; (- - -) DAM-44-2; (· · ·) DAM-36-1.

Table VI Dynamic Mechanical Analysis Results of PEUUs Representing the Transition Temperatures

Sample Code	Secondary Relaxation Temp ($^{\circ}\text{C}$)		$T_{g,S/S}$ ($^{\circ}\text{C}$)	
	From $\tan \delta$	From E''	From $\tan \delta$	From E''
DAM-26-2	-118	-128	-53	-59
-36-2	-124	-125	-56	-65
-44-2	-123	-130	-43	-69
MPD-26-2	-119	-130	-50	-58
-36-2	-125	-128	-43	-62
-44-2	-124	-126	-53	-69
PPD-26-2	-119	-127	-52	-64
-36-2	-116	-125	-55	-68
-44-2	-123	-129	-63	-70
DAM-36-1	-130	-130	-22	-40
MPD-36-1	-123	-128	-15	-38
PPD-36-1	-122	-125	-23	-43

not clearly detected. The glass transition temperatures of the S/S in Table VI are a little different from those indicated in the DSC tests, which may be due to the difference of testing conditions in respective tools. However, T_g 's estimated by loss modulus in DMA method are very close to those of the DSC method.

Microstructural Ordering of the H/S

The microstructure of hard domains could be identified by X-ray investigations or DSC tests. Figure 6 shows WAXD curves of the DAM series. MDI/DAM copolymers exhibit distinctive H/S reflection peaks at 11, 8.3, 4.6, 4.2, and 3.3 \AA ; other PEUU samples gave weak peaks at the same scattering angles. Therefore, those reflections are attributed to the H/S of PEUUs, but the crystallinity of all H/S should be very low. WAXD curves of the MPD and PPD series are not shown, but their reflection peaks are also weak and broad. Generally, DSC tests reveal that the crystalline H/S of PEUU elastomers melts above the degradation temperature because of their strong interurea interactions. Therefore, investigations of relative microstructural ordering of the H/S in the PEUU series were difficult by X-ray measurements or DSC methods.

The shift in IR peak positions of functional groups reflects their interactions between chemical

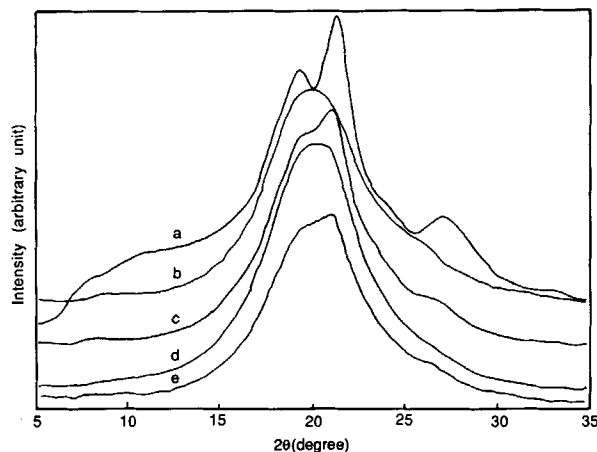
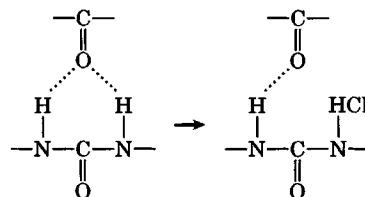


Figure 6 WAXD curves of the DAM series (film thickness: 1 mm): (a) MDI/DAM; (b) DAM-44-2; (c) DAM-36-2; (d) DAM-26-2; (e) DAM-36-1.

groups or their environment in macromolecular systems.^{8,13} The frequency shift of —NH and —C=O stretching peak for the PU system is generally regarded as a measure of hydrogen-bonding power of the H/S.^{24,25} In early studies, Ishihara et al.¹³ assigned the peak positions of hydrogen-bonded or free functional groups in the MDI-based PUU elastomers. The peak positions of NH_B , $\text{CO}_{F,UT}$, $\text{CO}_{B,UT}$, and $\text{CO}_{B,UA}$ including —CH stretching in PEUUs of this study are summarized in Table IV. The NH_F stretching vibration peak at around 3445 cm^{-1} and the $\text{CO}_{F,UA}$ peak at around 1695 cm^{-1} were not detected in this study. For all the samples, —CH stretching and $\text{CO}_{F,UT}$ absorption stay within a range of 1 cm^{-1} , indicating that the local environment around these groups does not change with sample composition or the kind of chain extenders.

