

# Thermal Degradation of Film Cast from Aqueous Polyurethane Dispersions

M. G. LU,<sup>1</sup> J. Y. LEE,<sup>2</sup> M. J. SHIM,<sup>3</sup> S. W. KIM<sup>1</sup>

<sup>1</sup> Department of Chemical Engineering, The University of Seoul, Seoul 130-743, Korea

<sup>2</sup> Technical Research Center, Han Yang Petrochemical Co., Ltd., Kyungki-Do 425-110, Korea

<sup>3</sup> Department of Life Science, The University of Seoul, Seoul 130-743, Korea

Received 19 July 2001; accepted 20 December 2001

**ABSTRACT:** In this paper, water-dispersible polyurethanes based on isophorone diisocyanate and polytetramethylene glycol were synthesized, and their thermal degradation behavior under nitrogen and air was studied by thermogravimetric (TG) analysis. The influence of NCO/OH ratio and functional group concentration was discussed. The thermal decomposition kinetics under nonisothermal conditions was analyzed using Ozawa method. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2552–2558, 2002

**Key words:** water-dispersible polyurethanes; isophorone diisocyanate; polytetramethylene glycol; thermal degradation; thermogravimetric analysis

## INTRODUCTION

For over 40 years, water-borne or water-based polyurethanes have been known, and the performance properties of these systems have been improved continuously with literally hundreds of papers and patents being issued during this period in the field of water-based polyurethanes.<sup>1–3</sup> There are at least three important reasons why aqueous polyurethanes (APUs) have become commercial important in the last few years. The first reason is environment concerns regarding (solvent) volatile organic compounds (VOC) being issued into the atmosphere and causing ozone depletion, acid rain, and possibly a imbalance of the earth's ecosphere. The second reason is eco-

nomics—organic solvent systems are expensive and aqueous polyurethanes do not bear the extra solvent cost. The third, and perhaps most important, reason related to the fact that the performance of aqueous polyurethanes have been improved to the point that they are comparable to or better than the conventional solvent-based polyurethanes for many specific applications.

A water-borne polyurethane dispersion can be defined as a binary colloidal system in which polyurethane particles are dispersed in a continuous aqueous medium.<sup>4</sup> APUs are usually prepared as a low molecular weight NCO-terminated prepolymer for ease of dispersion. Then, diamines are generally used to increase the molecular weight by reaction with the terminated NCO end groups (chain extension).<sup>5</sup> The presence of ionic species in APUs has a considerable effect on the physical properties.<sup>6</sup> Polyurethane ionomers are now one of the most rapid developing and active branches of polyurethane chemistry.

The degradation of thermoplastic polyurethanes has been extensively studied, and a num-

---

Correspondence to: S. W. Kim (swkim@uos.ac.kr).

Contract grant sponsor: Technological Innovation Development Business for SMEs, in Korea.

Contract grant sponsor: Han Yang Petrochemical Co., Ltd., in Korea.

*Journal of Applied Polymer Science*, Vol. 85, 2552–2558 (2002)  
© 2002 Wiley Periodicals, Inc.

ber of reviews are available.<sup>7,8</sup> Thermal degradations of ester- and ether-based thermoplastic polyurethanes are performed under vacuum, air, and nitrogen, allowing investigators to determine the mode of degradation.<sup>9–11</sup> Polyester-based thermoplastic polyurethanes exhibit rapid degradation in air and nitrogen, indicating that a non-oxidative mechanism is involved. In contrast, the significantly improved thermal stability of ether-based polyurethanes under vacuum and nitrogen indicates that the oxidative process plays a major role in the decomposition of ether-based thermoplastic polyurethanes. In general, the ester-based polyurethanes normally exhibit better thermal and oxidative stabilities than the ether-based ones.

The mechanism of thermal degradation of polyurethanes is very complex due to the variety of products formed. It is proposed that the thermal degradation of thermoplastic polyurethanes is primarily a depolycondensation process, which starts at about 250°C.<sup>12</sup> It presents a bimodal profile where the first mode is related to the hard segments, and polyurethane–urea is more stable than polyurethanes. Aqueous polyurethanes should exhibit some different features in thermal degradation due to their unique chain structure, for example, the salt-forming groups. Therefore, it is necessary to analyze their thermal degradation behavior to understand the structure–property relationship.

