

Differential Scanning Calorimetry Analysis of Silicon-Containing and Phosphorus-Containing Segmented Polyurethane. I—Thermal Behaviors and Morphology

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ABSTRACT: This article investigated thermal transition and morphology utilizing differential scanning calorimetry (DSC), which was performed on silicon-containing and phosphorus-containing segmented polyurethane (Si-PU and P-PU). The hard segments of those Si-PU and P-PU polymers investigated consisted of 4,4'-diphenylmethane diisocyanate (MDI) and diphenylsilanediol (DSiD), MDI, and methylphosphonic (MPA), respectively. The soft segment of those polymers comprised polytetramethylene ether glycol, with an average molecular weight of 1000 or 2000 (PTMG 1000 and PTMG 2000, respectively). Several thermal transitions appeared for on the Si-PU and P-PU polymers, reflecting both the soft-segment and hard-segment phases. The Si-PU and P-PU polymers with a lower hard-segment content exhibited a high degree of phase separating as indicated by the constancy of both the soft-segment glass transition temperature (T_{gs}) and the breadth of transition zone (ΔB). The polymers in which PTMG 2000 was used as the soft segment generally exhibited a crystalline melting endotherm about 10°C, while crystallization usually disappeared upon melt quenching. The hard segments of the Si-PU and P-PU polymers displayed multiple endotherms. The first endotherm was related to a short-range ordering of the hard segment domain (Region I), and the second endotherm was ascribed to a long-range ordering of the domain (Region II). The wide-angle X-ray demonstrated that the structure in Region I and Region II was almost completely amorphous. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3489–3501, 2001

Key words: silicon; phosphorus; polyurethane; thermal transition; morphology

INTRODUCTION

Segmented polyurethane elastomers are linear block copolymers of the (HS)_n type (H—hard seg-

ment; S—soft segment). The hard segments generally consist of aromatic diisocyanate chains extended with low molecular weight diols to produce blocks with a molecular weight in the range of 500–3000. The soft segments are typically a polyether or polyester diol with a molecular weight of 500–5000. The hard segments are, at room temperature, in a glassy or semi-crystalline state. In contrast, the soft segments exist in a rubbery or viscous state.

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Most segmented copolymers exhibit a two-phase microstructure due to the incompatibility of the two dissimilar segment types. This incompatibility is the driving force for phase separation in these systems because the urethane segments are more polar than the polyether or polyester segments. This driving force for phase separation is increased by the ability of the urethane segments to form interurethane hydrogen bonds. Experimental evidence has shown that the segmented polyurethane is not completely phase separated, but exhibit some degree of phase mixing.¹⁻⁷

In addition to the polar effect, other factors affecting the phase separation of these materials include the segment length, the ability of either segment to crystallize, the potential for soft-segment/hard-segment hydrogen bonding, material composition, sample preparation, and mechanical and thermal history. These materials have been exhibiting different physical properties and morphologies, depending on the composition and chemical structure of their hard and soft segments.¹⁻⁷ Furthermore, some unusual properties exhibited by these systems are directly related to their two-phase morphology, which is due to the fact that the hard segments act as physical crosslinks and as a reinforcing filler for the rubbery soft-segment matrix.

According to DSC analysis, these segmented polyurethanes may possess two melting points (if both phases crystallize) and two glass transition temperatures because of the two-phase structure.⁸ The soft-segment glass transition temperature (T_g s) generally appears as a baseline shift in the region of -80 to -10°C .⁹ The segmented polyurethanes with a longer soft-segment and a higher soft-segment content exhibited a soft-segment melting endotherm (T_m s) at about 10°C when a typically polyether or polyester was used for the soft segment.⁸⁻¹⁰

The behaviors of the hard-segment phase are uncertain or explained from a different aspect, because, due to its morphology, multiple endotherms appear when using DSC analysis. In early studies, a DSC endotherm, appearing at about 80°C , was ascribed to the dissociation of the urethane soft-segment hydrogen bonds, while an endotherm at around $150-170^\circ\text{C}$ was said to be related to the breakup of interurethane hydrogen bonds.^{11,12} Afterwards, Cooper and Seymour¹³ found that the DSC endotherms observed resulted from short-range and long-range ordering of the hard segment, which may all be due to

morphology, rather than to hydrogen-bond dissociation, as previously thought. In addition, a higher temperature melting endotherm for a microcrystalline hard segments was confirmed and observed in materials having longer aromatic urethane segments¹⁴ or higher hard-segment content.¹⁰

The temperature ranges and morphology of the hard segment phase of segmented polyurethanes has been studied by DSC analysis.^{9,13,15} A summary of the results is as follows.

In general, three hard segment-associated endotherms appeared in the DSC thermogram of an untreated sample. The first endotherm (Region I), observed in the range of $30-80^\circ\text{C}$, has generally been ascribed to a short-range ordering of an unknown nature. A subsequent endotherm (Region II) about the range of $120-190^\circ\text{C}$ was ascribed to a hard segment long-range ordering of an unspecified nature or to the onset of microphase mixing of the hard and soft segments.^{16,17} Finally, an endotherm (Region III) occurring above 200°C was ascribed to the melting of the hard-segment microcrystalline structure. However, segmented polyurethanes of low diisocyanate content (low hard-segment content resulting in short hard segments) are incapable of crystallization and appear only in Region I and II.^{13,18}

Recently, we incorporated silicon or phosphorus into the main chain of segmented polyurethane to improve the stability or flammability of polyurethane. Then we investigated the degradation properties of silicon- and phosphorus-containing segmented polyurethane (Si-PU and P-PU).¹⁹ There is interest in Si-PU and P-PU because the hard-segment endothermic behavior due to the silicon-containing or phosphorus-containing hard segment differs from that of typical hard segments based on 4,4'-diphenylmethane diisocyanate and 1,4-butanediol. In this article, we present the results of DSC studies on the thermal behavior and morphology of a series of Si-PU and P-PU polymers.

