MDI/1, 4-부탄디올/폴리 (에틸렌 아디프산)을 성분으로 한 폴리우레탄 내의 단단한 블록의 용융에 관한 연구

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Investigation of Melting Behavior in the Hard Block of Polyurethane Composed of MDI/Butanediol/ Poly(ethylene adipate)

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Abstract: The polyurethanes composed of methylene bis(4-phenylisocyanate) (MDI) and 1,4-butanediol as the hard segment and hydroxyl-terminated poly(ethylene adipate) as the soft segment were synthesized with varying the hard segment contents (15-40 wt.%) and investigated by differential scanning calorimetry and dynamic mechanical analyser. In the DSC thermogram two endotherm peaks were observed above the glass transition temperature of the hard segment. The experimental results for the different annealing time and heating rate in DSC showed that there existed two different crystal forms in the hard segment of the polyurethane. Form I crystal melts at 160°C and form II crystal melting at 190°C is thermodynamically more stable than form I. The endotherm peak of form II was always increased with falling off the endotherm peak of form I by annealing. These results were well correlated with the dynamic mechanical data by showing the dramatic change in dynamic shear modulus and a trough of loss tangent around 160°C caused by form I.

INTRODUCTION

The extent of microphase separation and the structure of the resulting components in the segmented polyurethane elastomer are now better understood. In particular, thermal analysis and X-ray scattering investigations have been found to show that the hard segments are separated to form discrete domains in a matrix of soft segment[1-7].

Factors affecting domain formation lay particular emphasis on the role of hydrogen bonding interactions but it remains obscure how far hydrogen bonding affects the thermochemical relaxation behavior[8-15].

Regarding the role of the hydrogen bond, it might be of interest to analyze the thermal transitions of segmented polyurethanes, especially above the glass transition temperature of the hard seg-

ment. A number of studies have recently been reported on the transition behavior of segmented polyurethanes. Most of the previous works had examined phase separation of hard segments into microdomains and domains softening with temperature for polyurethanes of different chemical compositions[16-18].

In the present study, an effort is made to investigate the crystalline melting and the annealing effect on the hard segments as well as its influence on the thermomechanical properties of linear segmented polyurethanes. The polyurethane elastomers were synthesized with methylene bis(4-phenylisocyanate) (MDI), poly(ethylene adipate) (PEA) and 1,4-butanediol (BD).

EXPERIMENTAL SECTION

Materials Hydroxyl-terminated poly(ethylene adipate) (PEA) was synthesized with ethanediol (ED) and adipic acid according to the method described elsewhere[19]. By titrations of hydroxyl end groups in PEA, the number average molecular weight ($\overline{Mn}$) of the PEA was measured[19]. By distilling out the excess of ED during the polycondensation, $\overline{Mn}$ of PEA was adjusted to 2,000 + 2%, since it is gradually increased by this process.

The synthesis of the polyurethanes (PU) carried out in dimethylformamide/methyl ethyl ketone (v/v: 1:1) solution at 75°C by the one shot technique[20]. The hard block contents in the polymer were varied between 15-40 wt.% by reacting various pro-

portions of MDI/BD/PEA at the equimolar concentration of isocyanate to hydroxyl groups. The composition and molecular weight of the PU are given in Table 1.

Differential Scanning Calorimetry A Du Pont 990 Thermal Analyzer equipped with a 910 DSC module was used. The thermogram was taken with 10.0 ± 0.2 mg sample under the heating rate of 10°K/min. The temperature and calorimetric calibrations were performed with indium as a standard material with an accuracy of ± 0.2°C.

Annealing Treatment A polyurethane sample, sealed in an aluminium capsule was heated to 230°C to erase the previous thermal history and then cooled rapidly to annealing temperature in the calorimeter. All samples were annealed on the DSC cell for the required time intervals isothermally. After a period of annealing, the capsule was cooled rapidly to –100°C and a DSC thermogram was scanned up to about 230°C with a definite heating rate. After cooling the specimen, scanning was repeated at the same heating rate as in the previous scan. Since the two scans were obtained one after the other, any drift occurred in the instrument can be almost cancelled out from the difference in the two curves. All the experiments were conducted under N_2 gas purge.