## EXPERIMENTAL

### Materials

Polytetramethylene glycol (PTMG,  $M_n = 2000$ , BASF, Inc.) was dried under vacuum before use. Dimethylol propionic acid (DMPA, Aldrich) was dried at 90°C. Triethylamine (TEA) was dried over 4 Å molecular sieves prior to use. Isophorone diisocyanate (IPDI, BASF, Inc.) and stannous octanoate (T-9, Air Products Co.) and the chain extender, ethylene diamine (EDA), were used as received.

### Preparation of Anionic Aqueous-Based Polyurethane Dispersions<sup>13</sup>

A reaction vessel equipped with a stirrer, condenser, nitrogen inlet, and thermometer was charged with 172.93 g of PTMG, 9.6 g of DMPA, 52.1 g of IPDI, and 20 g of N-methyl pyrrolone

(NMP). The amount of catalyst used was 0.02% based on the monomer weight. The reaction was carried out at a constant temperature. While stirring, the reactor was heated to 75°C until the desired extent of reaction was reached. The change of the NCO content during reaction was determined using a standard dibutylamine back-titration method (ASTM D1638). Then, the prepolymers were cooled to about 60°C, and 7.95 g of TEA and 12 g of NMP were added and stirred for another 30 min. The Polyurethane dispersions resulted from a high shear rate mixing of these prepolymers with a 400-mL aqueous solution of EDA (4.55 g). The final amino-terminated polyurethane dispersions had about 35% solids contents and pH 8.0 to 9.0.

### Film Preparation

Films were prepared by casting the aqueous dispersions on silicone-coated surfaces and allowed them to dry at room temperature for one week, and then at 60°C for another 12 h. After demolding, the films were kept into a desiccator to avoid moisture.

### Measurements

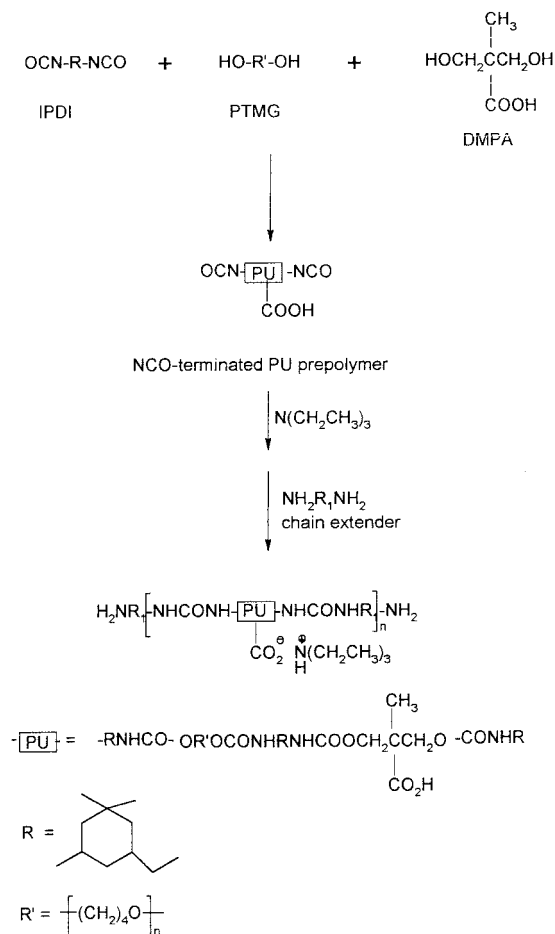
IR spectra of neat and films during thermal degradation were recorded using a MOMEM MB Series Fourier transform infrared (FTIR) spectrometer. The specimen films on KBr disks were put in an air oven at each specified temperature for various time periods to undergo thermal degradation. They are then removed from the oven and subjected to FTIR analysis at a 4 cm<sup>-1</sup> resolution in the mid-IR range, from 4000 to 600 cm<sup>-1</sup>.

The thermal stability and kinetics of degradation of APU films were carried out using a Setaram TG/DTG 92 simultaneous thermogravimetric/differential thermal analyzer from room temperature to 700°C at different heating rates from 5 to 30 K/min under air and nitrogen at a flow rate of 50 mL/min. The sample weights are 5–15 mg in all cases.