EXPERIMENT

Materials

Silicon-containing segmented polyurethane polymers (Si-PU) and phosphorus-containing segmented polyurethane polymers (P-PU) of various hard-segment contents and various soft-segment molecular weights were used in this study. The

silicon containing hard segments (Si-hard segment) consisted of 4,4'-diphenylmethane diisocyanate (MDI; Aldrich, UK) and diphenylsilanediol (DSiD; TCI, Japan). The phosphorus-containing hard segments (P-hard segment) consisted of MDI and methylphosphonic acid (MPA; Lancaster, UK). The soft segments were polytetramethylene ether glycol which had 56 or 112 hydroxy groups ($M_w = 2000$; PTMG 2000 or $M_w = 1000$; PTMG 1000, respectively) (Dupont, USA). Figure 1 describes the structure of the hard and soft segments of the Si-PU and P-PU polymers.

Preparation of the Polymers

The PTMG 1000 or PTMG 2000 was dissolved in *N,N*-dimethylformamide (DMF) (Fisher) in a dry nitrogen atmosphere in a 500-mL reaction flask at 70°C. A stoichiometrically calculated amount of MDI was added to the solution and stirred constantly for 1 h (PTMG 1000) or 80 min (PTMG 2000). Then, the appropriate amount of a DMF solution containing DSiD or MPA was added to the reactor. The final ratio of OH/NCO was approximately 1.0. After stirring for 1.5 h, Si-PU polymers or P-PU polymers of 35 wt % were obtained. The polymers were placed into a Teflon mold for 24 h at 100°C to form films from the polymer solution as the solvent evaporated. Subsequently, these polymer films dried by vacuuming at 60°C for 3 days; then these polymer films (untreated sample) were stored in a desiccator under room temperature for at least 7 days before undergoing DSC analysis. The synthesis and NMR measurement of these polymers were partially detailed in our recent article.¹⁹ The materi-

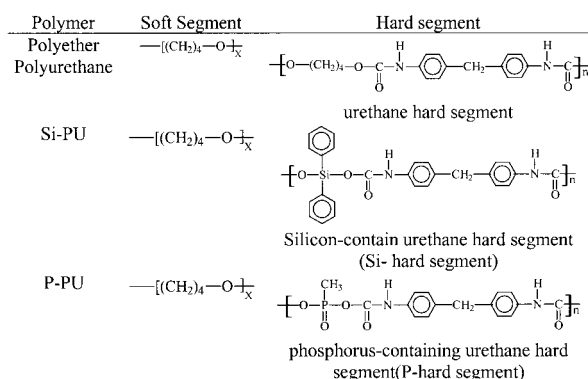


Figure 1 Hard-segment structure of silicon-containing polyurethane and phosphorus-containing polyurethane.

Table I Hard Segment Content of Materials

Sample ^a	Hard-Segment Number Average Molecular Weight (\overline{M}_w nh) ^b	Silicon/MDI Content (wt %) (Si-Hard Segment Content)
PD1-121	715	41.7
PD1-132	1174	54.1
PD1-143	1632	62.2
PD1-154	2106	67.9
PD1-165	2571	72.1
PD2-121	713	26.3
PD2-132	1179	37.1
PD2-143	1643	45.1
PD2-154	2106	51.3
PD2-165	2545	56.3

Sample ^a	Hard-Segment Number Average Molecular Weight (\overline{M}_w nh) ^b	Phosphorus/MDI Content (wt %) (P-Hard Segment Content)
PM1-121	597	37.3
PM1-132	941	48.5
PM1-143	1288	56.3
PM1-154	1631	62.0
PM1-165	1941	66.4
PM2-121	596	23.0
PM2-132	941	32.0
PM2-143	1289	39.2
PM2-154	1633	44.9
PM2-165	2000	49.7

^a Nomenclature is as follows: PD2-165 indicates silicon-containing PU, PTMG molecular weight of 2000, and a 1/6/5 molar ratio of PTMG/MDI/DSiD; PM2-165 indicates phosphorus-containing PU, PTMG molecular weight of 2000, and a 1/6/5 molar ratio of PTMG/MDI/MPA.

^b The hard segment number average weight was calculated by method⁸ of \overline{M}_w nh = M_n s(100-Sc)/Sc, where \overline{M}_w nh is the hard segment number-average weight, M_n s is the soft segment number-average weight, and Sc is the soft segment content (wt %).

als synthesized are summarized in Table I. The sample nomenclature, for example, PD1-143, indicates a silicon-containing segmented polyurethane with PTMG 1000 and a 1/4/3 molar ratio of PTMG/MDI/DSiD.

Measurement

Differential Scanning Calorimetry (DSC)

The DSC measurements were conducted using a Perkin-Elmer DSC-7 with an ice-water cooler in a nitrogen atmosphere. Indium was used to cali-

brate the temperature and heat of fusion. The weight of specimens was roughly 10 mg. The specimens of the initial scan were the untreated samples that were stored in a desiccator under 30°C for 7 days before any DSC analysis was performed. The specimens were measured starting from -100°C and heating to 250°C at a rate of 20°C/min in a nitrogen atmosphere. The melt-quenched specimens were the same as those in the initial scan. First, the specimens were heated to 230°C and held at this temperature for 1 min to remove their thermal history. Afterwards, the specimens were quenched to -110°C at a rate of 300°C/min. Subsequently, the thermograms of the specimens were again obtained by using a heating rate of 20°C/min from -100 to 250°C.

Wide-Angle X-Ray Diffraction (WAX)

Wide-angle X-ray scattering experiments were performed using a Rigaku Ru-HSR. The X-ray beam was nicked-filtered Cu K α radiation ($\lambda = 0.1542$ nm) from a sealed tube operated at a voltage of 30 kV and a current of 30 mA. Data was obtained from 5–60° at a scan rate of 4°/min.

RESULTS AND DISCUSSION

DSC thermograms of the initial and melt-quenched scans of the Si-PU and P-PU series polymers with a PTMG molecular weight 1000 and 2000 are displayed in Figures 2 and 3, respectively. The soft- and hard-segment glass transition temperature data is respectively summarized in Tables II and III for all of the samples.