In early studies, Bonart et al.¹¹ and Sung et al.⁶ suggested a three-dimensional hydrogen bond for both MDI- and TDI-based PEUUs where each urea carbonyl was bonded to two NH groups. According to Sung et al.⁶ and Wang and Cooper,¹² the $\text{CO}_{B,UA}$ peak shifts to a lower frequency above a critical content of the H/S. In Sung et al.'s studies of TDI-ED-based PEUUs, the hydrogen-bonded carbonyl ($\text{CO}_{B,UA}$) peak shifted from 1660 to 1640 cm^{-1} when the H/S content increased from 47 to 53%. In Wang and Cooper's studies using MDI-based PUUs extended with ED, the $\text{CO}_{B,UA}$ peak also shifted to a lower frequency, when the content of the H/S increased from 25 to 36%. They explained that this shift in $\text{CO}_{B,UA}$ is due to the increased number of three-dimensional hydrogen bonding. In our study, the MPD series has a NH_B peak at 3306 cm^{-1} and

$\text{CO}_{B,UA}$ at 1641 cm^{-1} irrespective of the H/S content. Therefore, urea linkage of the MPD series should have almost three-dimensional hydrogen bonding for all H/S contents within the experimental ranges (26, 36, 44%). In the case of the DAM series, the $\text{CO}_{B,UA}$ peaks varied with the content of H/S, i.e., shifted to 1651 cm^{-1} at an H/S content of 44% from 1643 cm^{-1} at an H/S content of 26%. This unusual phenomenon may be due to the remaining LiCl within the H/S that was added to the casting solution of DAM-44-2; the remaining Cl^{-} ion may interfere with the three-dimensional hydrogen bonding of urea linkages as follows:



A second reason may be purity of the H/S, i.e., an increase of solubilized S/S in the large hard domains could restrict the three-dimensional hydrogen bonding, resulting in an increase in conventional hydrogen bonding. The PPD series exhibited similar results as those of the DAM series, where PPD-36-2 and PPD-44-2 film also contained a chlorine ion that could be identified by the oxygen flask test. Generally, a frequency shift has been accepted as a measure of the strength of the hydrogen bond. In summary, the investigation of $\text{CO}_{B,UA}$ peaks of the DAM or PPD series revealed that hydrogen-bond strengths decreased with the increase in the H/S content in the PEUU series obtained from solvent-casting.

Thermal Stabilities

It is known that PUUs have better thermal stabilities due to the strong three-dimensional hydrogen-bonded interurea groups than those of corresponding PUs.^{4,8} In early studies, Grassie et al.¹⁶ examined the thermal degradation mechanism of polyester PU with a range of polyester contents. Their TVA (thermal volatilization analysis) and TG (thermogravimetry) tests demonstrated that the threshold degradation temperature of PUs increased with an increasing S/S content, i.e., polyester chain segments are more stable than are the urethane units. They explained that thermal stability could be increased through the stabilization of a urethane link by hydrogen bonding of —NH groups with ester carbonyl groups.