## RESULTS AND DISCUSSION

### Formation of Aqueous Polyurethane Prepolymers and Films

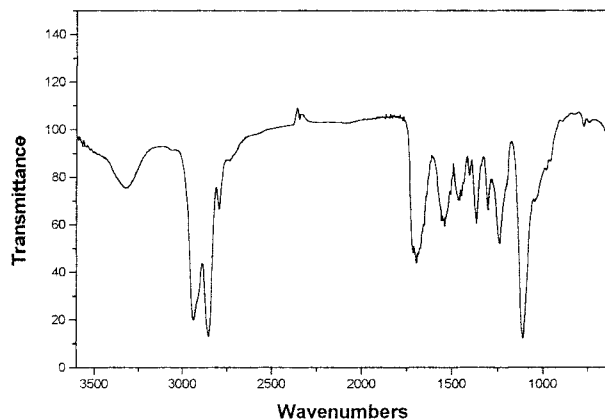
The physical properties of the polyurethane films depend on the molecular structure; they also depend on the content of functional groups. The



**Figure 1** Preparation of water-based polyurethane dispersions.

isocyanate used in work was IPDI, which has good thermal stability, low vapor pressure, low toxicity, and relatively high stability. DMPA, a carboxylic group containing diol, can be used to form water-dispersable urethane prepolymer without any significant reaction between the carboxylic group and isocyanate group because the hydroxyl group is much more reactive relative to aliphatic isocyanate component.

The reaction scheme for the prepolymer preparation and the processes of dispersion and chain extension is given in Figure 1. Almost all of the infrared research on polyurethane has been focused on two principle vibrational regions: the N—H stretching vibration ( $3200\text{--}3500\text{ cm}^{-1}$ ), and the C=O stretching vibration ( $1700\text{--}1730\text{ cm}^{-1}$ ). In Figure 2, the infrared spectrum of the aqueous polyurethane film shows a carbonyl stretching of carboxylic group at  $1708\text{ cm}^{-1}$ , an amide I band (urethane and urea carbonyl

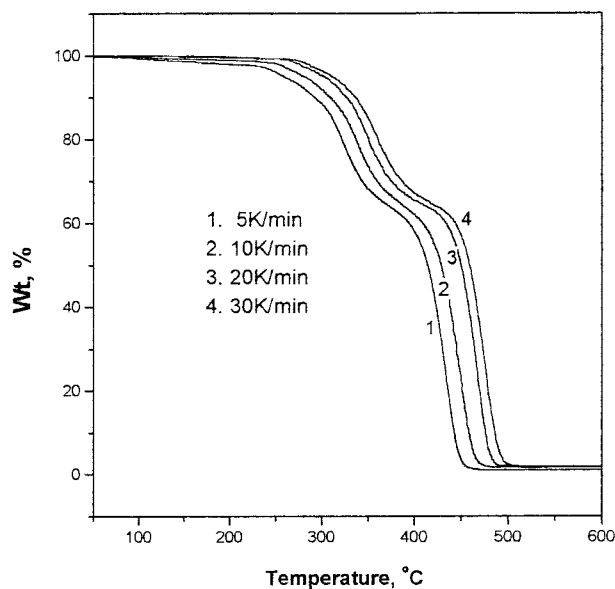


**Figure 2** Infrared spectra of APU54.

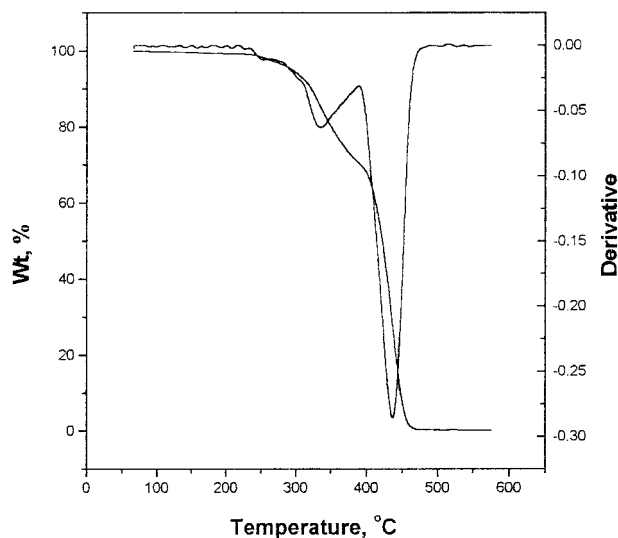
stretching vibrations) at  $1645\text{ cm}^{-1}$ , and an amide II band (N—H bending vibrations) at  $1553\text{ cm}^{-1}$ . The N—H stretching vibration is at  $3320\text{ cm}^{-1}$ . The hardness of films was increased with increasing the ratio of NCO/OH and DMPA content as expected due to the increased hard segment content.

