

## Characterization for Pyrolysis of Thermoplastic Polyurethane by Thermal Analyses

Suk-Hwan Kang, Dong-Cheol Ku, Jung-Hun Lim, Yun-Kyu Yang,  
Noh-Seok Kwak, and Taek-Sung Hwang\*

*School of Chemical Engineering, Chungnam National University, Daejeon 305-764, Korea*

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**Abstract:** The pyrolysis kinetics of polyurethanes synthesized from polycaprolactone diol (PCL) and diisocyanate (HDI, H<sub>12</sub>MDI) using catalysts such as dibutyltin dilaurate (DBTDL) were studied by a thermogravimetric (TG) technique, which involved heating the sample at the rates of 10, 20 and 30 °C/min. The effect of the kind of diisocyanate and the hard segment contents on the activation energy and reaction order were examined at conversions ranging from 1 to 100%. The activation energies at first increased slowly with increasing conversion. Also, differential scanning calorimetry (DSC) was used to investigate the structural differences in each polyurethane. DSC can reveal the melting behavior, in terms of the glass transition temperature ( $T_g$ ), which is known to vary as a function of the stoichiometry and processing conditions.

*Keywords:* polyol, diisocyanate, activation energy, glass transition temperature.

### Introduction

Polyurethanes are used in a wide range of applications in industry and in daily life. They appear in a surprising variety of forms: foams, elastomers, adhesives, coatings, shape-memory, etc.<sup>1,2</sup> The flexible polyurethane slab foams are in furniture, carpet underlay, bedding, and molded polyurethane foam in transportation. Polyurethanes are used as adhesives with different solvents (ketones, etc.) in the shoe sector as well as in the bonding of foams with superficial treatment for the bonding of PVC.<sup>3</sup> Also, thermoplastic polyurethane elastomers (TPU) can be repeatedly melted and processed due to the absence of the chemical networks that normally exist in rubber. In recent years, TPU was used in the spindle and shrink-proof processing.<sup>4,5</sup>

In general, TPU was synthesized with polyol and isocyanate under the catalyst such as dibutyltin dilaurate (DBTDL) and was known that it was linear segmented block copolymers having hard segments (HS) and soft segments (SS). The HS are made from diisocyanate, e.g. diphenylmethane-4,4-diisocyanate (MDI) or 1,6-hexamethylene diisocyanate (HDI), by addition of a chain extender, e.g. butanediol (BD). The SS consist of the long flexible polyether or polyester chains that interconnect two hard segments.<sup>6-8</sup> Therefore, the characteristics of TPU can be determined by contents of HS

or SS.

Several investigators have studied the thermal decomposition mechanisms and characterization of polyurethane polymers. Font *et al.* have reported on the release of aromatic and aliphatic hydrocarbons, and toxic gases such as ammonia and hydrogen cyanide from the polyurethane.<sup>3</sup> Frick and Rochman have observed by thermal analysis (DSC) the characteristics of TPU with specific properties by varying the synthesis and process conditions.<sup>4</sup> Herrera *et al.* have practiced that TPU based on MDI decomposed in the incineration oven, and the gas products desorbed and analyzed off-line by GC/MS.<sup>9</sup> Rotival *et al.* used thermogravimetric analyzer (TGA) to study the thermal decomposition of polyurethane adhesive. Gases, such as CO, CO<sub>2</sub> and HCN, carbonyl compounds and phenyl isocyanate were monitored.<sup>10</sup> Takamoto and Petrich investigated the production of oils from the pyrolysis of polyurethane scrap at 450 °C.<sup>11</sup>

The results of a pyrolysis study of a polyurethane based adhesive are reported. The results are compared with those for varnish waste.<sup>12</sup> The releases of aromatic and aliphatic hydrocarbons, and toxic gases such as ammonia and hydrogen cyanide from the polyurethane are also reported.

In this work, for observing the pyrolysis characteristics of polyurethanes, the materials used in TPU based on polyol (polycaprolactone diol, PCL) and aliphatic isocyanate (1,6-hexamethylene diisocyanate, HDI and cyclohexylmethane diisocyanate, H<sub>12</sub>MDI). The TGA and DSC were used to observe the thermal properties such as activation energy,

\*e-mail: tshwang@cnu.ac.kr

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reaction order and glass transition temperature ( $T_g$ ) of synthesized TPU.

