Differential Scanning Calorimetry Analysis of Silicon-Containing and Phosphorus-Containing Segmented Polyurethane. II Annealing Effect

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ABSTRACT: The effect of thermal annealing on the multiple endothermic behavior and morphological changes in the silicon-containing and phosphorus-containing segmented polyurethane (Si-PU and P-PU) has been studied by differential scanning calorimetry (DSC). In the amorphous hard segments of the Si-PU and P-PU polymers that were annealed below T2, both the T1 temperature, and magnitude of T1 endotherm increased linearly as a function of the logarithmic annealing time (log t_a). This result demonstrated that the endothermic behavior (T1 endotherm) is typical of enthalpy relaxation resulting from the physical aging of the amorphous hard segment. Furthermore, the P-PU polymer was unstable than the Si-PU polymer due to the fact that the phosphorus-containing hard segment produce aged more easily. Dissociation of domains and enthalpy relaxation of hard segments for the Si-PU polymer was associated with T2 endothermic behavior. However, the enthalpy relaxations of the T2 endothermic behavior for P-PU polymer was absent, which could be attribute to the behavior of degradation in the temperature range of T2 endotherm. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3502–3513, 2001

Key words: silicon; phosphorus; polyurethane; annealing

INTRODUCTION

In our previous study,[1] the silicon-containing segmented polyurethane (Si-PU) and phosphorus-containing segmented polyurethane (P-PU) displayed multiple endotherms that were associated with the short-range ordering of the hard segment domain at a lower temperature range (Renge I) and the long-range ordering of the hard segment domain at a higher temperature range (Region II). However, the formation of those domains were strongly affected by heat treatment (annealing effect), except for the hard-segment length and hard-segment content, which was presented in the previous study.[1]

Cooper et al.[2–4] indicated that the temperature ranges of Renges I and II in segmented polyurethane were affected by annealing. They demonstrated that the endothermic temperature of Range I (T1) could be improved by annealing, resulting in a consistent upward temperature shift of T1 until its merger with the endothermic

Table I   Composition

Sample	Hard-Segment Molecular Weight (M_w nh)	Silicon/MDI Contetnt (wt %) (Si-Hard Segment Content)	Phosphorus/MDI Contetnt (wt %) (P-Hard Segment Contetnt)
PD1-143	1632	62.2	
PM1-143	1288		56.3

temperature of Region II (T2). The higher the annealing temperature, the greater the upward shift. They also found that the T2 could be shifted to a higher temperature range by annealing also, and even merged with the endothermic temperature range of the microcrystalline hard segment domain by severe annealing over long periods of time if the hard segments possessed a sufficient length to produce a microcrystalline domain.

Previously, the cause of the endothermic behavior of Regions I and II was uncertain or explained from different aspects. Early studies suggested that the endothermic behavior was due to the destruction of urethane hydrogen bonds.[5,6] Cooper and Seymour,[3] in the study of infrared spectroscopy, verified that hydrogen-bond dissociation does occur, increasing steadily as the temperature is raised above the hard-segment T_g. However, it is important to note that there is still significant hydrogen bonding at 200°C, and that the thermal behavior of the hydrogen bonds is insensitive to morphological details. Furthermore, they also indicated that hydrogen bonding plays no observable role in the DSC analysis, which is not surprising due to the fact that ΔH and ΔS values are varying slowly, and contribute to only a minor fraction of the observable thermal response. Therefore, the DSC endotherms observed resulted mainly from morphological effects. Afterward, Cooper et al.,[7] in a study of different annealing conditions, ascribed the endotherms of Regions I and II of segmented polyurethane as an effect of the dissociation of the hard segment domains. Koberstein et al.,[8,9] however, in their study on conventional polyether polyurethanes, suggested that the endothermic behavior of Region I may be explained by solubility effects embodied in the microdomain model of Koberstein and Stein.[10] Recently, Chen et al.[11] studied endothermic behavior of the Region I in a polyurethane based on 4,4′-diphenylmethane diisocyanate and 1,4-butanediol, and suggested that the nature of the behavior was typical of enthalpy

relaxation resulting from the physical aging of the amorphous hard segment. In our previously article,[1] the thermal behavior and morphology of a series of Si-PU and P-PU polymers was presented. This article will investigate the effect of annealing on the morphology and the nature of Regions I and II.

EXPERIMENTAL

Materials

According to our previous results,[1] the melt-quenched samples PD2-143 and PM2-143 exhibited amorphous hard segment domains in Region I and II and a higher phase separation after upon DSC measurement. Therefore, both of these samples were used in our investigation of the annealing effect. The composition of PD2-143 and PM2-143 listed in Table I.

Measurement

The preparation of the melt-quenched samples PD2-143 and PM2-143 (unannealed sample) were the same as those in our previous study.[1] The melt-quenched samples were first heated to 230°C, held at this temperature for 1 min to remove thermal history, quenched to 20°C at a rate of 300°C/min, and then kept at this temperature until thermal equilibrium was reached. Subsequently, thermograms of the samples were measured at a heating rate of 20°C/min. The weight of the samples was roughly 10 mg. Because the characteristic temperatures of the hard segment domains (Regions I and II) appeared above room temperature in this study, the DSC thermograms of the melt-quenched samples were only measured from room temperature under different annealing conditions. The different annealing conditions are illustrated in Figs. 1, 3, 4, 6, 8, and 10–18. Furthermore, the samples underwent an-

nealing for more than 24 h while inside a test tube in a nitrogen atmosphere. The test tube was put into a vacuum oven and kept at a constant temperature for a predescribed amount of time.

The magnitude of enthalpy relaxation resulting from annealing was calculated from the net area obtained by subtracting the DSC thermogram of an unaged sample from that of an aged one. This is the generally accepted method according to the literature.[11–13] The peak position was measured by using vertical cursors to locate the peak position.