### Thermal Degradation

A number of experimental indices are often used to characterize the process of thermal decomposition, including what follows:



**Figure 3** TG thermograms of APU56 at different heating rates under nitrogen.



**Figure 4** TG and DTG curves of APU54 at 10 K/min under nitrogen.

1. The temperature of initial decomposition ( $T_{d,onset}$ ). This is the temperature at which the loss of weight during heating is just measurable (inclination point of the loss of weight/temperature curve).
2. The temperature of half-decomposition ( $T_{d,1/2}$ ). This is the temperature at which the loss of weight during heating reaches 50% of its final value.
3. The temperature of the maximum rate of decomposition ( $T_{d,max}$ ), measured as the rate of loss of weight (at a standardized rate of temperature increase).
4. The average energy of activation ( $E_d$ ), determined from the temperature dependence of the rate of loss of weight.

These indices, especially the characteristic temperatures, are dependent on the heating rate

applied during the pyrolysis. Typical TG curves for the thermal degradation of APU films under nitrogen are shown in Figures 3 and 4. The TG thermograms in Figure 3 shifted to higher temperatures as the heating rate increases from 5 to 30°C/min. The shift of onset to higher temperature with increasing heating rate is due to the shorter time required for a sample to reach a given temperature at the faster heating rates. The initial decomposition temperature  $T_{d,onset}$ , the temperature of half-decomposition  $T_{d,1/2}$ , and the temperature of the maximum rate of decomposition  $T_{d,max}$  for different samples at heating rate of 10°C/min are listed in Table I.

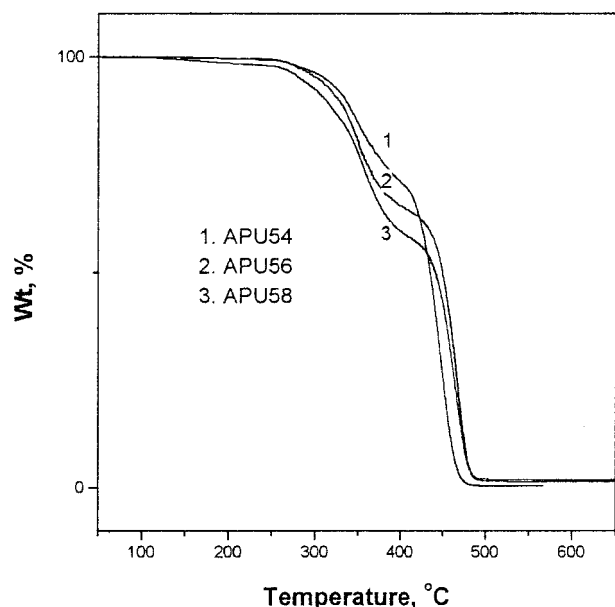
It has been reported that the pyrolysis product for PTMG-based polyurethane in the first stage of thermal decomposition is mainly carbon dioxide, whereas the main gas product in the second stage is butyl ether.<sup>14</sup> It is said that the early stage degradation occurred mainly in the hard segments for the polyether-type polyurethanes. Grassie et al. studied the thermal degradation of polyurethane and proposed a detailed mechanism—that is, urethane groups first undergo depolymerization, resulting in individual monomers, which then further react to produce carbon dioxide.<sup>15</sup> So we believe that there are also two stages in thermal degradation of APUs: the first stage is caused by the degradation of hard segments; and the degradation of soft PTMG segments is responsible for the second stage.