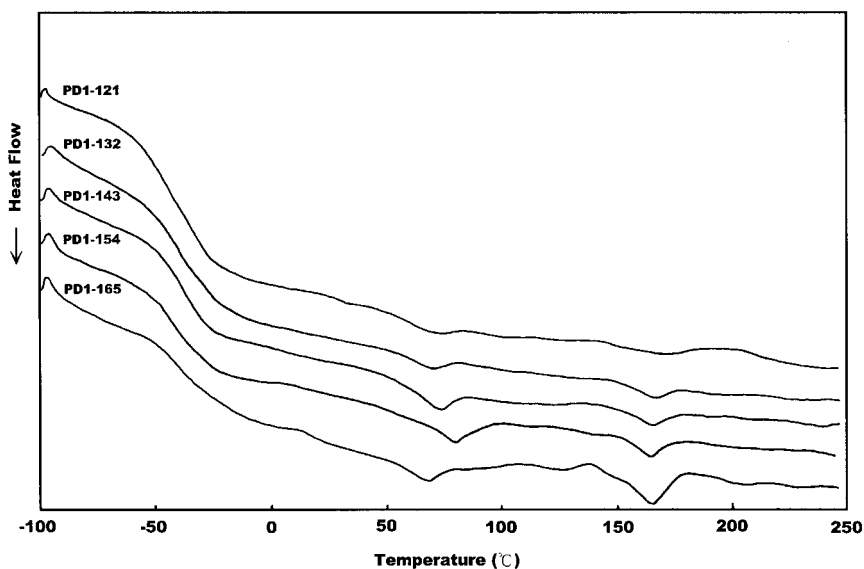
Soft Segment Transition

$T_{g,s}$ Region: Soft-Segment Glass Transition Temperature

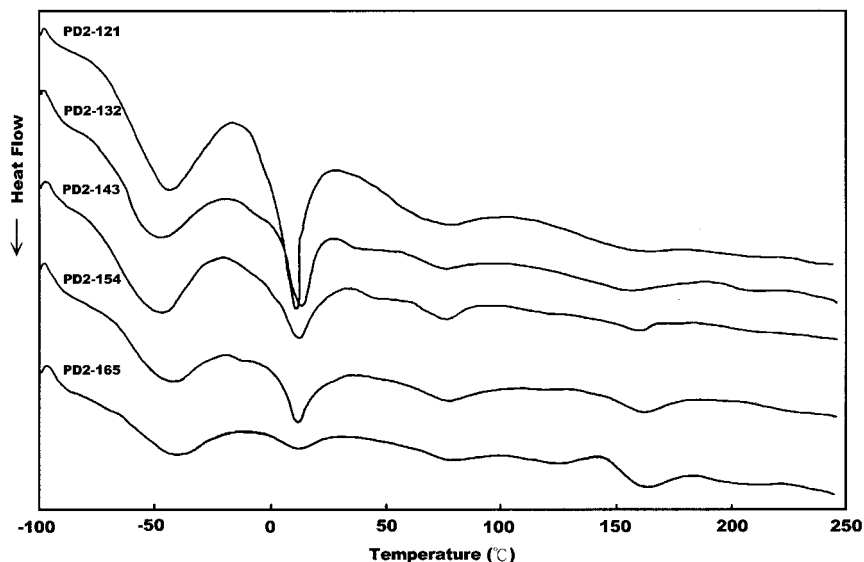
The soft-segment glass transition temperatures ($T_{g,s}$) of the samples utilizing the soft segment of PTMG appeared below 0°C, as shown in Table II. In general, the $T_{g,s}$ are primarily affected by the amount of hard segments dispersed in the soft-segment phase (the extent to which the hard segments and soft segments mix), and is often used as a relative measure of the degree of phase separation. Moreover, the breadth of the transition zone (ΔB) may also be used as a qualitative measure of the degree of phase separation. However, the ΔB is affected to a large extent by segmental

mixing at the interface in addition to the mixing in each phase.²⁰ For each of the Si-PU and P-PU series polymers having the same soft-segment molecular weight on both the initial scan (Fig. 2) and the melt-quenched scan (Fig. 3), the $T_{g,s}$ and ΔB remained nearly constant as seen in Table II, except for those samples with a higher hard-segment content. The constant $T_{g,s}$ and ΔB indicated that those samples had a high degree of phase separation, that is, in the samples, the $T_{g,s}$ was well defined and unaffected by heating and quenching. Also, the soft segment regions were quite pure. However, the Si-PU and P-PU polymers with a higher hard-segment content did not exhibit a high degree of phase separation as shown by the higher $T_{g,s}$ values and broader ΔB zone on the initial scan or melt-quenched scan. Moreover, in these samples, the $T_{g,s}$ and ΔB increased slightly with an increase of the Si-hard segment or P-hard segment content, as presented Table II. The results depict that the higher hard-segment content samples have a low degree of phase separation, that is, the more the soft-segment domains are contaminated with dissolved high glass transition temperature hard segments, the higher will be the PTMG domain's $T_{g,s}$. These results were similar to those of conventional polyurethane using a polyether or polyester as the soft segment, in which there was an increase in the number of hard segments dispersed in the soft-segment phase in those polymers having a low soft-segment content.^{21,22}

Besides the effect of the amount of hard segments dispersed in the soft segment phase (the factor of soft and hard phase mixing), hard-segment content and hard-segment length, the $T_{g,s}$ was also affected by the soft-segment molecular weight. Table II showed that increasing the PTMG molecular weight resulted in a narrower ΔB , which was centered at a lower temperature. Similar results have been reported previously for polyether polyurethane, polyester polyurethane, and poly(urethane-imide) copolymers.^{10,21–23} Schneider and Paik Surg²¹ suggested that the reason the $T_{g,s}$ decreased with an increase in the soft-segment molecular weight was due to a decrease of phase mixing and hydrogen bonding. Critchfield et al.^{22,23} noted that homopolymers generally display a decrease in T_g with decreasing molecular weight, which is ascribed to as increased volume associated with the chain ends leading to increased mobility. They ascribed the increase in the $T_{g,s}$ with decreasing molecular weight in segmented copolymers to the decrease in free volume and mobility due to the bonding of the



(a) Si-PU1 series polymers



(b) Si-PU2 series polymers

Figure 2 DSC thermograms of the initial scan for all samples.