Linear Dynamic Mechanical Property Measurement The Rheometrics mechanical spectrometer was employed in dynamic plate-plate mode at high temperatures. The disc type specimens were prepared by compression molding. A strain of 2-5%

Table 1. The Composition and Molecular Weight of Synthesized Polyurethane

Sample number	Molar ratio (MDI/BD/PEA)	Hard block[a] weight %	$\overline{Mn} \times 10^{-3}$ [b]	$\overline{Mw} \times 10^{-3}$ [b]	Polydispersity
AJ-1	1.20/0.28/0.92	15	15.3	30.8	2.0
AJ-2	1.20/0.52/0.69	20	30.0	83.4	2.8
AJ-3	1.20/0.66/0.54	25	51.7	122.5	2.4
AJ-4	1.20/0.77/0.43	30	57.0	142.5	2.5
AJ-5	1.20/0.85/0.35	35	58.4	140.1	2.4
AJ-6	1.20/0.91/0.29	40	59.7	137.3	2.3

a; Calculated from the molar ratio of MDI/BD/PEA

b; Measured by Waters Gel Permeation Chromatography (Waters Series 122)

was generally imposed in all the measurements.

RESULTS AND DISCUSSION

Synthesis of PEA and PU Hydroxyl-terminated poly(ethylene adipate) (PEA) was synthesized with adipic acid and 1,2-ethanediol[19].

During the polycondensation $\overline{Mn}$ of the PEA was checked by the end group titration.[19] In order to obtain $\overline{Mn}$ of PEA 2,000, the 1,2-ethanediol (ED) formed by ester interchange reaction during polycondensation was removed continuously.

Polyurethanes (PU) were synthesized by one shot method[20]. PU having different hard block contents were prepared and precipitated in methanol by pouring THF solution of PU several times to exclude low molecular weight of the PU. Their molecular characteristics are given in Table 1.

Since the changes in physical properties of PU with the molecular weight are leveled off above $\overline{Mw}$ = 30,000[2], the difference in $\overline{Mw}$ of the PU synthesized would hardly show any effects on the physical properties we intend to measure.

As the polyurethanes containing 30 and 40 wt.% of hard segments were mainly investigated in this study, they were abbreviated as PU30 and PU40, respectively.

Differential Scanning Calorimetry Measurement
The thermal responses of linear PU elastomer were investigated by the DSC technique. The differential thermograms obtained with PU of various hard segment contents are shown in Fig. 1.
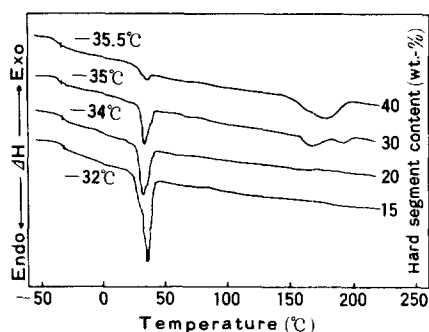

Fig. 1. DSC thermograms of PU containing various hard segment contents.

The distinct glass transition temperature of the soft segment occurs in the temperature range from –35.5 to –32.5°C. The transition temperatures (T_g) are very slightly decreased with an increase in hard segment contents. As the hard segment content increased, the soft segments should be better segregated from the hard segment.

The endothermic peaks around 39°C in Fig. 1 are believed to be arisen from the melting of the crystalline soft segments. The fact that the peak area per unit mass are increased with the soft segment contents supports that the endotherm peaks are attributed to the melting temperature(T_m) of soft blocks.

The T_m of the hydroxyl-terminated PEA($\overline{Mn}$ = 2,000) was measured and found to be 47°C, which is about 8°C higher than the T_m of the soft block in PU. The intermolecular hydrogen bonding by terminal hydroxyl groups of PEA render a high crystallinity to PEA itself. However, when PEA is incorporated as soft blocks in PU, hydroxyl groups are destroyed and chain ends are immobilized by the formation of urethane groups, and hence crystalline formation should be impeded more or less. Consequently by the incorporation of PEA in PU as soft blocks, their T_m were lowered.

For the PU30 and PU40, the slope changes associated with the glass transigion of the hard segments are found around 85°C in Fig. 1. Two broad endothermic peaks are observed at temperatures above 140°C, which are due to the melting of hard blocks. However, the thermal responses of T_g and T_m, arised from the hard blocks, are too small for the PU of low hard block contents (15 and 20 wt.%) to be detected.