The above hypothesis is in good agreement with the results observed in our experiments. Figures 3 and 4 show clearly that there are two different degradation steps involved. The second stage begins at about 400°C in all cases although little difference can be observed, which probably results from the molecular weight, particle size, etc. The reaction during this stage is indeed caused by the degradation of polyether segments,

**Table I** The Characteristic Temperatures of APUs at Heating Rate of 10 K/min

Sample	$T_{d,onset}$ (°C)		$T_{d,1/2}$ (°C)		$T_{d,max}$ (°C) <sup>a</sup>	
	N <sub>2</sub>	Air	N <sub>2</sub>	Air	N <sub>2</sub>	Air
APU36	283.6	164	413.9	322	347.1, 436.8	266, 341, 471
APU54	297.2	167	421.9	314	334.6, 436.3	216, 269, 330, 479
APU56	260.0	163	426.6	308	337.6, 448.3	198, 277, 350, 481
APU58	260.4	161	409.7	304	356.0, 445.6	199, 258, 349, 472
APU86	243.9	155	411.8	295	336.6, 438.8	251, 320, 475

<sup>a</sup> The temperatures at different peaks.



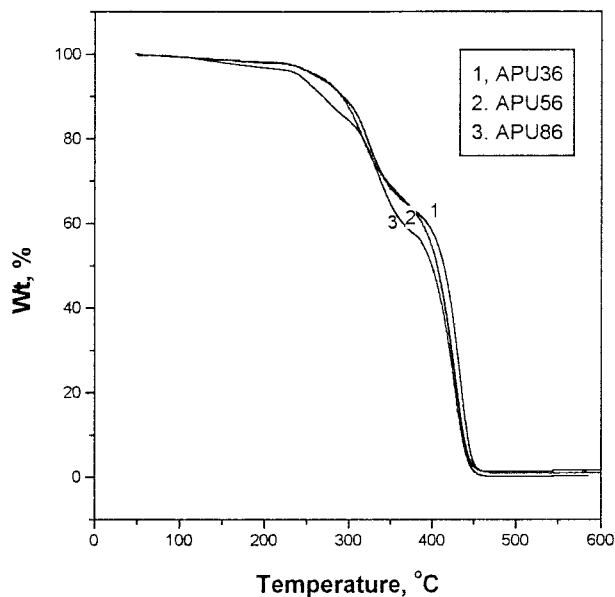
**Figure 5** Influence of NCO/OH ratio on thermal degradation of APUs.

which was seldom affected by the chemical composition and structure of polyurethane. In other words, the polyurethane structure only changes the decomposition process in the first stage, or the degradation of hard segments. The different degradation stages can be more clearly described by the behavior of differential weight loss (DTG) curves as showed in Figure 4, where two peaks were observed. The same results can be found for other samples.

The influence of NCO/OH ratio on thermal stability under nitrogen is given in Figure 5. As can be found, high weight loss was observed for samples with high NCO/OH ratio since it contains high hard segment contents.

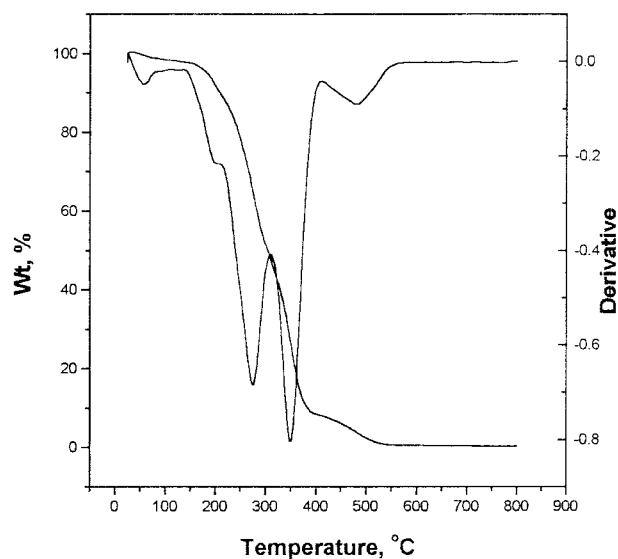
Figure 6 shows the effect of DMPA content. It is clear that the functional monomer decreases the thermal stability under nitrogen of resulted polyurethane film. Although the detailed mechanism is absent, it is possible to associated with the presence of tertiary carbon atom connected with carboxyl group. It is commonly accepted that the tertiary carbon is more easily attacked by organic radical to form new active species.<sup>15</sup>