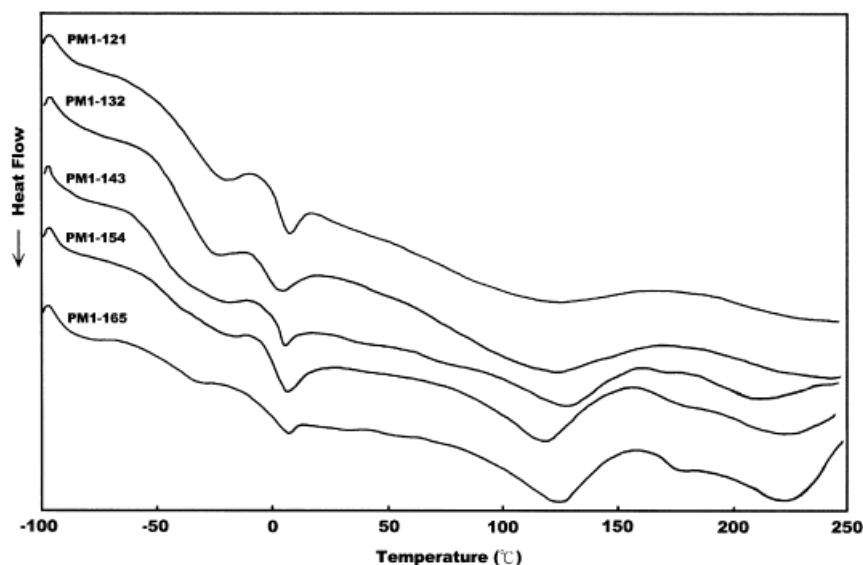
soft segments to the rigid isocyanate blocks. Chuang et al.,¹⁰ in their studies on the poly(urethane-imide) copolymers, suggested that the copolymers with a shorter soft segment have a higher T_g s due to the copolymer of the softer segments, causing more steric hindrance to rotation because of the MDI and imide group attached.

Comparing these conclusions with the results of Table II with regard to the effect of soft-segment length, the decrease of the ΔB and T_g s zone as the soft-segment molecular weight increased

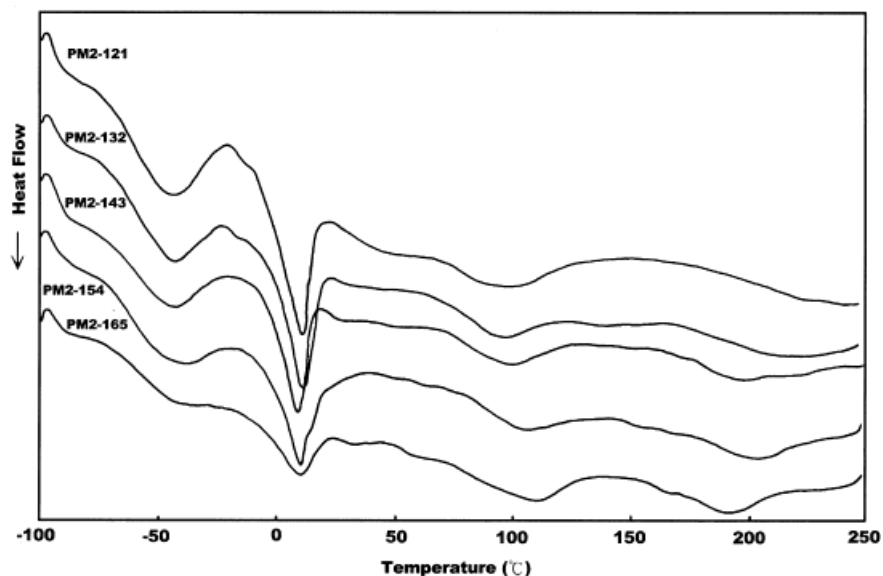
was a result of the decreasing influence of chain-end restrictions, steric hindrance, and interfacial effects as the soft-segment chain length increased. According to the discussions in this section, those samples having a short soft segment had a lower degree of phase separation.

T_ms Region: Soft Segment Melting

After the soft-segment glass transition endotherm, there is an obvious endotherm between 0