RESULTS AND DISCUSSION

In our previous study[1] the morphological formation of the hard-segment domains (Regions I and II) for Si-PU and P-PU except for its hard-segment length and content was affected by its thermal history during preparation. Because all samples were heated at 100°C for 24 h to remove the solvent and dried by vacuuming at 60°C for 3 days before the initial scan, there was an annealing
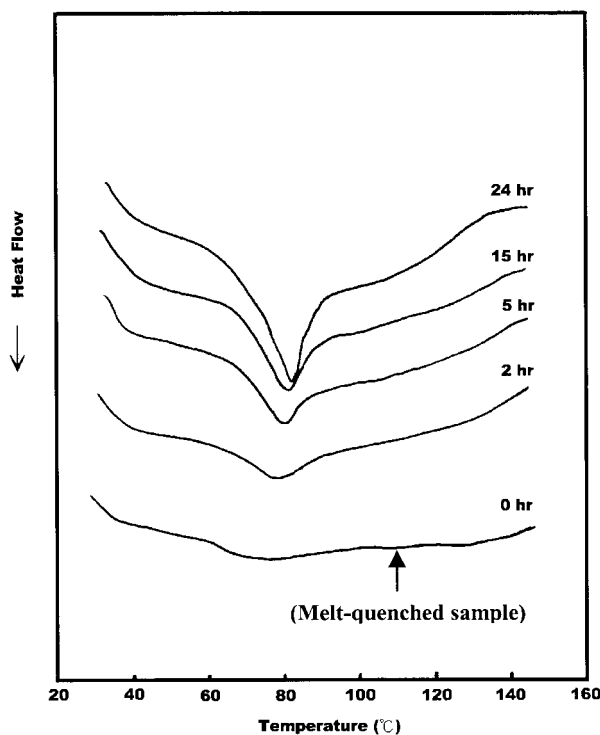

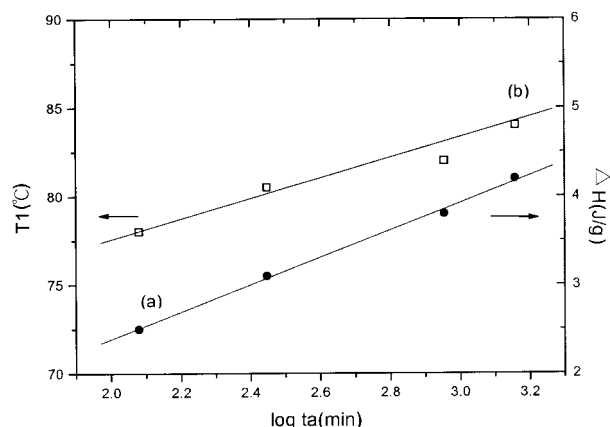**Figure 1** DSC thermograms of the melt-quenched PD2-143 samples, which were annealed at 60°C for different periods of time.

Figure 2 (a) Relationship of the endotherms magnitude, ΔH, and (b) relationship of the endothermic peak position, T1, with respect to the logarithm of the annealing time. Both (a) and (b) result from the DSC thermograns in Figure 1.

effect appearing in the results of the initial scan of the DSC measurement. Obviously, different annealing temperatures and annealing times may affect the morphological formation, so different annealing conditions were employed to further investigate the effect of annealing on the nature of the morphological formation of the hard segment domains for the Si-PU and P-PU polymers in this study.

Effect of Sub-T1 Annealing

Si-PU Polymers

Figure 1 illustrates the DSC thermograms of the melt-quenched PD2-143 samples after further annealing at 60°C for different periods of time. We found that a small endotherm appearing in the vicinity of T1 progressively shifted to a higher temperature and grew larger in magnitude as the annealing time (t_a) increased. Figure 2 illustrates that there is a linear relationship between the logarithm of annealing time (log t_a) and both the endotherm's magnitude (ΔH) and its peak position T1. Obviously, well-ordered Si hard-segment domains (Region I) can be better formed after annealing at 60°C for a period of time.

Furthermore, Figure 3 illustrates the DSC thermograms of the melt-quenched PD2-143 samples that were further annealed at different temperatures (T_a) for 1 h. The greatest endothermic peak appeared for $T_a = \text{T1}(T_g) - 20°C$. Comparing the results of Figures 1–3 with those of Tenbrinke
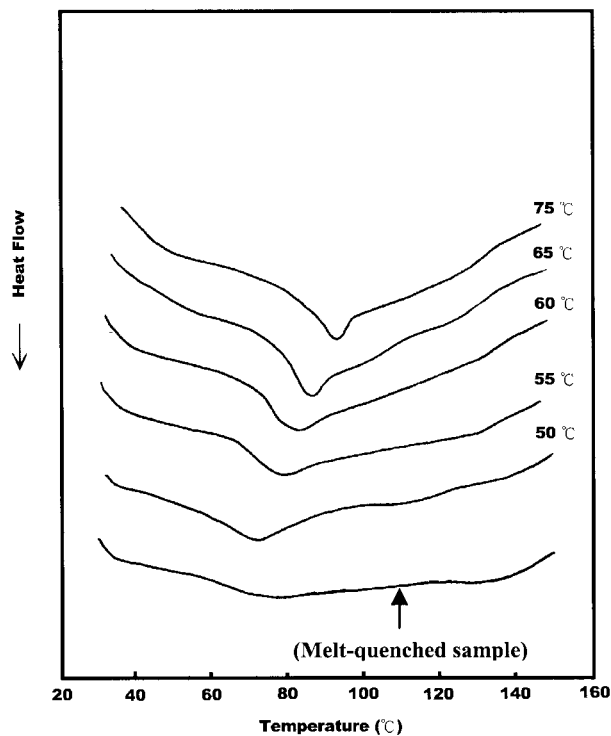
Figure 3 DSC thermograms of the melt-quenched PD2-143 sample, which were further annealed under different anealing temperatures, T_a, for 1 h.

et al., in their article[16] they reviewed all the enthalpy relaxation behaviors from the physical aging of amorphous polymers and summarized the results as follows:

1. The magnitude of the endothermic peak in the proximity of T_g increases linearly with the logarithm of the annealing time (t_a), when the aged glass is not in equilibrium.[17-22]
2. The position of the endothermic peak also increases linearly with log t_a under the same conditions.[17,20,23-25]
3. The maximum height of endothermic peak is a function of annealing temperature when $T_a = T_g - 20°C$.[20,26]

Therefore, we suggested that the T1 behavior of our Si-PU polymers from Sub-T1(T_g) annealing is an enthalpy relaxation behavior originating from the physical aging of amorphous Silicon-urethane hard segments.

