

# Effects of NCO/OH Ratio and Catalyst Concentration on Structure, Thermal Stability, and Crosslink Density of Poly(urethane-isocyanurate)

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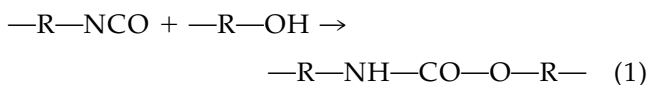
**ABSTRACT:** Poly(urethane-isocyanurate)s were synthesized by reacting toluene diisocyanate and poly(propylene glycol) with various stoichiometric ratios (1–3) in the presence of different concentrations of dibutyltin dilaurate (DBTDL) and ferric acetylacetonate (FeAA). The influence of the NCO/OH ratio and the catalyst type and concentration on the extent of urethane and isocyanurate formation were examined using Fourier transform IR spectroscopy. No trimer formation was observed in the presence of the FeAA catalyst. The percentage of the trimer group and the trimer/urethane content were found to be increased with increasing the stoichiometric ratio or DBTDL concentration. The thermal decomposition of the copolyurethanes in an inert atmosphere was studied by means of thermogravimetry (TG). The TG curves showed three decomposition steps with the principal degradation temperature at about 355–385°C. The

effects of the NCO/OH ratio, catalyst type and concentration, and heating rate on the thermal stability of the copolyurethanes were determined. The Flynn–Wall, Kissinger, and Ozawa methods were used to calculate the activation energies of thermal decomposition. The swelling behavior of solid copolyurethanes in toluene showed that, as the DBTDL concentration and/or NCO/OH ratio increased, the swelling ratio and average molecular weight between crosslinks were decreased whereas the crosslink density was increased. The sol fraction of solid copolyurethanes was examined and found to be reduced when the percentage of DBTDL or the stoichiometric ratio was raised. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 963–972, 2003

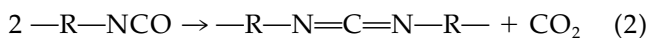
**Key words:** polyurethanes; isocyanurate; organometallic catalysts; Fourier transform IR; thermogravimetric analysis

## INTRODUCTION

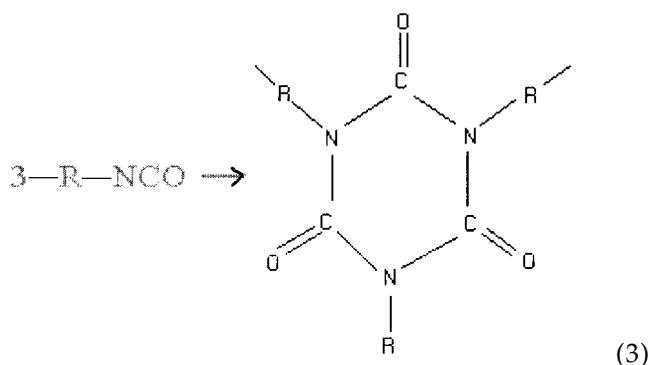
Polyurethanes (PUs) are used in a wide range of industrial applications such as foams, adhesives, and elastomers.<sup>1,2</sup> Although these polymers provide good mechanical properties, they are not generally suitable for the applications that require heat resistance because of the low thermal stability of the urethane groups. In order to increase their thermal stability, PUs could be modified by substituting some of the urethane groups with more heat-resistant heterocyclic groups such as isocyanurate rings in the polymer chain. The reactions that lead to the formation of urethane and isocyanurate structures are described by the following expressions for urethane formation:



carbodiimide formation:



and isocyanurate formation:



Various catalysts, including organometallic compounds, accelerate the formation of urethane. Some of them can also catalyze the trimerization reaction if an excess amount of isocyanate is present. In both cases the catalysis operates through formation of transient complexes between the catalyst and isocyanate.<sup>1,2</sup> The trimerization of isocyanate groups shown in reaction (3) results in crosslinking and formation of a polymer network. Therefore, the isocyanurate-modified PU that is sometimes called poly(urethane-isocyanurate) or PUIR has greater thermal stability, improved fire resistance, and higher dimensional stability than conventional PU.<sup>3,4</sup>

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TABLE I  
Chemicals Used for Synthesis of PUIRs

Materials	Specifications	Supplier
Toluene diisocyanate (TDI)	Molecular weight: 174.16 g/mol Purity: 99.67% Equivalent weight: 87.37 g Percent of NCO: 48.09% Isomer ratio: $\frac{2,4\text{-TDI}}{2,6\text{-TDI}} = \frac{80}{20}$	Merck (Germany)
Poly(propylene glycol)	Molecular weight: 2000 g/mol Purity: >99% Hydroxyl no.: $55 \frac{\text{mg KOH}}{\text{g}}$ Equivalent weight: 1020 g	Fluka (Switzerland)
Ferric acetylacetonate	Molecular weight: 353.18 g/mol Purity: >99%	Merck (Germany)
Dibutyltin dilaurate	Appearance: red-colored powder Molecular weight: 631.56 g/mol Purity: >99% Appearance: yellowish viscous liquid	Merck (Germany)

Since polymers containing too few isocyanurate rings do not possess the desired properties and those containing too many isocyanurate rings are brittle and friable, it is necessary to evaluate and control the amount of trimer groups formed. Hence, comprehensive knowledge of the effects of several parameters such as the stoichiometric ratio, type and concentration of catalyst, and reaction temperature on the relative amounts of trimer and urethane groups is vital to obtain optimum properties. Several studies have examined the effects of trimerization and crosslinking on the physical and mechanical properties of copolyurethane networks.<sup>3-12</sup> Although some of these studies have focused on the thermal properties and effects of crosslinking on the swelling behavior and sol/gel fraction of PUIRs, there have been few fundamental studies on PUIRs with a base of toluene diisocyanate (TDI) and poly(propylene glycol) (PPG).<sup>13,14</sup>