Figure 7 shows the TG and DTG curves of APU56 conducted under air atmosphere. Similar results can be observed for other samples. The TG curves with a shoulder at about 10% of weight were different from those obtained under nitrogen. Under air atmosphere, the thermal degrada-



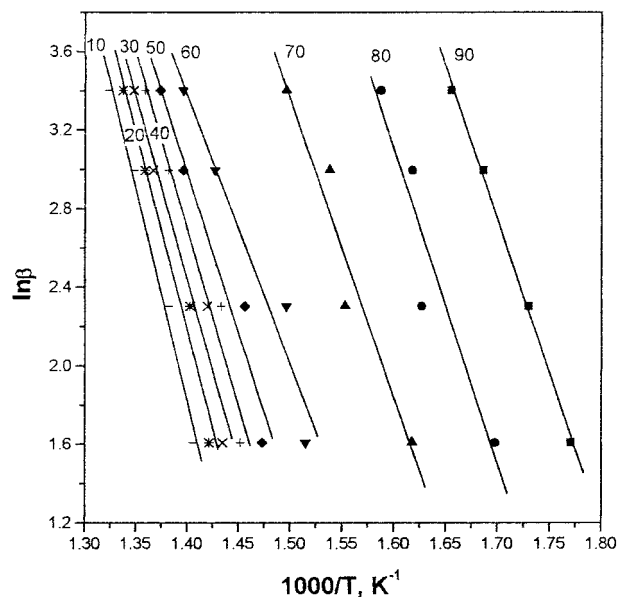
**Figure 6** TG thermograms of samples containing 6% of DMPA at 5 K/min.

tion started from a lower temperature and was more complex. The peaks in DTG curve can be considered as evidence. The curve showed clearly that there are different stages of degradation that are sometimes not perceptible in TG thermograms, giving the close relation and mutual influence between degradation process of hard and soft segments in oxidation conditions. The final decomposition stage that was absent under nitro-



**Figure 7** TG and DTG curves of APU56 at 10 K/min under air.





**Figure 8** Osawa plots for APU 36 at different conversions.

gen perhaps was from the predominant crosslinking reactions, as compared with chain scission reactions in the course of heating under nitrogen. Crosslinking reactions are believed to be accompanied with chain scission reactions for many polymers during heating in air through a free-radical mechanism. Shieh et al. reported the degradation process of a thermoplastic polyurethane elastomer based on 4,4'-diphenylmethane diisocyanate (MDI) and polyester polyol, which has almost same initial decomposition temperatures under both air and nitrogen.<sup>16</sup> Therefore, we believe that, as was the case with the thermoplastic polyurethanes, the oxidation process is indeed important in the thermal degradation of APUs under air atmosphere.

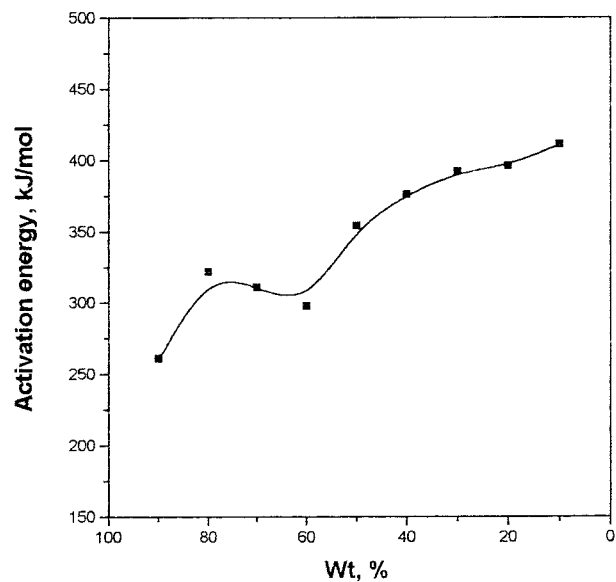
### Kinetic Analysis

Random thermal degradation can usually be described as a first-order reaction (loss of weight as a parameter) if the decomposition products are volatile. Although several methods for calculating kinetic parameters are reviewed in our previous work, it is commonly believed that nonisothermal methods can describe thermal degradation process better.<sup>17</sup> Here, the degradation kinetics of APUs under nitrogen were analyzed by using Osawa expression, which can be used to describe the influence of conversion on activation energy.<sup>18</sup>