To further verify the view of physical aging, the melt-quenched samples PD2-143 were further an-

nealed at 30°C for extended periods of time. Figures 4 and 5 show that the position and magnitude of the endothermic peak also increase linearly with the logarithm of the annealing time. These results confirm that this endothermic behavior of short-range ordering of the Si-hard segment domains (Region I) is probably an enthalpy relaxation resulting from prolonged physical aging.

P-PU Polymer

The results of the DSC thermograms of the melt-quenched PM2-143 samples after further annealing at 60°C for different periods of time period were similar to those of the PD2-143 polymer, and are presented in Figures 6 and 7. However, the endotherm's magnitude (ΔH) of the melt-quenched PM2-143 polymers was higher than that of the melt-quenched PD2-143 polymers at the same of annealing conditions. If we accept that the T1 behavior in sub-T1 annealing is an enthalpy relaxation behavior resulting from the physical aging of the amorphous hard segments, then we may reasonably assume that the P-hard
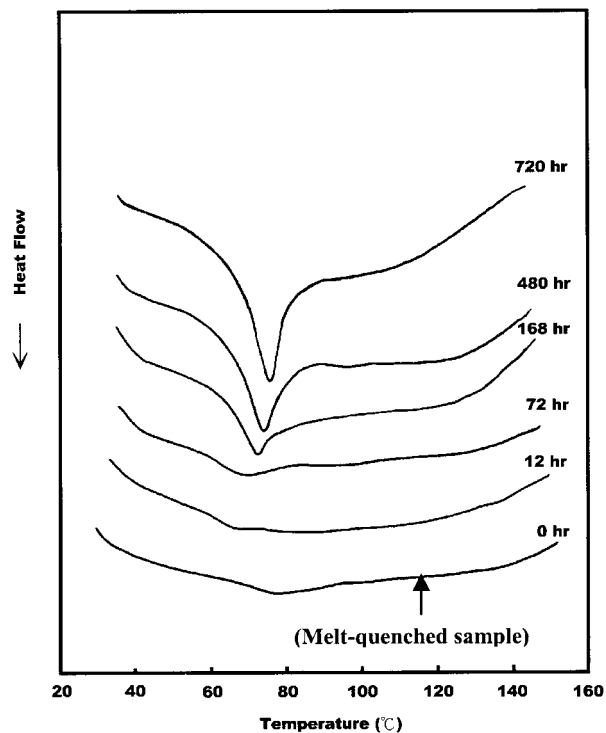

Figure 4 Enthalpy relaxation behaviors of the melt-quenched PD2-143 samples, which were further annealed for different periods of time at 30°C.
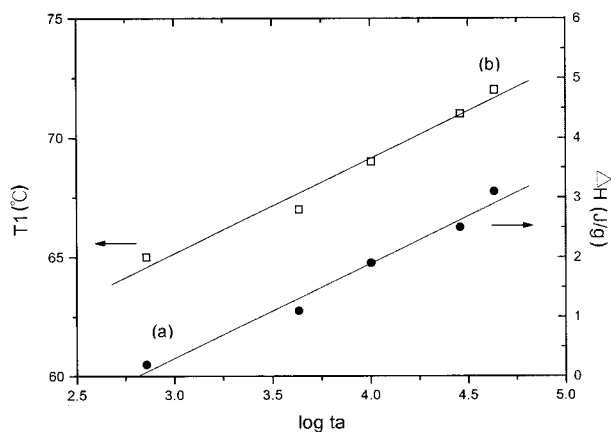
annealed for different periods of time at 30℃.

Figure 5 (a) Relationships of the endothermic magnitude, ΔH, and (b) relationship of endothermic peak position, T1, with respect to the logarithm of the annealing time, t_a. Both (a) and (b) result from the DSC thermograms in Figure 4.

segments age more quickly than the Si-hard segments. Therefore, the Si- hard segment is more stable than the P-hard segment.

In order to further demonstrated this assumption, the melt-quenched samples PM2-143 were further annealed at 30°C for long periods of time as depicted in Figure 8. Figure 9 illustrates the linear relationship between the peak position T1 and log t_a, and between the magnitude ΔH and log t_a (the logarithm of the annealing time). Comparing the ΔH of the melt-quenched PM2-143 samples and with that of the melt-quenched PD2-143 samples reveals that the melt-quenched PM2-143 samples have a higher ΔH. Furthermore, Figure 10 shows that the melt-quenched PM2-143 samples that were further annealed at different temperatures (T_a) for 1 h had the greatest endothermic peak appears at $T_a = \text{T1}(T_g) - 20°\text{C}$. The results of Figures 6–10 verify that the T1 behavior for PM2-143 polymers is also an enthalpy relaxation originating from the physical aging of the amorphous P-hard segment. These results further verify the thermal instability of the P-hard segment, which agrees with a previously study of degradation by TGA.[12]

Super-T1 Annealing

Figures 1 and 6 show that the reordering or reforming endotherm was terminated at about
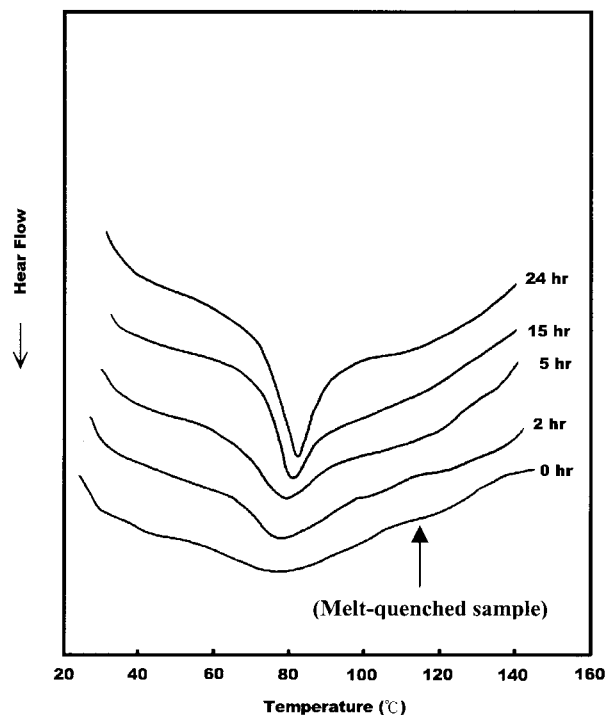

Figure 6 DSC thermograms of the melt-quenched PM3-143 samples, which were annealed at 60°Cfor different periods of time.