(c) P-PU1 series polymers

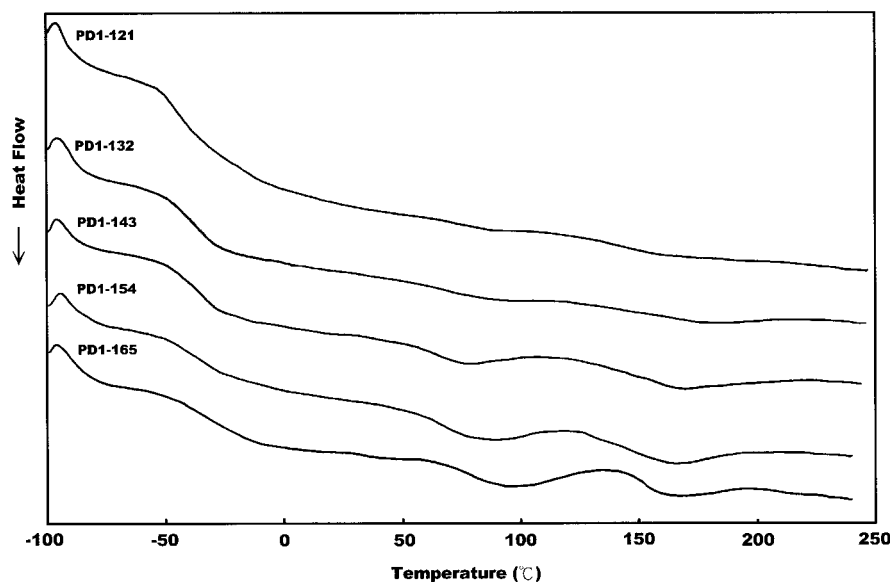


(d) P-PU1 series polymers

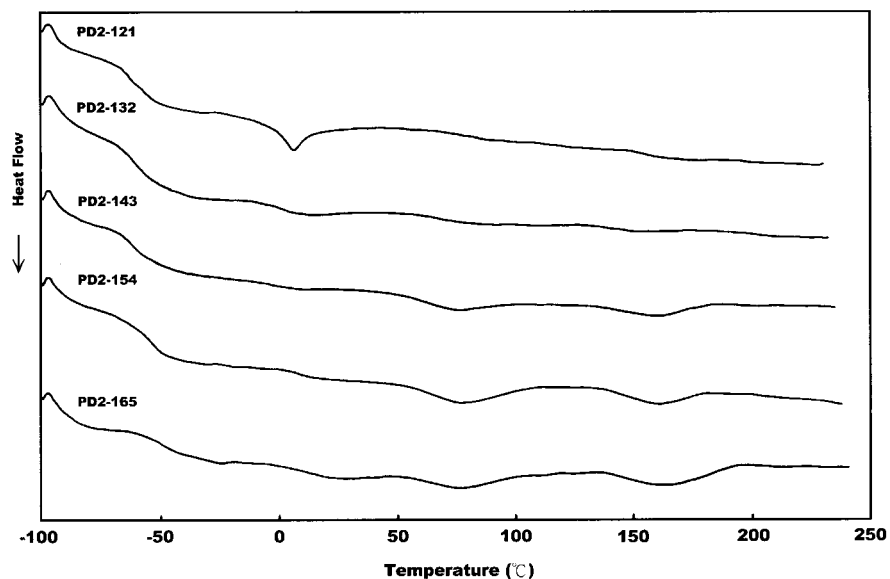
Figure 2 (Continued from the previous page)

and 20°C, which corresponds to the melting of the soft-segment crystalline (T_m s). On the initial scan, the T_m s only occurred for the Si-PU polymers utilizing PTMG 2000 (Si-PU2) and for all of the P-PU polymers as presented in Table II and Figure 2. Furthermore, the position of the T_m s in the samples using PTMG 2000 was centered at about 10°C. However, the magnitude of the endotherm decreased as the hard-segment content increased as shown in Figure 2. The length of the soft segment was an obvious

factor in determining the occurrence and position of T_m s because it affected the steric resistance and the soft-segment mobility. The T_m s of Si-PU polymer using PTMG 1000 (Si-PU1) had no T_m s, while the T_m s of the P-PU polymer using PTMG 1000 (P-PU1) shifted to a lower temperature. The results illustrated that the shorter soft-segment length led to a higher steric resistance from hard segment, and that the steric resistance of the Si-hard segment was higher than that of the P-hard segment. In the



(a) Si-PU1 series polymers

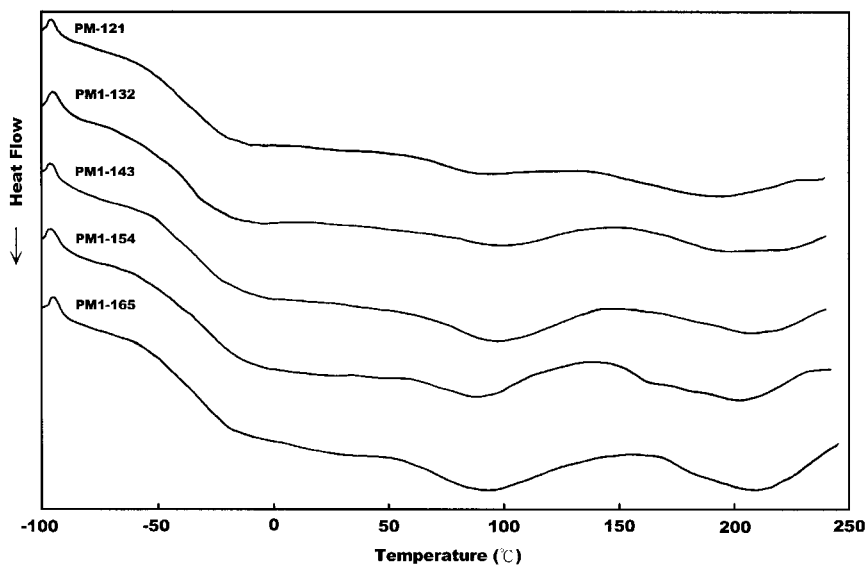


(b) Si-PU2 series polymers

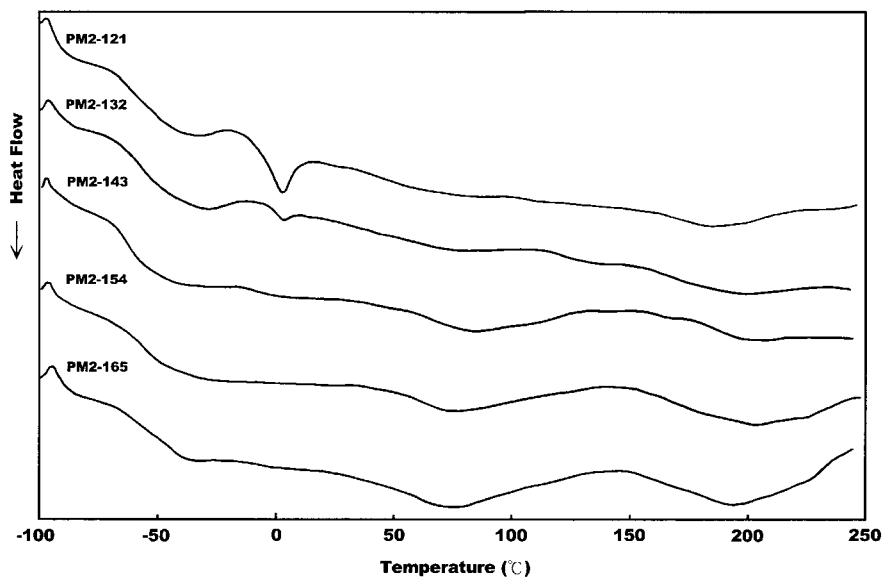
Figure 3 DSC thermograms of the melt-quenched scan for all samples.

melt-quenched polymers, the T_m s only occurred for the PD2-121, PM2-121, and PM2-132 samples all having a lower hard-segment content, and it, too, had shifted to a lower temperature. The factors behind this phenomenon include the mobility of the soft segment, steric resistance, and the melt-quenched effect. The samples with a longer soft-segment and a lower hard-segment content had a higher mobility and lower steric resistance. Therefore, the hard segment domains exerted less of a filler effect, which al-

lowed crystallization. Furthermore, the samples after melt-quenching, changed into an amorphous glass state below T_g s. Upon heating, the soft segment crystallized after passing through its T_g s. A lower soft-segment T_g allows crystallization to occur at a lower temperature (see Table II). Lower temperature crystallization, however, resulted in smaller crystallite size and a less-ordered crystalline structure, which meant the soft segment melted at a lower temperature.