### Theory

The mathematical model used to describe the kinetics of a system undergoing chemical change is usually expressed as the following equation:<sup>13</sup>

$$\frac{dX}{dt} = f(X)k(T) \quad (1)$$

As polymer degradations are often chain reactions,  $f(X)$  represents the net result of a series of elementary steps, each of which has its own activation energy, with the corresponding response to temperature change. The rate constant  $k$  changes with absolute temperature according to the Arrhenius equation. This model is used almost universally to express the temperature dependence on the rate constant of the reaction and  $k(T)$  is defined as:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

Among the various methods proposed for estimation of overall kinetic parameters from non-isothermal TG data, Friedman's method, which was adopted in the present study, is most widely used.<sup>14</sup> This can be expressed as

$$\frac{dX}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-X)^n \quad (3)$$

$$\ln \frac{dX}{dt} = \ln[A(1-X)^n] - \frac{E}{RT} \quad (4)$$

The plot of  $\ln(dX/dt)$  versus  $(1/T)$  is a straight line with a slope equal to  $-E/R$  and an intercept equal to  $\ln[A(1-X)^n]$ . The reaction order can be evaluated by means of eq. (5). The left-hand side of eq. (5) is constant as the intercept of eq. (4). Therefore, the plot of  $\ln[A(1-X)^n]$  versus  $\ln(1-X)$  is a straight line with a slope equal to  $n$ .

$$\ln[A(1-X)^n] = \ln A + n \ln(1-X) \quad (5)$$

### Experimental

**Materials.** The materials used were the thermoplastic polyurethane synthesized at 65°C with PCL, HDI and H<sub>12</sub>MDI. PCL (Aldrich Chemical Co. USA) was used as a polyol, which the weight averaged molecular weight ( $\overline{M}_w$ ) was 1,250 or 2,000. HDI (Aldrich Chemical Co. USA) and H<sub>12</sub>MDI (Bayer Chemical Co. Germany) as diisocyanates were used.

Also, 1,4-BD as a chain-extender and dibutyl tin dilaurate (DBTDL) as a catalyst were purchased from Aldrich Chemical Co. USA, respectively. The solvents, dimethyl sulfoxide (DMSO) and methanol (Duk-San Chemical Co. Korea) were of pure grade over 95%. The component ratio of polyol, diisocyanates and chain extender in the synthetic reaction is shown in Table I. Also, the mean molecular weights of polyurethanes synthesized are shown in Table II. Synthesis of polyurethane followed two-step reactions including the formation of prepolymer, as shown in Figure 1.

**Thermal Analysis.** Thermal analysis for the synthesized polyurethane of solid state were performed with thermogravimetric analyzer (TA2050) of Dupont Co. and differential scanning calorimetry (DSC-2010) of TA Instruments Co. Runs of TGA were conducted in the dynamic mode (heating

**Table I. Composition of Polyurethane with HDI and H<sub>12</sub>MDI**

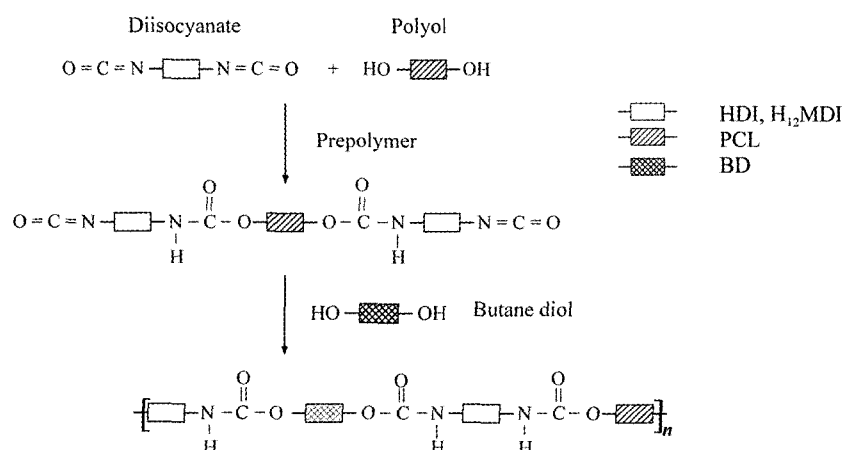
Sample	Mole Ratio PCL/HDI/BD	Hard Segment (wt%)	Sample	Mole Ratio PCL/H <sub>12</sub> MDI/BD	Hard Segment (wt%)
H-1-121	1/2/1	26	H <sub>12</sub> -1-121	1/2/1	33
H-1-132	1/3/2	35	H <sub>12</sub> -1-132	1/3/2	44
H-2-121	1/2/1	18	H <sub>12</sub> -2-121	1/2/1	23
H-2-132	1/3/2	25	H <sub>12</sub> -2-132	1/3/2	32

H-1; The molecular weight of PCL is 1,250. H-2; The molecular weight of PCL is 2,000.