160°C, and that the Region II structure was not obviously improved by annealing at 60°C for any of the time periods. This phenomenon may be because the hard segment domains were not disrupted, that is, the hard segment domains could
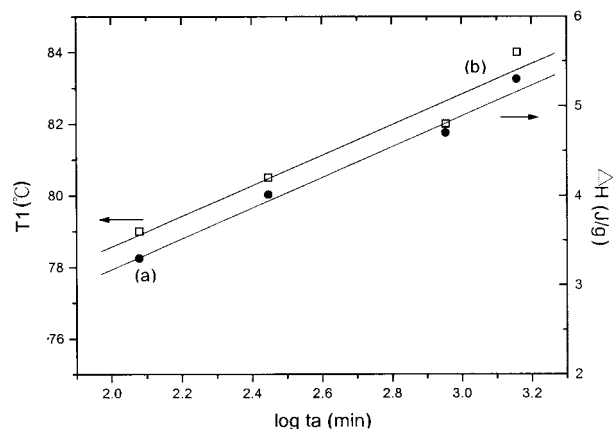

Figure 7 (a) Relationship of the endothermic magnitude, °H, and (b) relationship of the endothermic peak position, T1, with respect to the logarithm time. Both (a) and (b) result from the DSC thermograms in Figure 6.
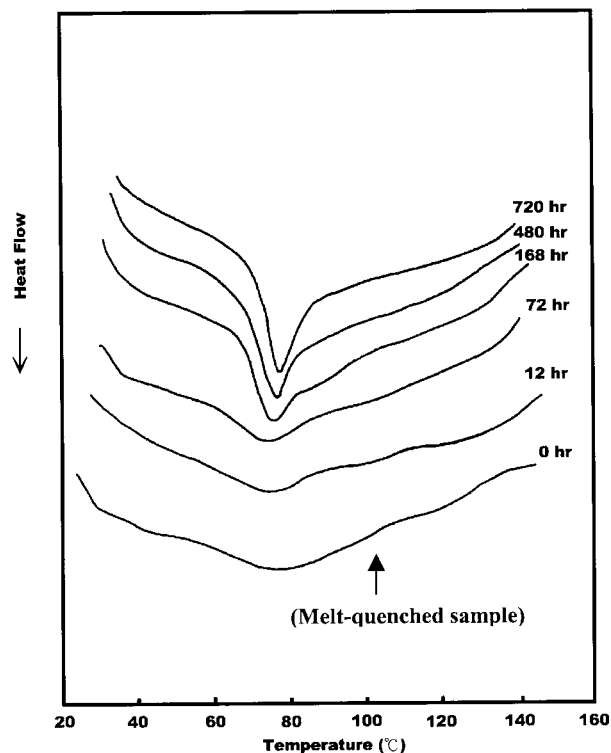
Figure 8 Enthalpy relaxation behaviors of the melt-quenched PM2-143 samples, which were further annealed for different periods of time at 30°C.

Figure 10 Figure 3 DSC thermograms of the melt-quenched PM2-143 samples, which were under different annealing temperatures, T_a, for 1 h.

not be reformed or ordered in Region II under the annealing conditions. However, we found that if we had the melt-quenched samples PD2-143 and
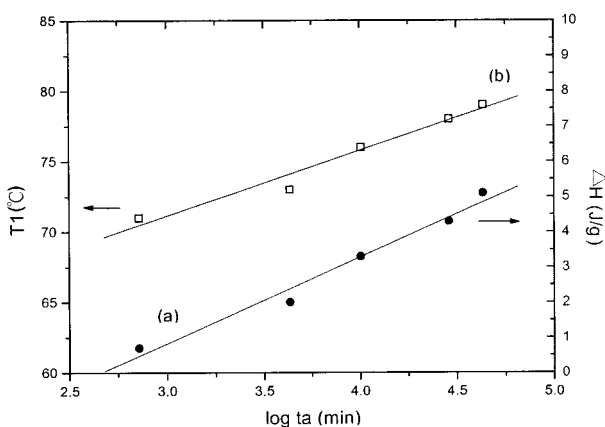

Figure 9 (a) Relationship of the endothermic magnitude, ΔH, and (b) relationship of endothermic peak position, T1, with respect to the logarithm of annealing time, t_a. Both (a) and (b) result from the DSC thermograms in Figure 8.
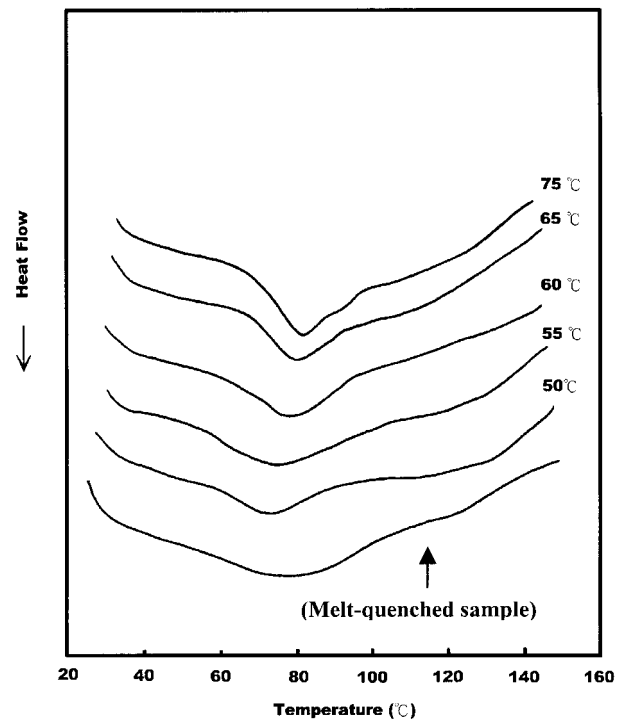
PM2-143 annealed at 150°C for a period of time, an ordered structure could be form.