(c) P-PU1 series polymers



(d) P-PU2 series polymers

Figure 3 (Continued from the previous page)

Hard Segment Transition

Cooper et al. studied different segmented polyurethanes by DSC^{9,13,14} and discovered that there were three significant endothermic regions that were associated with the hard-segment domains. After careful examination of Figures 2 and 3, three endothermic regions (Region I, II, and III) were not displayed by all the samples on either the initial scan or the after melt-quenched scan. The formation of these regions may be affected by

the hard-segment content, the type of hard-segment used, length of the soft segment, and heat treatment. We described the endothermic regions of Si-PU and P-PU polymers as follows:

Region I: Short-Range Ordering of the Hard Segment Domain

Region I displayed a distinct endotherm (T1) between about 65–80°C for the Si-PU1 polymers on the initial scan. The T1 of the Si-PU2 polymers

Table II Thermal Transitions: Soft-Segment Glass Transition and Melting Temperatures (All Values in °C)

Sample	Initial Scan			Melt-Quenching Scan		
	T_g s ^a	ΔB ^b	T_m s ^c /(ΔH KJ/mol)	T_g s ^a	ΔB ^b	T_m s ^c (ΔH KJ/mol)
PD1-121	-46	11	—	-43	10	—
PD1-132	-46	11	—	-43	11	—
PD1-143	-45	12	—	-42	10	—
PD1-154	-45	13	—	-39	12	—
PD1-165	-41	16	—	-33	16	—
PD2-121	-63	7	9 (42)	-63	7	6 (4)
PD2-132	-63	7	13 (31)	-60	6	—
PD2-143	-64	7	12 (18)	-62	7	—
PD2-154	-60	10	12 (15)	-59	9	—
PD2-165	-60	13	12 (5)	-50	15	—
PM1-121	-43	12	8 (4)	-43	11	—
PM1-132	-43	11	5 (5)	-39	11	—
PM1-143	-48	10	5 (3)	-37	13	—
PM1-154	-42	15	5 (6)	-39	15	—
PM1-165	-44	19	6 (1)	-40	19	—
PM2-121	-62	8	11 (44)	-63	7	3 (9)
PM2-132	-62	9	12 (43)	-60	8	3 (1)
PM2-143	-63	10	10 (38)	-60	7	—
PM2-154	-62	9	11 (25)	-57	10	—
PM2-165	-56	15	10 (18)	-55	12	—

^a T_g s: Soft-segment glass transition temperature determined from the midpoint of the change in baseline height.

^b ΔB : breadth of T_g s determined by the intersection of the baseline and a tangent through midpoint.

^c T_m s: melting temperature of the soft-segment crystalline.

were centered between 70–75°C. The narrow T1 range indicated that the Si-PU2 polymers with a long soft-segment length had a higher phase degree of separation or a more well-defined Si-hard segment domain than Si-PU1 polymers, which agrees with our previous results. Furthermore, the low Si-hard-segment content samples PD1-121, PD2-121, and PD1-132 exhibited a flatter and smaller endothermic peak than those samples having a high Si-hard segment contains, as shown in Figure 2(a) and (b). According to the literature,^{4,15,23} the flat endotherm and small endothermic peak could be attributed to the disordering of the ordered hard-segment region or to a lower degree of ordering. Obviously, the high short-range ordering of the Si-hard segment domains did not form on the Si-PU polymers with a low silicon content under the conditions of this study. The sample PD1-165 had a low T1 (about 65°C), which may be attributed to low phase separation due to the conditions under which the sample was prepared, which resulted in more soft segments being dispersed in the Si-hard-segment phase (phase mixing).

Figure 2(c) and (d) shows that the behavior of P-PU series polymers in Region I on the initial scan displayed a broader endothermic peak than the Si-PU polymers. Moreover, the P-PU series polymers had a higher and broader endothermic range of temperatures (T1 was between 60 and 120°C). Furthermore, the endothermic range and T1 temperatures of the P-PU series polymers were much higher than those of the Si-PU series polymers. These results may be explained by enthalpy relaxation resulting from the easy physical aging of the amorphous P-hard segment. This point of view will be verified in a separate article (annealing effect).²⁴

Figure 3 shows the DSC thermograms of the melt-quenched Si-PU series and P-PU series polymers. We found that the endothermic behavior of Region I was absent on the low hard-segment content samples. However, the high hard-segment content samples displayed a smaller and broader endotherm than those displayed on the initial scan. This diminution or disappearance of endothermic behavior on the melt-quenched scan was presumably because quenching was too fast

Table III Thermal Transition: Hard Segment Transition

Sample	Initial Scan		Melt-Quenching Scan	
	T1 (°C)	T2 (°C)	T1 (°C)	T2 (°C)
PD1-121	71	—	—	—
PD1-132	70	166	—	162
PD1-143	72	164	75	162
PD1-154	80	164	88	163
PD1-165	67	165	93	165
PM1-121	121	—	—	—
PM1-132	123	—	—	—
PM1-143	129	—	98	—
PM1-154	118	—	90	162
PM1-165	124	175	95	—
PD2-121	75	—	—	—
PD2-132	74	—	—	—
PD2-143	75	159	75	160
PD2-154	75	163	79	162
PD2-165	72	164	75	162
PM2-121	—	—	—	—
PM2-132	96	—	—	—
PM2-143	100	—	83	—
PM2-154	106	—	76	—
PM2-165	113	162	75	165

for the ordered structures present in the initial scan to reform. However, this phenomena (a decreasing or absent endotherm) can be improved by annealing, which will be detailed in another article.²⁴