**Table II. Synthetic Conditions of Polyurethane with HDI and H<sub>12</sub>MDI**

Sample	$\overline{M}_w$	$D$	Sample	$\overline{M}_w$	$D$
H-1-121	19,100	1.947	H <sub>12</sub> -1-121	17,700	1.952
H-1-132	19,200	1.944	H <sub>12</sub> -1-132	17,900	1.945
H-2-121	20,400	1.940	H <sub>12</sub> -2-121	20,000	1.940
H-2-132	22,170	1.930	H <sub>12</sub> -2-132	21,700	1.932

$\overline{M}_w$ ; The mean molecular weight of polyurethane.  $D$ ; Degree of dispersion.



**Figure 1.** Schematic procedure of polyurethane formation.

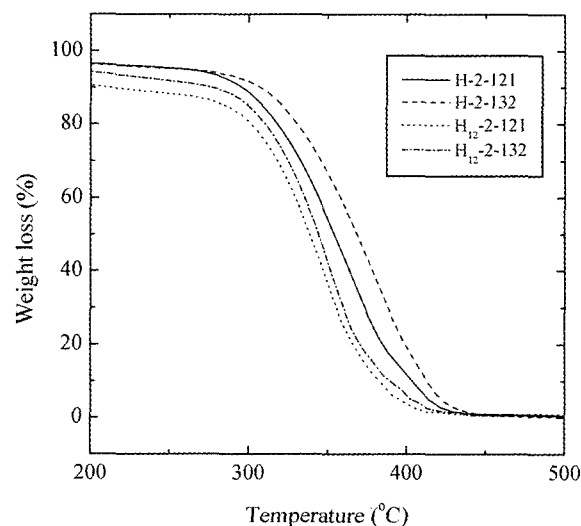
rates 10, 20 and 30 °C/min) under nitrogen atmosphere and the temperature was varied in the range of 30~600 °C. Sample weights were approximately 5 mg. Runs of DSC were performed in the temperature range of -100~200 °C under nitrogen atmosphere (heating rate : 10 °C/min).

## Results and Discussion

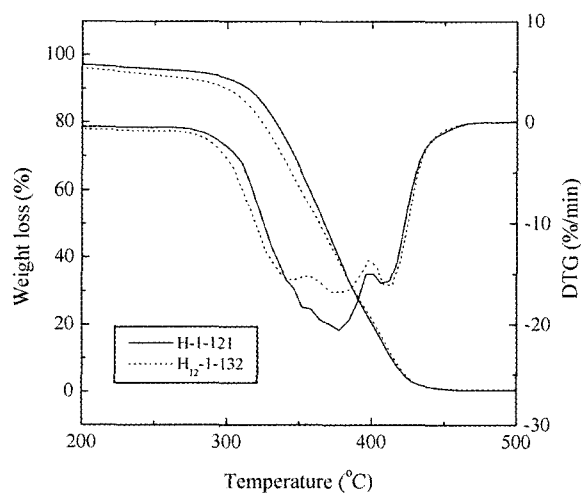
Polyurethanes synthesized with polyol and isocyanate can be prepared by a variety of methods and applied for various object. There are advantages and disadvantages to each method. The one-shot polymerization results in more random block polymers and the prepolymer method is a two-step process that gives less random and more block polymers.<sup>6</sup> These polyurethanes consist of alternating segments of hard and soft blocks. The hard segments are formed by extension of an aromatic or aliphatic diisocyanate and the soft segments are polyethers or polyesters.<sup>7</sup> Also, for applying of polyurethane as an additive for improving the form stability of fiber, it has been superiority thermostability. Therefore, in this study, there is concentrate up on examining its thermal characteristics on the operating conditions.