Si-PU Polymer

Figure 11 displays the DSC thermograms of the melt-quenched samples PD2-143 after annealing at 150°C for different periods of time. Three endotherms appeared between 160 and 200°C. According to the previous literature,[3,7,8,27–29] these endotherms are associated with a dissociation of the noncrystalline ordered hard segment domains (Region II) in the temperature range T2. Multiple peaks after annealing at a high temperature were frequently encountered before.[7,11,28] However, the first peak appeared at about 170°C, which is just 20°C above the annealing temperature. As mentioned earlier, this phenomenon is probably attributable to an enthalpy relaxation of the Si-hard segment resulting from physical aging. Furthermore, another two endothermic peaks appeared at a temperature approximately 30°C above the annealing temperature. We reviewed the literature[3,7] on the effect of high-temperature annealing on the thermal behavior of polyure-
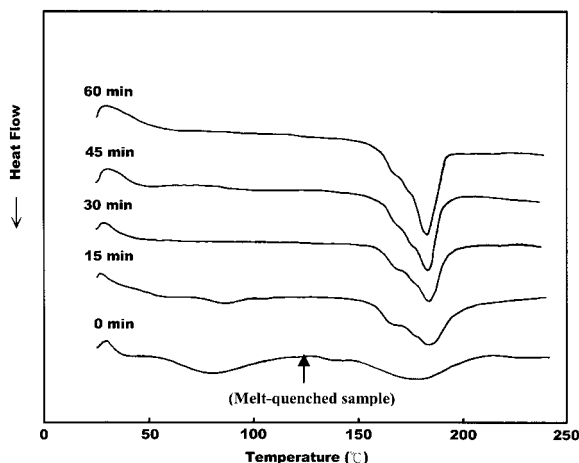
Figure 11 DSC thermograms of the melt-quenched PD2-143 samples, which were annealed at 150°C for different periods of time.

thanes. Comparing these studies with our results, annealing at a temperature of 150°C may have contributed to the mobile, disordered Si-urethane hard segments reassociating into a more stable Si-urethane hard segments because only higher temperature endotherms remain after annealing. That is, the diordering long range of the Si-hard segments coming form aggregations that are disrupted by the annealing conditions are reformed into the ordering long range of the Si-urethane hard segment domains, which then dissociate at a temperature approximately 30°C above the annealing temperature. Furthermore, after annealing, the endotherms exhibited a larger peak area, which increased with the increase of the annealing time, as shown Figure 11, suggesting an increased domain size and improved ordering. The peaks were nearly all at about the same temperature, indicating that the position of the higher temperature endotherms appears to be independent of annealing time. Similar behavior has been reported in the literature.[7,28,30]

To further investigate the annealing effect above temperature T2, the melt-quenched PD2-143 samples were annealed at T2 between 160 and 190°C for 1 h, as shown in Figure 12. The DSC thermograms displayed two endothermic peaks at a temperature about 20 and 30°C above the annealing temperatures, respectively, which indicated that enthalpy relaxation of the Si-hard segments and dissociation of ordered Si-hard segments occurred during the period of annealing. Furthermore, Figures 11 and 12 also display a

high temperature on the annealing effect on T1 behavior. We found that T1 was completely absent above 150°C when the annealing temperature was above 150°C for a period of time.

Cooper et al.[3,7] in their study of traditional polyurethane also noted that the T1 endotherm disappeared after annealing at a high temperature for a period of time. Also, such annealing moved the position of the endothermic peak to higher and higher temperatures until it merged with T2, and eventually only a single endotherm appeared. Moreover, the T1 (Region I) peak may also be moved by annealing without a well-developed T2 (Region II) peak. Therefore, we had the melt-quenched PD2-143 samples annealed at a middle range temperatures between 110 and 140°C for 1 h, as presented in Figure 13, to help our better understand this type of T1 behavior and the morphological changes associated with it. Figure 13 reveals that a small endothermic peak appeared at a temperature about 20°C above the annealing temperatures (110, 120, and 130°C, respectively), which agrees with the relationship T_a = T1$-T_a$_20°C. However, this small peak disappeared after annealing at 140°C, and was incorporated into the endothermic range of Region II. Furthermore, the position and size of T2 were nearly identical when the annealing temperature was between 110 and 130°C, while the size of T2 was obviously change when the annealing temperature reached 140°C due the T1 peak (Range I) arriving at the T2 temperature range and com-
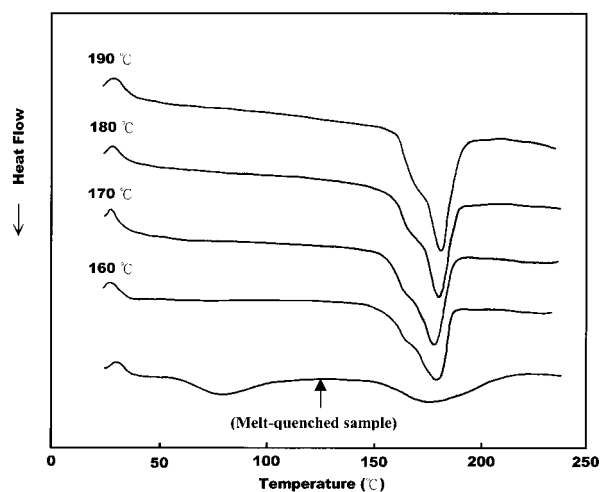