In an attempt to obtain further information about the two peaks in the melting range of hard block in PU, the heating rate were varied during DSC measurements as shown in Fig. 2. The variation of the heating rate in DSC measurements affected the position and the area of the peaks. However, the fact that two distinct peaks remained unchanged under these conditions lead to the conclusion that there are two crystal forms in the hard segment in PU, which will be designated form I and II melting at
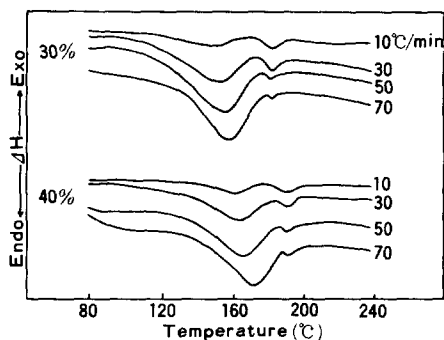
Fig. 2. DSC thermograms of PU containing hard segment content 30 and 40 wt.% at various heating rates.
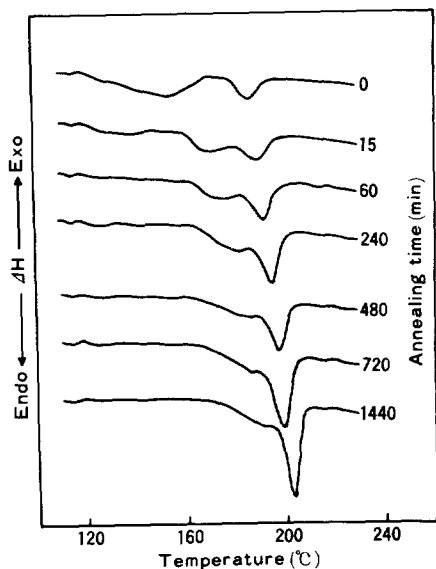

Fig. 4. DSC thermograms of PU containing 40 wt.% hard segment after different annealing times at 160°C.
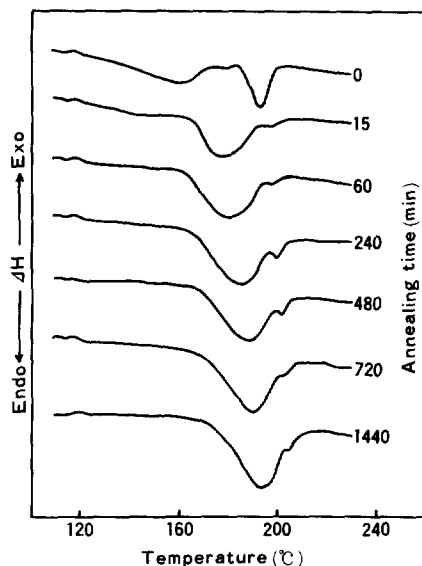

Fig. 3. DSC thermograms of PU containing 30 wt.% hard segment after different annealing times at 160°C.

low (160°C) and high (190°C) temperature, respectively. The thermograms in Fig. 2 show that T_m of the form I is about 30°C lower than that of form II, and that the form I is becoming more endothermic than form II by increasing the heating rate.

Annealing experiments were done just below the melting point of form I(160°C) to induce further growth and/or transformation of the crystal forms. The thermograms of PU30 and PU40 with different annealing time are shown in Fig. 3 and 4, respectively. The two distinct endotherm peaks arising from melting crystalline form I and II of the hard

block are found in each thermogram.

By extending the annealing time, the both endotherm peaks of PU30(Fig. 3) are shifted progressively to higher temperature and the area of the first peak was decreased with increase in the second peak area. Under the same condition, the shift of peaks of PU40 (Fig. 4) shows a similar trend to Fig. 3, but contrary to the Fig. 3 the area of the first peak is not changed.

The constancy of the relative peak area suggests that the first endotherm whose phase is presumably of lower order never merges with the second endotherm by annealing. The time dependence of the increase in the peak temperatures was examined in Fig. 5. It is interesting to note that the first endotherm PU30 eventually merges with that of PU40 at 203°C and the second endotherms of the both polymers merge at 218°C.

The areas of the melting peak around 200°C in Fig. 3 are increased with falling off the other peaks and it suggests that the crystal structure of that peak might be more compact and thermodynamically more stable than the other crystal structure.

In the thermogram of PU40 (Fig. 4) the second melting peak are not merged to the first peak,

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whereas an opposite phenomenon was observed in the thermogram of PU30 (Fig. 3). This seems to arise from the differences in the length of hard block; the hard block length in the PU40 is one and half times longer than that of PU30. The thermogram of the PU containing hard block more than 40 wt.% showed always the same trend as shown in Fig. 4 as well as the pure hard block of PU.[4] There should be a critical length or content of hard block in order to form similar crystal forms and melting behavior of the hard block in PU.

Recently Briber et al.[21] have reported that two crystal forms, type I and II, were found in the hard block (77 wt.%) of PU composed of MDI/BD/poly (ethylene oxide) by the optical investigations. Type I crystals were intrinsically disordered and exhibited only a few diffraction ring in X-ray studies whereas type II crystals were lath shaped and formed a highly ordered array. The melting temperatures of type I and II were reported to be around 206 and 225°C, respectively. This is consistent with the results we obtained; ie, there exsists two crystal forms in the hard segment composed of MDI/BD in PU.