Typical variations of temperature and conversion rate in terms of the weight loss of polyurethane at the non-isothermal condition for polyurethanes based on HDI and H<sub>12</sub>MDI can be seen in Figures 2 and 3 (including DTG curves), respectively. As can be seen in Figure 2, the thermal decomposition of HDI-based PU takes place. Little differences of *T<sub>i</sub>* values can be noticed in the first steps of the degradation process, regarding the temperature of the degradation threshold. The residue for the decomposed PU at 500 °C is below about 0.3%. In addition, the profile of pyrolysis by H<sub>12</sub>MDI-based PU in Figure 3 is similar to that of HDI-based PU.

The DTG thermograms of polyurethane are shown in Figure 3. The thermal decomposition for polyurethanes took place the two step reactions. The decomposition component of the first degradation step can be shown the carbon diox-



**Figure 2.** Experimental TG curves of HDI-based and H<sub>12</sub>MDI PU at heating rate 20 °C/min.



**Figure 3.** TG and DTG-curves of H-121 and H<sub>12</sub>-132 at heating rate 20 °C/min.

**Table III. Thermogravimetric Analysis of Polyurethanes in Nitrogen Atmosphere at 20°C/min Heating Rate**

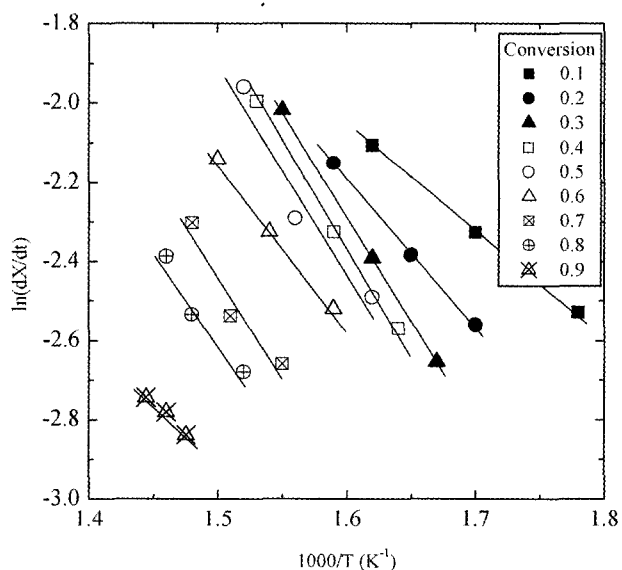
Samples	$T_i$ (°C)	$T_{mr}$ (°C)	$T_f$ (°C)	$\Delta T^a$	$\Delta W^b$ (%)
H-1-121	157	378	509	221	99.7
H-1-132	165	377	562	212	100
H-2-121	140	369	575	229	100
H-2-132	122	385	594	263	99.8
H <sub>12</sub> -1-121	129	348	597	219	99.8
H <sub>12</sub> -1-132	139	379	596	240	99.6
H <sub>12</sub> -2-121	88	353	554	265	99.9
H <sub>12</sub> -2-132	110	352	591	242	99.8

<sup>a</sup> $\Delta T = T_{mr} - T_i$ , <sup>b</sup> $\Delta W =$  Weight loss at  $T_f$ .

ide as the main evolving product. On the other hand, in the second step the evolution of water, HCN which was decomposed the butane diol (1,4-BD) used as chain extender or some nitriles can be shown.<sup>9</sup>

In order to determine the thermal stability of the polyurethanes, the characteristic temperature such as  $T_i$  (temperature corresponding to initial 2% weight loss),  $T_{mr}$  (temperature of maximum rate weight loss) and  $T_f$  (temperature corresponding to final weight loss) were calculated and reported in Table III. The values of  $T_i$  for the HDI are appeared generally higher than that of H<sub>12</sub>MDI.