Figure 12 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed under different annealing temperatures, T_a, for 1 h.
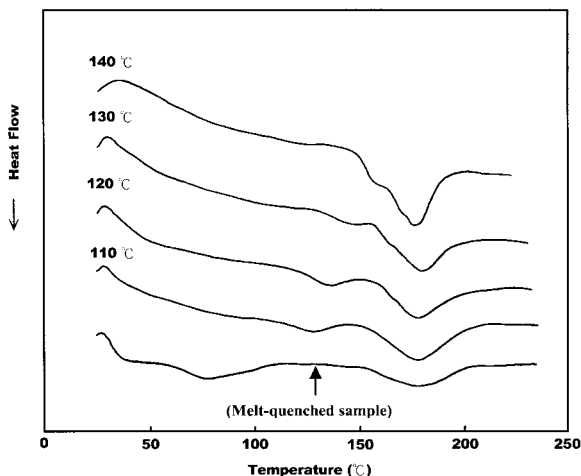
Figure 13 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed under different annealing temperatures, T_a, for 1 h.

Figure 15 (a) Relationship of the endothermic magnitude, ΔH, and (b) relationship of endothermic peak position, T1, with respect to the logarithm of annealing time, t_a. Both (a) and (b) result from the DSC thermograms in Figure 14.

bined with T2 (Range II). The results demonstrated that the Range II structure of the Si-PU could not be changed below an annealing temperature of 140°C.

The melt-quenched PD2-143 samples were annealed at 120°C for different time periods, as shown in Figure 14, to further demonstrate the T1 behavior of enthalpy relaxation in the middle temperature range. Figure 14 indicates that the position and magnitude of the T1 endotherm progressively increased with an increase of the annealing time. Figure 15 again shows the linear
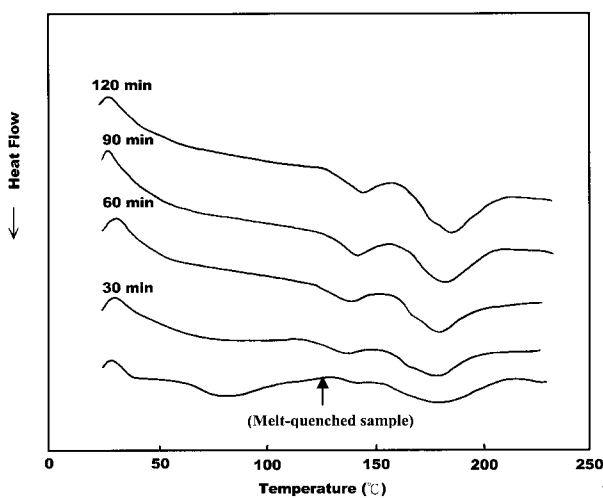
relationship between each of the position and magnitude of the T1 endotherm and the logarithm of the annealing time (log t_a). According to the results of Figures 13 and 14, this T1 behavior is also an enthalpy relaxation resulting from physical aging of the Si-PU polymer.

P-PU Polymer

Figure 16 shows that the melt-quenched PM2-143 samples annealed at 150°C for different periods of time exhibited a large endothermic peak between 160 and 240°C. These endothermic peaks were

Figure 14 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed at 120°C for different periods of time.
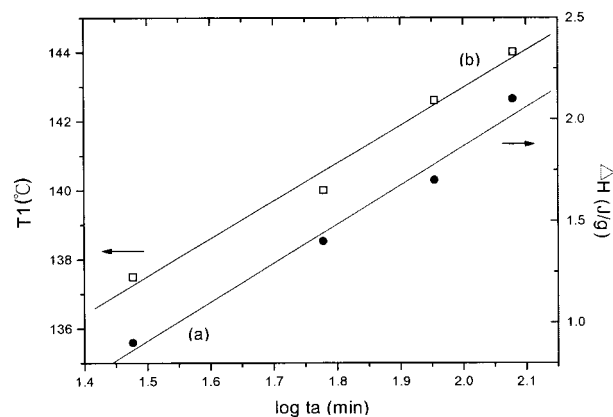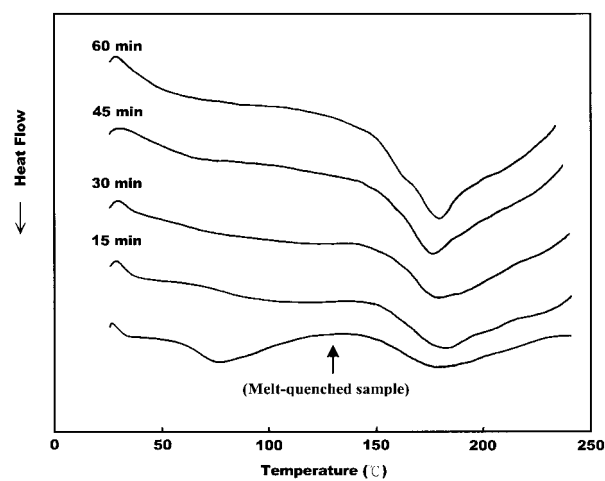

Figure 16 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed at 150°C for different periods of time.
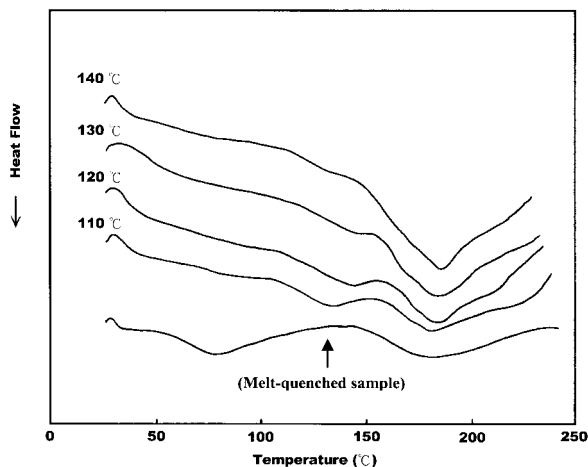
Figure 17 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed under different annealing temperatures, T_a, for 1 h.