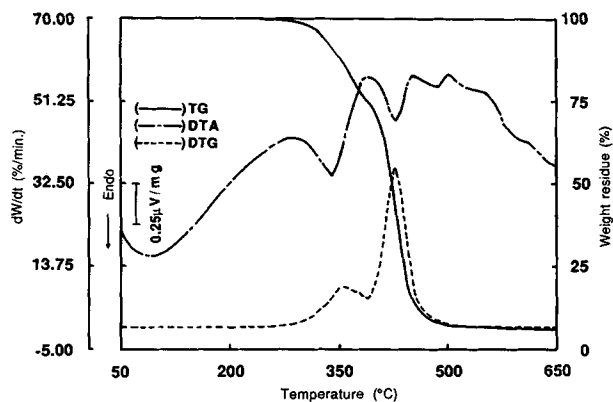


Figure 7 TG/DTA thermograms of DAM-26-2 with a heating rate of 20°C/min in a nitrogen atmosphere.

Until now, the effect of the microstructure of the H/S on the thermal stability of PUU elastomer has not been fully studied. In this study, we examined the TG/DTA analysis of PEUU films under a nitrogen atmosphere at a heating rate of 20°C/min. A thermal degradation curve of DAM-26-2 is shown in Figure 7. It is clear that thermal degradation occurs in two steps and that the endothermic peak corresponding to the first step is larger. The TG/

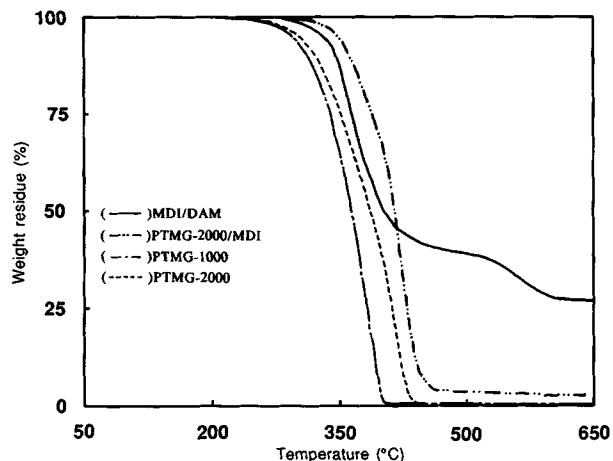


Figure 8 TGA thermograms of MDI/DAM polymer, PTMG-2000/MDI polymer, PTMG-1000, and PTMG-2000.

DTA data of all PEUU elastomers are summarized in Table VII. Figure 8 shows TG thermograms of the H/S analogous MDI/DAM copolymer, PTMG-2000, PTMG-1000, and the S/S analogous PTMG-2000/MDI copolymer. The PTMG-2000 started to degrade at about 260°C and has a maximum deg-

Table VII TG/DTA Data of PEUU Elastomers at a Heating Rate of 20°C/Min under a Nitrogen Atmosphere

Sample Code	T_{di} (°C)	ΔH_d , 1st ^a ($\mu\text{v} \cdot \text{s}/\text{mg}$)	T_d^m , 2nd ^b (°C)	DTG (%/min) ^c	Ash Content (%)
DAM-26-2	296	48	426	35.3	4.5
DAM-36-2	275	80	430	28.9	7.5
DAM-44-2	270	135	430	23.5	12.1
MPD-26-2	282	52	431	34.9	5.6
MPD-36-2	270	75	427	28.0	10.2
MPD-44-2	272	105	430	24.1	12.5
PPD-26-2	288	71	425	34.0	3.7
PPD-36-2	269	78	427	31.2	7.5
PPD-44-2	268	130	430	22.0	12.5
DAM-36-1	296	86	431	22.7	4.9
MPD-36-1	275	83	429	24.6	6.5
PPD-36-1	282	95	429	23.5	5.1
PTMG-2000	263	4	421	34.1	0.0
PTMG-1000	260	—	386	32.7	0.0
PTMG-2000/MDI	321	18	423	37.4	2.8
MDI/DAM (H/S)	298	350	372	20.8	26.9

^a Heat of degradation (in the 1st step) measured by DTA peak areas.

^b Maximum degradation temperature (in the 2nd step).