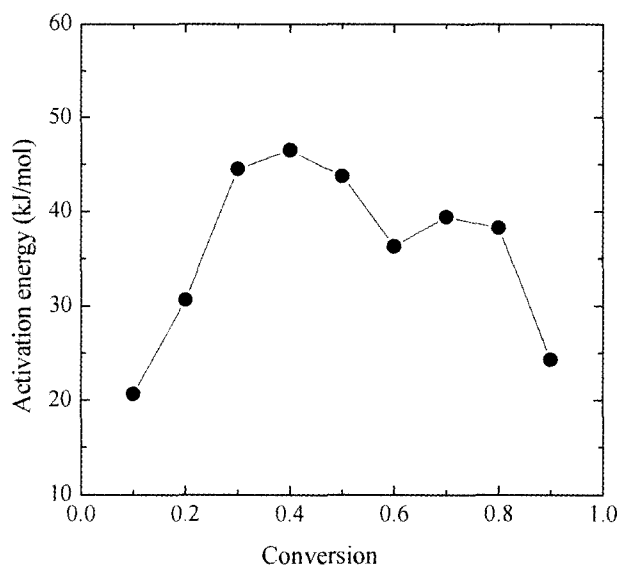
Kinetic analysis of the thermal degradation was carried out according to the Friedman method.<sup>14</sup> The activation energy was obtained from the plot of  $\ln(dX/dt)$  versus  $(1/T)$  by using eq. (4) at a fixed conversion. Results in the range



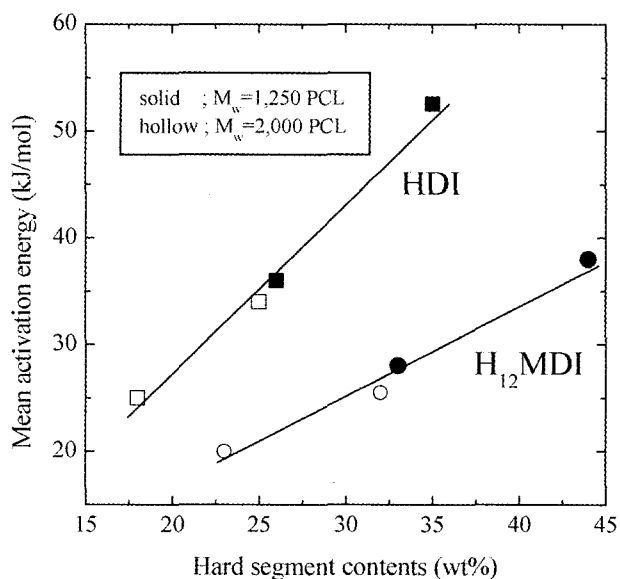
**Figure 4.** Kinetic analysis of PU (H-1-121) by the Friedman method.

of conversion from 0.1 to 0.9 for the polyurethane (H-1-121) are shown in Figure 4. The activation energy can be calculated easily from these slopes.

The calculated activation energy at different conversion levels of polyurethane (H-1-121) can be seen in Figure 5. In this Figure, the value of activation energy doesn't tend to increase or decrease specially with increasing conversion level. The activation energy ranges from 21 to 47 kJ/mol according to the change of conversion level. It has been understood that the polyurethane could be decomposed into various compound. With starting to decomposition of the



**Figure 5.** Calculated activation energies for PU (H-1-121).



**Figure 6.** Effects of hard segment contents on the mean activation energy for each conversion.

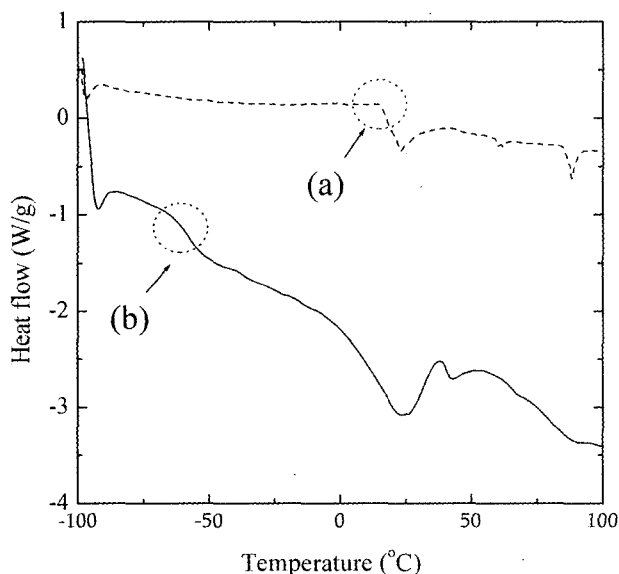
polyurethane melting, the carbon-hydrogen chemical compound, that the carbon length is short relatively, and the hydrogen bonded main-chain can be decomposed. Therefore, with increasing the reaction time, decomposition of the C-C bond or others bond of main-chain occurred gradually.<sup>15</sup>

As mentioned above, the mechanical as well as thermal properties of polyurethane was affected by the hard segment contents. Effect of hard segment contents on the mean activation energy for each conversion is shown in Figure 6. As can be seen in Figure 6, the activation energy for the HDI and H<sub>12</sub>MDI increased linearly with increasing hard segment contents.