Figure 18 DSC thermograms of the melt-quenched PD2-143 samples, which were further annealed at 120°C for different periods of time.

different from those of the melt-quenched PD2-143 samples. According to our previous study on Region II,[1] we suggest that the endothermic behavior (T2 peak) is a dissociation and degradation resulting from long-range ordering and disordering of the P-hard segment domains. Therefore, the enthalpy relaxation resulting from physical aging may be absent when annealing under higher temperatures due to the degradation of the P-hard segments having occurred during the annealing period. Also, it is possible that the disordering of the long-range P-hard segments may be could not reassociated into the ordering of the long-range P-hard segment.

The melt-quenched samples PM2-143 were also annealed in the middle range temperature (between 110 and 140°C), as shown in Figure 17, and displayed an endothermic peak (T1) between 120 and 160°C. This T1 peak also increased as the annealing temperature increased. The T2 endotherm slightly increased with an increase of the annealing temperature. However, the T2 positions are nearly all the same, at about 185°C, when the annealing temperature was between 110 and 130°C, while the T1 peak merged with the broad T2 peak at 140°C. Figure 18 shows the melt-quenched PM2-143 samples annealed at 120°C for different periods of time. Figure 19 shows the relation of the position of the T1 peak and the magnitude of endotherm to the logarithm of the annealing time (log t_a). The results were similar to the melt-quenched PD2-143 samples. However, the magnitude of the endotherms was
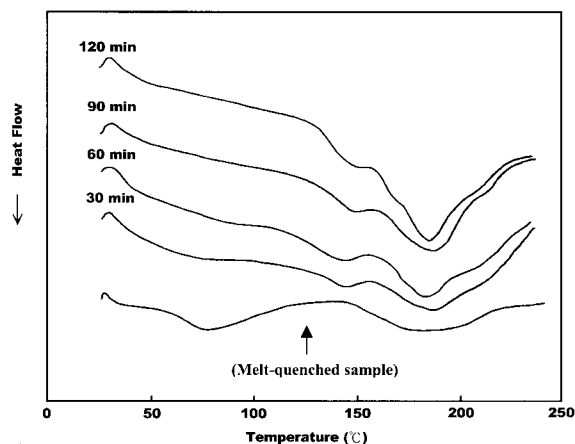
higher than that of the melt-quenched PD2-143 samples under the same annealing conditions. This may be due to the P-hard segments being more mobile than the Si-hard segments. Therefore, we suggest that this T1 behavior of the P-PU polymer is also enthalpy relaxation resulting from the physical aging of P-hard segments.

Figure 20 illustrates the wide-angle X-ray (WAX) diffraction of the melt-quenched samples PD2-143 and PM2-143 when annealed at 150°C annealing for 1 h. The diffraction intensity and pattern of WAX showed that an almost completely amorphous, which indicated that the en-
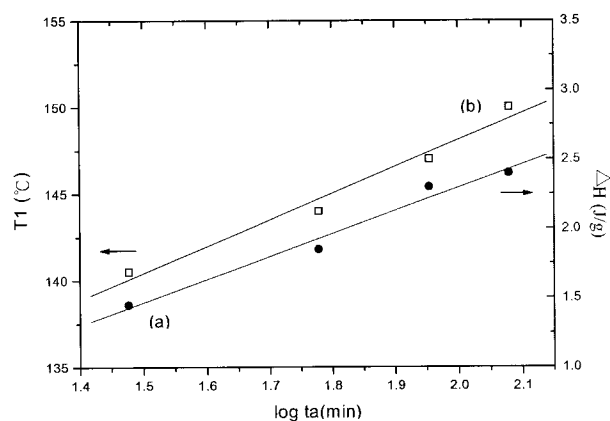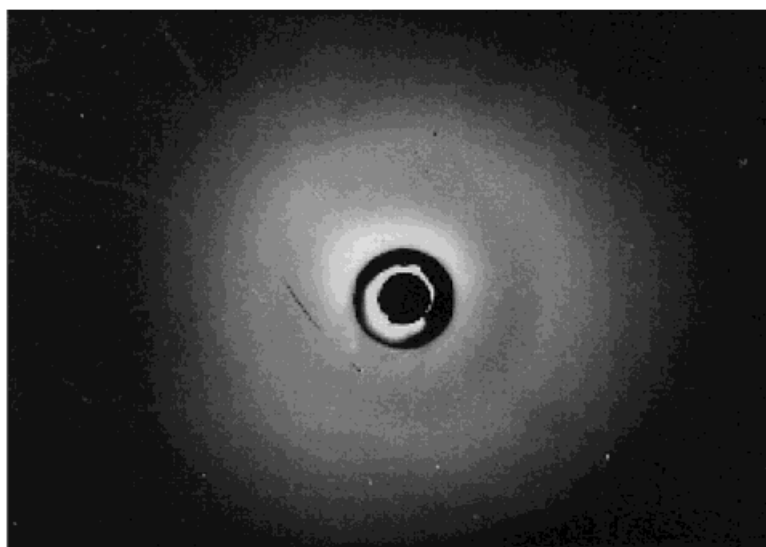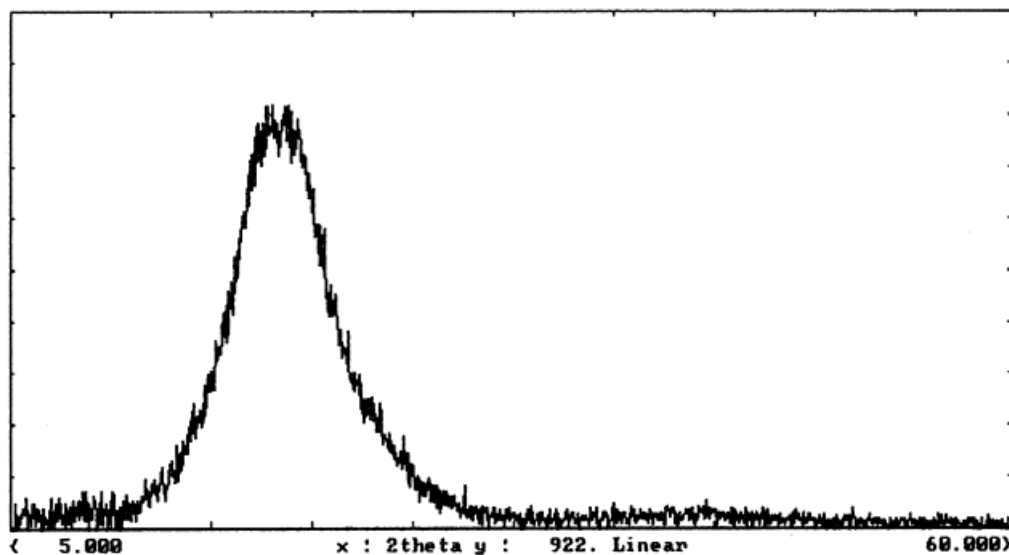