^c Differential thermogravimetry (dw/dt , weight loss percentage per minute at T_d^m , 2nd).

radiation temperature of 421°C (in Table VII); on the other hand, the PTMG-2000/MDI copolymer has a high threshold degradation temperature of 321°C, but the maximum degradation temperature was also about 420°C. This difference may be due to structural effects, i.e., PTMG-2000 is an oligomer having reactive hydroxyl end groups, but PTMG-2000/MDI is a high MW crystalline polymer due to stable interurethane H-bonding.

The thermal stabilities of the DAM series having different H/S contents and different MW's of PTMG are depicted in Figure 9. All four samples showed two-step degradation behavior, but the threshold degradation temperatures were different, i.e., the DAM-26-2 sample, having the lowest H/S content, showed the highest degradation temperature of 296°C and the DAM-44-2 sample, having the highest H/S content, showed the lowest degradation temperature of 272°C; on the other hand, DAM-36-1 started to degrade at 296°C. To explain this phenomena, we thought that a systematic approach to the relationship of the structural factor and degradation behavior should be taken into account.

First of all, we analyzed which segment principally degraded in each degradation step in the course of the two degradation steps of the PEUU series from PTMG 2000. Figure 10 shows the DTG curves of the DAM series. It is clear that the maximum degradation temperature of the H/S analogous MDI/DAM polymer is 372°C, but that of the S/S analogous PTMG-2000/MDI polymer is 423°C. Additionally, degradation became more active in the second step with an increase in S/S content. This reflects that the principal degradation of PTMG-

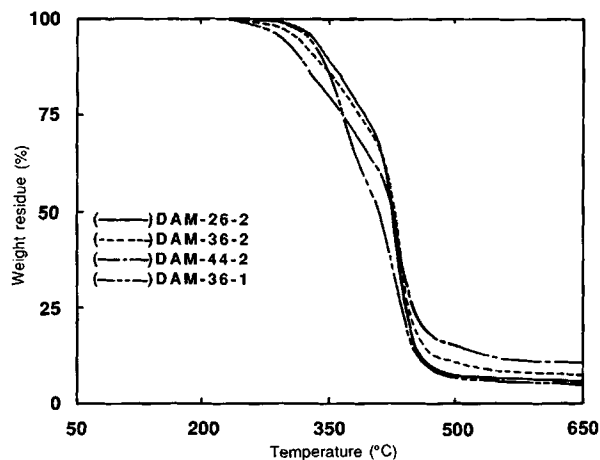


Figure 9 TGA thermograms of the DAM series with a heating rate of 20°C/min in a nitrogen atmosphere.

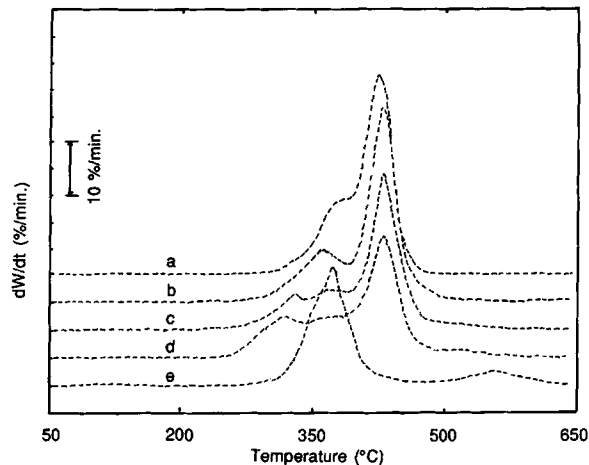


Figure 10 Differential thermal gravimetry curves of the DAM series: (a) PTMG-2000/MDI; (b) DAM-26-2; (c) DAM-36-2; (d) DAM-44-2; (e) MDI/DAM.