Region II: Long-Range Ordering of the Hard Segment Domain

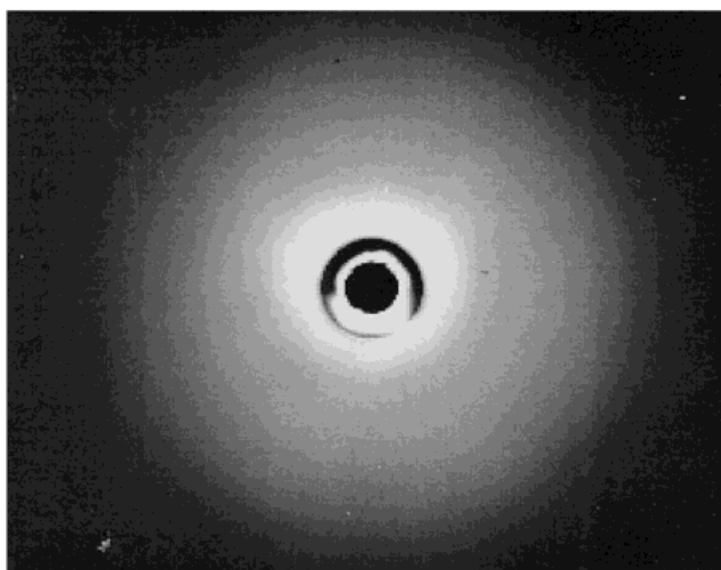
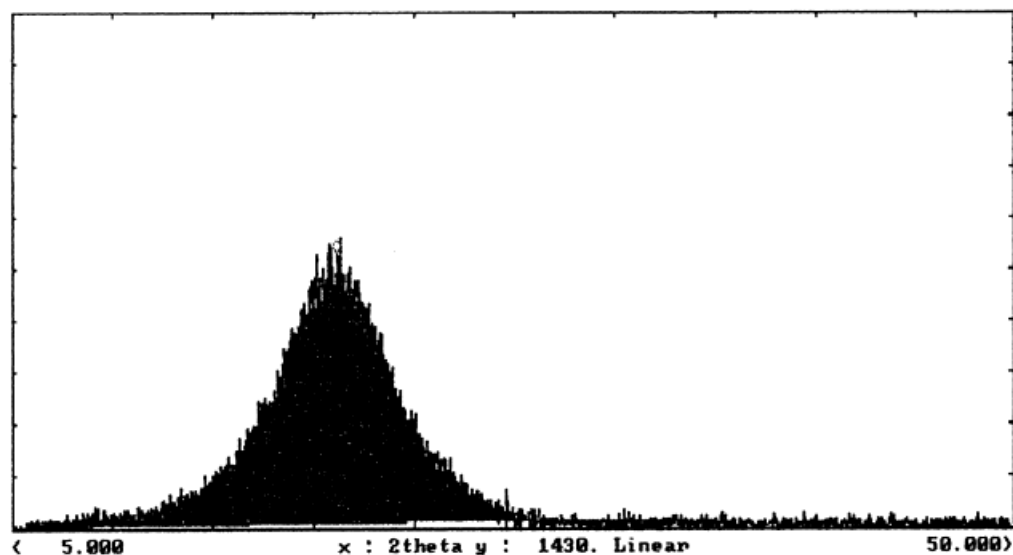
Region II was usually ascribed to a dissociation of long-range ordering of the hard segment domain. Figure 2(a) and (b) illustrate that the endotherm of Region II (T2) appeared at around 165°C on the initial scan for those Si-PU series materials with a high hard-segment content. However, those Si-PU series polymers having a hard-segment content below 45 wt % and having only one or two Si-hard segment units ($Mnh \approx 715$ or 1179), as shown in Table III and Figure 3, did not display a clear Region II endotherm on the initial scan. The results suggested that the polymers having only a few Si-hard segment units (less than three) could not form a well-defined Region II structure under the conditions of this study. The position of T2 (about 160°C) of Si-PU1 and Si-PU2 polymers on the initial scan were not greatly affected by the

soft-segment length, as shown in Table III. However, the magnitude of the endotherm increased as the Si-hard-segment content increased, as illustrated in Figure 2(a) and (b).

Figures 3(a) and (b) illustrate that the Region II structure of the melt-quenched Si-PU polymers with a lower Si-hard-segment content was absent while the melt-quenched Si-PU polymers with a higher Si-hard-segment content displayed a small and broad endotherm. The results were similar to the results of Region I, because melt-quenching diminished Region II structure and increased the degree of disorder in the Si-hard-segment domains.

The P-PU series polymers on the initial scan displayed a large, distinct endotherm peak between 160–250°C following the Region I endotherm as shown in Figure 2(c) and (d). Moreover, the endothermic peak was larger and broader than the endothermic peak of the Si-PU series polymers in the Region II. The melt-quenched P-PU series polymers similarly displayed a large endothermic range between 160–250°C, as shown in Figure 3(c) and (d). It is worthwhile noting that the Region II endotherm of those samples with a low P-hard-segment content did not disappear after melt-quenching. Thus, the endothermic behavior of P-PU polymers differs from the Si-PU series polymers in the Region II. According to our other study,¹⁹ the temperature at the onset of degradation of the P-PU polymers occurs at about 170°C and the weight loss is about 10 wt % between about 170–250°C. Obviously, the P-PU series polymers displayed a degradation endotherm on the initial scan or melt-quenched scan. Therefore, the degradation behavior expressed why a large endotherm between 160–250°C was always displayed on the initial and melt-quenched scans.