Figure 19 (a) Relationship of the endothermic magnitude, ΔH, and (b) relationship of endothermic peak position, T1, with respect to the logarithm of annealing time, t_a. Both (a) and (b) result from the DSC thermograms in Figure 18.

(5.000   x : 2theta y :   922. Linear   60.000>


(a) PD2-143

Figure 20 Wide-angle X-ray (WAX) diffraction intensity and pattern of the melt-quenched sample PD2-143 and PM2-143 at 150°C annealing for 1 h.

dothermic behavior after annealing is not a melt of the crystalline in Region I and II.

CONCLUSIONS

These extensive annealing studies on the melt-quenched samples having a high degree of phase separation were performed by DSC, and provide further evidence for high degree of phase separation, which would exclude the possibility of Region I formation. The endothermic behavior of Region I for the Si-PU and P-PU polymer is an enthalpy relaxation resulting from the physical aging of amorphous hard segment. Furthermore, the magnitude of the endotherm of Region I increased as the annealing time increased, which illustrates an increased Region I structure and an
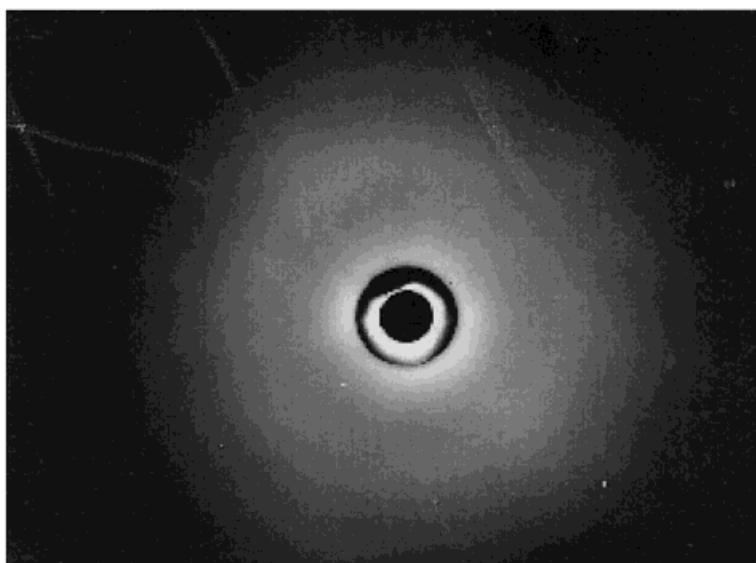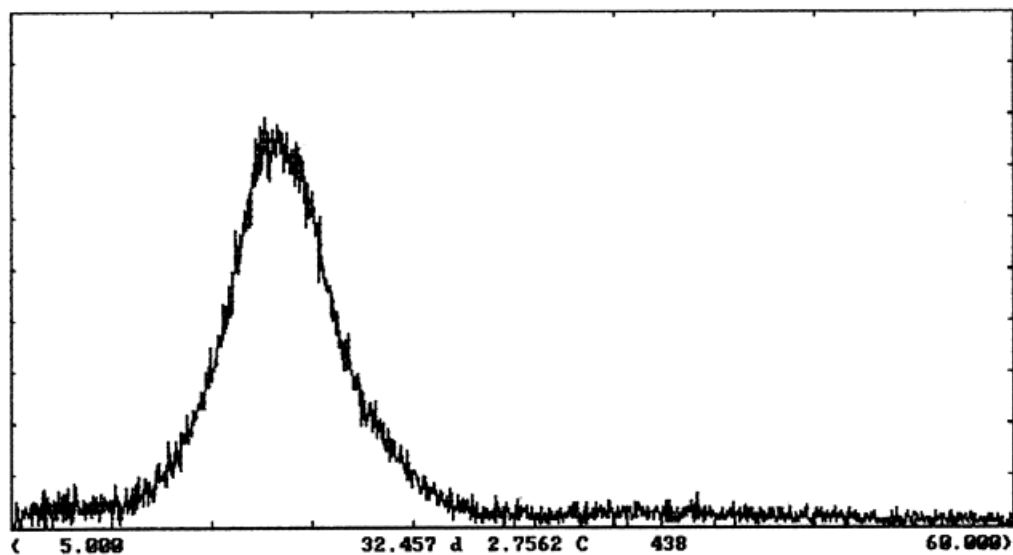
(b) PM2-143

Figure 20 (*Continued from the previous page*)

improved ordering of hard segment in Region I. The T1 endothermic peak was absent at annealing temperatures above 150°C, and shifted into the T2 endothermic range as the annealing temperature increased. The Region II structure of the Si-PU polymer also improved by high-temperature annealing over a period of time. Although the magnitude of the T2 endotherm of the Si-PU polymer increased with an increase of the annealing temperature, the endothermic peaks maintained a constant temperature about 180°C. The endothermic behavior of Region II for the Si-PU polymer was related to enthalpy relaxation and the dissociation of the amorphous hard segment. The higher temperature endotherm of the P-PU polymer exhibited a large endotherm, which was primarily caused by the degradation of the unstable P-hard segment. Furthermore, enthalpy relaxation of amorphous hard segment provides a reasonable explanation for why the thermal stability

of the P-hard segment is lower then that of the Si-hard segment.

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