2000 (S/S) of the PEUU elastomer takes place in the second step. Table VIII supports this suggestion, i.e., comparing the weight loss of each sample after the first degradation step with the H/S content, DAM-26-2 is 26.4%, DAM-36-2 is 29%, and DAM-44-2 is 37.1% respectively. Therefore, the H/S degraded in the first degradation step. Samples prepared from the wet process, i.e., coagulated in water, exhibited results more closely corresponding to the stoichiometry of the sample composition. Also, the heat of degradation in the first degradation step was dependent on the H/S content (Table VII), i.e., the endotherm of the first degradation step is due to the degradation of the H/S, which also supports the above suggestion. From these analyses, it is clear

Table VIII Effect of Sample Preparation Methods on the Degradation Behavior of PEUU Elastomers

Sample Code	As-cast (Dry)		Wet Process	
	$T_{d,i}$ (°C)	Wt Loss (%) in the 1st Degradation Step	$T_{d,i}$ (°C)	Wt Loss (%) in the 1st Degradation Step
DAM-26-2	296	26.4	282	22.7
-36-2	275	29.0	276	34.4
-44-2	272	37.1	278	40.2
MPD-26-2	282	26.2	264	26.7
-36-2	270	32.2	259	34.2
-44-2	272	35.0	257	37.9

that the initial degradation reaction is governed by the characteristics of the H/S of the PEUU elastomer. Above all, microstructural ordering of the H/S appears to be closely related to the threshold degradation temperature of PEUU elastomers. In the previous sections, we discussed the microstructural ordering of the H/S—in other words, the hydrogen-bonding power between the H/S. For example, in the DAM series, the DAM-26-2 sample has strong three-dimensional hydrogen bonding between the H/S, but DAM-44-2 has relatively weak hard-domain bonding forces because of the remaining LiCl and/or solubilized S/S among the hard domain. In summary, it appears that the thermal stabilities of PEUU elastomers are deeply related with microstructural ordering of the H/S. In contrast to Grassie et al.'s suggestion that an important factor for the thermal stability of PU is the stabilization of the urethane link by hydrogen bonding of —NH groups with ester carbonyl of the S/S, we found that three-dimensional hydrogen bonding between the H/S is the decisive factor in the case of PUU.

Three DAM samples obtained from the wet process in which LiCl or the monomer is thoroughly removed by washing did not show a large difference in $T_{d,i}$ (282–276°C), but overall degradation behavior is similar to the samples from the as-cast method (Fig. 11). The MPD series, which did not require LiCl in the casting step, also showed similar results in both preparation methods; however, all samples from the as-cast method (dry) are more thermally stable than those prepared by the wet process.

DAM-36-1 has a threshold degradation temperature of 296°C, higher than that of DAM-36-2 with the same H/S content. According to the DSC anal-

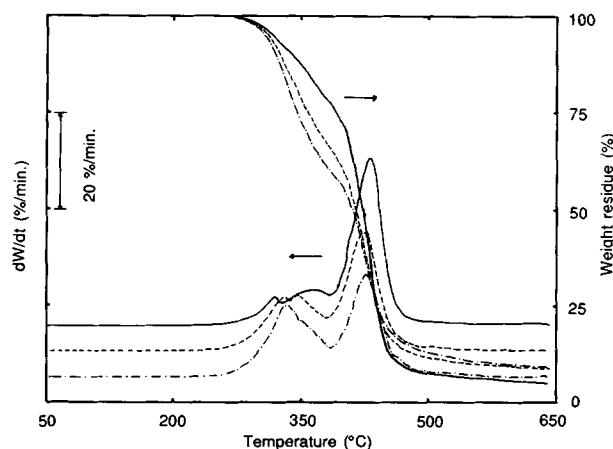


Figure 11 TG/DTG thermograms of the DAM series obtained by the wet process: (—) DAM-26-2; (---) DAM-36-2; (- - -) DAM-44-2.