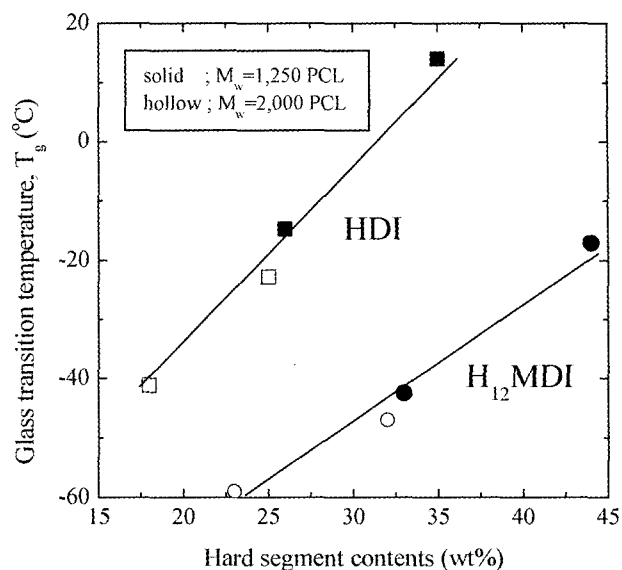
With increasing the hard segment contents of polyurethane, thermostability, which defined the storage modulus to change temperature rapidly, tends to improve. Also, the degree of phase separation in segmented polyurethanes is relatively higher, and the compatibility between hard segment and soft segment is low.<sup>16</sup>

Polyurethanes based HDI have higher hydrogen bond ability than H<sub>12</sub>MDI. The tensile strength of polyurethanes reported by Kim & Hwang appeared lowly because the inflexibility of backbone chain was insufficient in the case of them which were synthesized with HDI, but it was showed the value which is higher than H<sub>12</sub>MDI.<sup>5</sup> Therefore, it could be judged with because the attraction between molecules increased.

DSC thermograms for polyurethanes (H-1-121 and H<sub>12</sub>-2-132) are shown in Figure 7. In Figure 7, the thermal properties of polyurethanes as the glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) can be determined by each thermograms. Effects of hard segment contents on the  $T_g$  obtained from them are shown in Figure 8.



**Figure 7.** DSC thermograms for polyurethanes: (a) H-1-132 and (b) H<sub>12</sub>-2-121.



**Figure 8.** Relationship between hard segment content and  $T_g$  of SS.

As are shown in Figure 8, with increasing the hard segment contents of polyurethane,  $T_g$  of SS for the all HDI-based and H<sub>12</sub>MDI-based polyurethanes increased linearly. The  $T_g$  values of polyurethanes based H<sub>12</sub>MDI is generally low since the H<sub>12</sub>MDI which was the hexagon ring structures has been lower upright characteristic than the HDI which has a linear structure. The HDI forms the hard crystalline structure after it reacts with the BD as a chain extender. On the other hand, the decomposition of H<sub>12</sub>MDI is quickly advanced, because the compounds of cis-trans, trans-trans and cis-cis isomer which are attained the configuration of the chair form and the boat form are not crystallized easily. As the hard segment contents of polyurethane went up, the high  $T_g$  values appeared. This could be due to crystallization of the hard segment as stronger interaction among polymer chains.

## Conclusions

Pyrolysis of polyurethane synthesized with polycaprolactone diol and diisocyanate has been successfully analyzed by adopting the Friedman method in TGA. The activation energy was distributed in the range from 19 to 52 kJ/mol by the effect on the kinds of diisocyanate and the contents of hard segment. Specially, thermostability of all the HDI-based and H<sub>12</sub>MDI-based polyurethane tends to improve, with increasing the hard segment contents.

Also, the glass transition temperature ( $T_g$ ) of polyurethanes by DSC thermograms could be investigated. With increasing the hard segment contents as stronger interaction among polymer chains,  $T_g$  for the all polyurethanes based HDI and H<sub>12</sub>MDI were increased. The  $T_g$  values of polyure-

thane based with HDI which formed easily the hard crystalline structure were, generally, higher than those based with H<sub>12</sub>MDI because of the configuration of the chair and boat form.

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