Also, the large endothermic behavior of P-PU series polymers was mainly the result of the degradation of the phosphorous urethane segment, and not a melt of the crystalline structure (see Fig. 4). However, the same type of Region II endotherm may exist in the P-PU polymers with a high hard-segment content as previously discussed with the Si-PU polymers, because the samples PM1-165 and PM2-165 displayed a small endotherm at about 165°C and its hard-segment structure was similar to the Si-PU materials. Therefore, we presume that the endothermic behavior of Region II for P-PU polymers is dissociation due to a long-range ordering of the hard-segment domain accompanied by a large number



(a) PD1-161

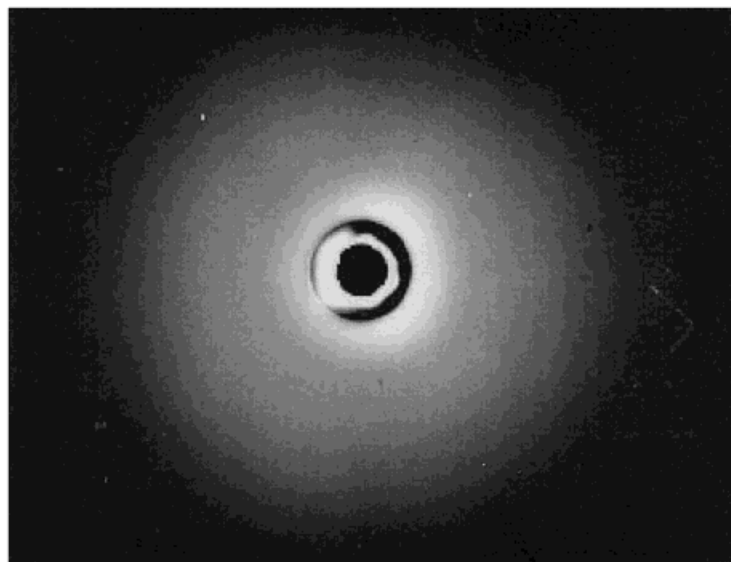
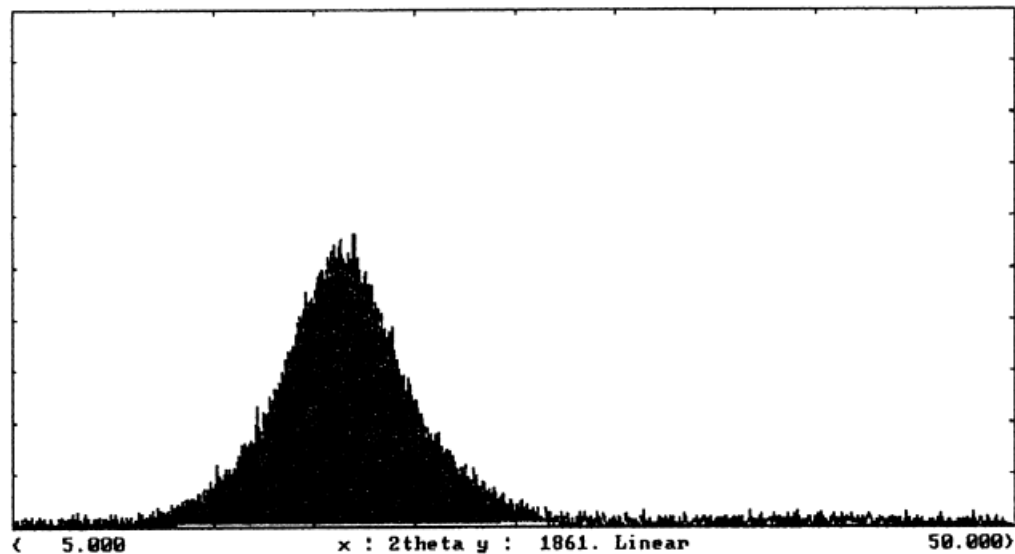
Figure 4 Wide-angle X-ray (WAX) diffraction intensity and pattern.

of endotherms from the degradation of the P-hard segment.

Region III: Microcrystalline Hard-Segment Domain Melting

Figure 4 shows the wide-angle X-ray (WAX) diffraction intensity and patterns of the untreated sample (before melt quenching) PD1-165 and PM1-165. The diffraction intensity and pattern of

WAX presented an almost completely amorphous structure, which indicates that the previously discussed endothermic behavior of Region I and II is not a melt of crystalline structure. Furthermore, the WAX diffraction analysis also illustrated that the Si-PU and P-PU series polymers having a hard-segment content of below 70 wt % (M_w below 2600) had no Region III structure in this study. According to Petrovič,⁸ studies of the seg-



(b) PM1-161

Figure 4 (Continued from the previous page)

ment polyurethane show that the M_w at about 8000 (the hard-segment unit about 13) had a clear melting endotherm of crystalline. Therefore, the Si-PU and P-PU series polymers did not display a melting endotherm of the microcrystalline structure above 200°C, probably because the hard-segment length of those Si-PU and P-PU series polymers did not have enough hard-segment length. However, the endotherms above 200°C on the

DSC thermograms of the P-PU series polymers were merely a degraded behavior of the P-hard segment.

CONCLUSIONS

The DSC analysis of Si-PU and P-PU polymers demonstrated the thermal behaviors of the soft-

segment and hard-segment phases. The soft-segment phase of Si-PU and P-PU polymers exhibited a glass state below 0°C. Furthermore, Si-PU and P-PU polymers having a lower hard segment content of exhibited an almost stable T_g s and ΔB , indicating that the polymers had a high degree of phase separation. This high degree of phase separation generally could improve the mechanical properties of the segmented polyurethane. If the soft segment had enough length and a small enough steric resistance, the soft segment also crystallized. Thus, the T_m s appearing on the initial scan for P-PU1 series polymers using PTMG 1000 indicated that the steric resistance of the P-hard segment was lower than that of the Si-hard segment. The T_m s disappeared after melt quenching except for samples PD2-121, PM2-121, and PM2-132, whose T_m s shifted back to a lower temperature.

The formation of the amorphous Region I and Region II structures were affected by the hard-segment content, type of hard segment, and thermal history. Nearly all the samples on the initial scan displayed the endotherm of Region I, while melt quenching resulted in a smaller endotherm or the its disappearance altogether. The Si-PU series polymers having more than three Si-hard segment units could form the Region II structure with an endotherm at about 160°C. Similarly, after melt-quenching, the Si-PU polymers with a higher Si-hard-segment content exhibited a small or broad endotherm. These decreasing or absent endotherm after melt quenching indicated that those hard segments could not form a well-defined Regions I and II structure. Region II of the P-PU series polymers displayed a large endotherm due to the degradation, which occurred over the endothermic range of the region. Therefore, the endothermic behavior of P-PU polymers in the Region II could be attributed to dissociation of a long-range ordering of the hard-segment domain and the P-hard segment of the degradation. Furthermore, heat treatment (annealing) also affected the domains (Regions I and II structure), which will be presented in a separate article.²⁴

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