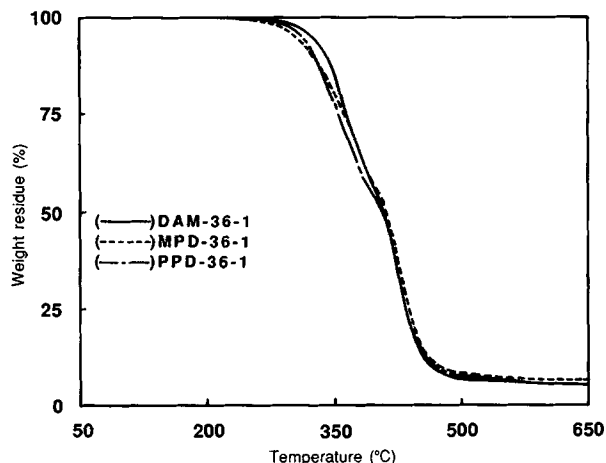


Figure 12 Change of initial degradation temperature for PEUU elastomers with different chain extenders.

ysis, the degree of phase separation of PTMG-1000 series is lower than that of PTMG-2000 series, but the mechanical properties of the PTMG-1000 series show quite phase-separated behavior. The analysis of microstructure and hard-domain morphology of the PTMG-1000 series will be helpful in the clarification of these phenomena. Knutson and Lyman²⁶ suggested that the relatively pure polyurethaneurea hard domains and the polyether matrix in the PTMG-1000 series are separated by a rather broad interfacial zone. Futamura et al.²⁷ studied 2,4-TDI/aromatic diamine-based PEUUs and suggested that the morphology having the very small hard domains dispersed in the polyether matrix with very diffuse boundaries by SAXS. We also thought that some hard segments form domains of very small size, because the urea carbonyls in the PTMG-1000 series were observed to be nearly completely hydrogen-bonded.¹² Therefore, it could be suggested that the degree of phase separation of the PTMG-1000 series is low, but that the microstructural ordering of the H/S itself is quite high, which could be identified by the IR peak positions and WAXD tests. The threshold degradation temperature of PEUU elastomers is primarily dependent upon the microstructural ordering of the H/S and not upon the degree of phase separation in the domain scale.

Figure 12 illustrates TG curves of PEUUs having different chain extenders; threshold degradation temperatures are in the order of the DAM > PPD > MPD series, although the differences are small. These results suggest that thermal stabilities might be deteriorated by the remaining LiCl in PPD-36-1 or the kink structure of the H/S in the MPD-36-1 sample.

CONCLUSIONS

DSC, dynamic mechanical, FTIR, and X-ray experiments were carried out to characterize the phase-separation behavior and hard-domain structure of polyether polyurethaneureas (PEUU) of systematically varied H/S content, S/S molecular weight, and type of aromatic diamine chain extender.

The synthesized PEUU series showed different solubility in DMF according to the chain extender and H/S content, i.e., some samples became soluble only with the aid of LiCl in DMF solvent.

The PTMG-2000 samples exhibited a higher degree of phase separation than that of the PTMG-1000 samples, but the effect of the H/S content or type of chain extender on the phase-separation behavior seemed to be small.

The presence of three-dimensional hydrogen bonding between the H/S was identified by FTIR measurements, and the relative microstructural ordering of hard domains with various H/S composition could be estimated by the shift of the hydrogen-bonded urea carbonyl group ($\text{CO}_{\text{B,UA}}$). Microstructural ordering of the H/S were disrupted by the remaining LiCl that was added to solubilize polymers (some of DAM and PPD series).

TG/DTA analyzes were used to characterize the thermal stabilities of PEUU elastomers that showed a two-step degradation behavior at a heating rate of 20°C/min under a nitrogen atmosphere. The H/S was mostly degraded in the first degradation step and samples with well-ordered H/S showed higher threshold degradation temperatures. Therefore, it could be suggested that threshold degradation temperatures are dependent upon the microstructural ordering of the H/S and not upon the degree of phase separation in the domain scale. The threshold degradation temperature was higher in the sample with low H/S content (26%) than those with H/S content of 36 or 44% and in the order of the DAM > PPD > MPD series at the same H/S content (26%).

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