Considering Briber's data as well as our results, form I is supposed to be a mesomorphic phase probably of a nematic order as was usually observed in rigid aromatic polymers, although there are little morphorogical evidence on this matter. However,

the endotherm of form I may not rule out a certain contribution of dissociation of the hydrogen bond in PU.

Dynamic Mechanical Measurements The changes in dynamic mechanical properties were investigated at high temperatures to elucidate their correlations with the structural changes of the PU. The temperature dependence of the storage shear moduli(G') is shown as a function of the hard block contents in Fig. 6. The storage modulus for the PU containing 35 wt.% hard segment exhibited a small plateau above the glass transition around 80-100°C and showed a drastic decline around analyzer. Two endotherms were observed above the glass transition temperature of the hard segment. By variation of heating rate in the DSC measurement and of duration of sample annealing, these two peaks seem to be arisen from two different crystalline structures in the hard segment of the PU. We have designated as crystal form I and II, which are melting around 160 and 190°C, respectively. These results were consistent with those obtained by Brieber et al., who had observed two different crystal forms in the
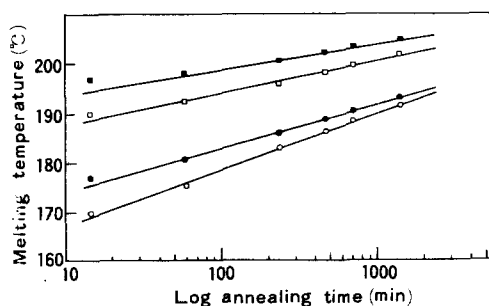

Fig. 5. Plot of T_m vs. log annealing time for PU containing 30 and 40 wt.% hard segment as determined from DSC data.
(□○; high and low T_m of PU containing 30 wt.% hard segment, ■ ●; high and low T_m of PU containing 40 wt.% hard segment)
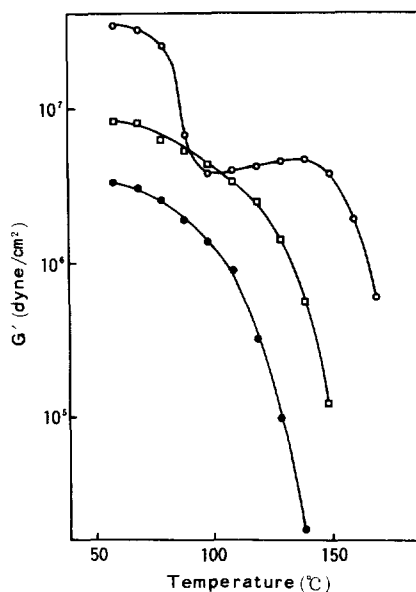

Fig. 6. Dynamic storage modulus of PU as a function of temperature with various hard segment contents. (○;35, □; 25, ●; 20 wt.%)
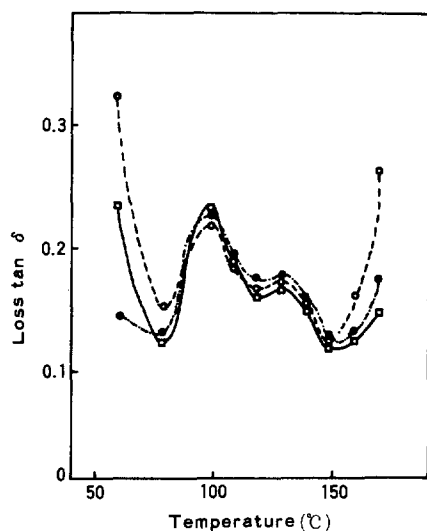
Fig. 7. Loss tangent of PU containing 35 wt.% hard segment as a function of temperature at various oscillation frequencies. (○; 1.18, □; 8.59, ●; 5.0 rad/sec)

hard segment of the PU composed MDI/BD/poly (propylene oxide) by electron microscopy and X-ray diffractions.

The form I is supposed to be a mesomorphic phase probably of a nematic order as was usually observed in a liquid aromatic polymer. The crystal form II was found to be thermodynamically more stable than the form I, since the endotherm peak of form II was always increased with falling off that of form I by annealing.

Finally the dynamic mechanical data were correlated well with the DSC results; the melting transition of form I crystal was accompanied by a dramatic change in the dynamic shear modulus. The loss tangent of PU also showed a trough at 150°C, which supports the idea of existence of the crystal form I in the PU.

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