**Table II** Activation Energy Values from Osawa Method

Wt (%)	Activation Energy, kJ/mol				
	APU36	APU54	APU56	APU58	APU86
90	282	348	261	261	262
80	293	353	322	337	289
70	276	429	311	311	278
60	270	514	298	281	296
50	298	549	354	342	336
40	326	573	376	357	354
30	337	584	392	366	342
20	361	600	396	379	367
10	387	587	411	388	361

Figure 8 shows a typical Osawa plots. The activation energy values for APUs are given in Table II. As can be seen, the values decrease with increasing DMPA content and NCO/OH ratio, consistent with the results from TG thermograms. It is observed that the high DMPA and NCO/OH make the thermal degradation easier; the dependence of activation energy on conversion is given in Figure 9. In the first stage of degradation resulting from the hard segment decomposition, the activation energy value increased gradually with the decrease of W%. This implies that there are different reactive species involved during this stage. It is because the hard



**Figure 9** The dependence of thermal degradation activation energy on conversion of APU56.

segments contain different chemical bonds. For example, urea is more stable than urethane linkages. The second stage of degradation has high activation energy values and remains practically constant, which is caused by the polyether degradation.

## CONCLUSIONS

The thermal degradation experiments herein show that the ratio of NCO/OH and DMPA content will decrease the thermal stability of aqueous-borne polyurethanes. The thermal decomposition consists of two stages, which result from degradation of hard and soft segments, respectively. An oxidation process plays an important role during the thermal degradation of this polyether-based polyurethane. Therefore, under air atmosphere, the thermal degradation was much easier than under nitrogen. The activation energy for degradation of polyurethane was not a constant throughout the whole process, and also contained different periods, corresponding to the degradation stages.

This work was supported by Technological Innovation Development Business for SMEs (2001) and Han Yang Petrochemical Co., Ltd. in Korea.

## REFERENCES

1. Dieterich, D. *Prog Org Coat* 1981, 9, 281.
2. Frisch, K. C.; Klempner, D. *Adv Urethane Sci Technol* 1987, 10, 121.
3. Ruscall, R.; Corner, T.; Stageman, J. F. *Polymer Colloids*; Elsevier: New York, 1985.
4. Dieterich, D. *Angew Chem Int Eng Ed* 1970, 9, 40.
5. Oertel, G. *Polyurethane Handbook*, 2nd ed.; Carl Hanser Verlag: Munich, 1993.
6. Lorenz, O.; Hugo, H. *Angew Makromol Chem* 1978, 72, 115.
7. Tarakanov, O. G.; Orlov, V. A.; Beliakov, V. K. *J Polym Sci Part C* 1968, 23, 193.
8. Engel, J. H.; Reegen, S. L.; Weiss, P. *J Appl Polym Sci* 1967, 7, 1679.
9. Tarakanov, O. G.; Orlov, V. A.; Beliakov, V. K. *J Polym Sci Part C* 1968, 23, 117.
10. Madorsky, S. L.; Straus, S. *J Polym Sci* 1959, 36, 183.
11. Dulog, L.; Storck, G. *Makromol Chem* 1966, 91, 50.
12. Grassie, N.; Zulfqar, M. *J Polym Sci* 1978, 16, 1563.
13. Houston, D. J.; Williams, G.; Satguru, R.; Padget, J. D.; Pears, D. *J Appl Polym Sci* 1998, 67, 1437.
14. Chang, T. C.; Chiu, Y. S.; Chen, H. B.; Ho, S. Y. *Polym Degrad Stab* 1995, 47, 375.
15. Grassie, N.; Scott, G. *Polymer Degradation and Stability*; Cambridge University: Cambridge, 1985.
16. Shieh, Y. T.; Chen, H. T.; Liu, K. H.; Twu, Y. K. *J Polym Sci Part A: Polym Chem* 1999, 37, 4126.
17. M. G.; Lu, M. J.; Shim, Kim, S. W. *J Appl Polym Sci* 2000, 75, 1514.
18. Osawa, T. *J Therm Anal* 1970, 2, 301.