In this article, the catalyzed synthesis of PUIRs on bases of TDI and PPG in the presence of the organometallic catalysts dibutyltin dilaurate (DBTDL) and ferric acetylacetonate (FeAA) is studied. The extent of urethane and isocyanurate formation at different NCO/OH ratios and catalyst concentrations is evaluated using Fourier transform IR (FTIR) analysis. The thermal behavior of the copolyurethanes is discussed and the activation energy of thermal degradation is calculated from three different methods. The effects of trimerization and crosslinking on the thermal stability, swelling behavior, and sol fraction of the PUIRs are also characterized.

## EXPERIMENTAL

### Materials

The specifications and sources of chemicals used for the synthesis of PUIRs are given in Table I. The purity

and percent NCO of TDI and the hydroxyl number of PPG were determined according to ASTM D 5155 and ASTM D 4274, respectively.<sup>15,16</sup> The DBTDL and FeAA catalysts were used without any prior treatment.

### Synthesis of PUIRs

All the reactions were carried out in a 250-mL three-necked round-bottom glass reactor at isothermal conditions in a bath. The reactor was equipped with a mechanical stirrer and a nitrogen inlet. In the first step, 50.0 g of PPG ( $[\text{OH}]_0 = 0.9427 \text{ mol/L}$ ) was mixed properly with a calculated quantity of catalyst (DBTDL or FeAA) for about 20 min. Then, TDI was added dropwise in order to maintain a certain NCO/OH ratio. The reaction was followed under nitrogen purging at a mixing rate of 200 rpm until a visible viscosity change was observed; otherwise, it was continued for 30 min. The curing was allowed to proceed in a closed bottle at the same temperature for 24 h in an oven and then at room temperature for 1 week. Identical experiments were carried out with changes in the catalyst concentration, NCO/OH ratio, and reaction temperature. The reaction conditions of the synthesized PUIRs and their physical states are given in Table II.

### FTIR spectroscopy

The FTIR analysis of the PUIRs was performed on a Bruker IFS-48 spectrophotometer in the mid-IR range from 4000 to 400  $\text{cm}^{-1}$  and with a resolution of 4  $\text{cm}^{-1}$  using KBr pellets. An isocyanurate ring was detected by an absorption peak at 1410  $\text{cm}^{-1}$ ; the urethane group was characterized by the summation of the absorption bands at 3350, 1730, 1530, and 1230  $\text{cm}^{-1}$

TABLE II  
Specifications of Synthesized Copolyurethanes

Sample	$r$ (NCO/OH)	Catalyst Concentration <sup>a</sup> (wt %)	Reaction Temp. (°C)	Appearance
A	1	1	50	Viscous liquid, colorless
B	2	1	50	Rubber-like, yellowish
C	3	1	50	Rubber-like, yellowish
D	2	2	50	Rubber-like, yellowish
E	2	3	50	Rubber-like, yellowish
F	3	2	50	Rubber-like, yellowish
G	3	3	50	Rubber-like, yellowish
J	0.85	$5 \times 10^{-6} \frac{\text{mol}^b}{\text{g PU}}$	72	Viscous liquid, colorless
K <sup>a</sup>	0.85	$5 \times 10^{-6} \frac{\text{mol}^c}{\text{g PU}}$	72	Viscous liquid, red colored
L	3	0	50	Viscous liquid, colorless
M	2	1	70	Rubber-like, yellowish
N <sup>a</sup>	3	3	50	Viscous liquid, red colored

<sup>a</sup> All of the samples except K, L, and N are catalyzed with DBTDL. Samples K and N are catalyzed with FeAA.

<sup>b</sup> 0.316 wt %.

<sup>c</sup> 0.177 wt %.

$(A_{3350} + A_{1730} + A_{1530} + A_{1230} = A_U)^{2,4,12}$  Although an absolute estimation of isocyanurate formation is not possible, because no calibration curve could be built to use the Lambert–Beer law, it is possible, however, to obtain comparative results by using the absorbance ratios of the trimer to the urethane group or to the sum of the total functional groups in the structure of PUIR. Despite the fact that this ratio merely provides comparative results, it is nevertheless an index of the quantity of isocyanurate formed.<sup>2,4,5</sup> The use of absorbance ratios, on the other hand, makes the quantitative analysis independent of the optical paths of different samples.

#### Thermogravimetric analysis (TGA)

A Du Pont 951 TG analyzer was used, which was calibrated with calcium oxalate. About 50–100 mg of PUIR sample was used to obtain TG and derivative TG (DTG) profiles. The heating rates were 5, 10, 15, and 20°C/min under a nitrogen atmosphere at 30 to 700°C.

#### Density measurements

The densities of the solid PUIR samples ( $\rho_p$ ) were measured using a pycnometric method. The experimental accuracy of this method was about  $\pm 0.004 \text{ g/cm}^3$ .<sup>17</sup>

#### Swelling measurements

The swelling characteristics and crosslink densities of the PUIRS were measured by immersing the polymer specimens in toluene at room temperature (25°C).<sup>12,17</sup> In order to measure these properties, small blocks

(approximately  $1 \times 1 \times 0.5 \text{ cm}$ ) were weighed and immersed in toluene at room temperature for 72 h until swollen equilibrium was obtained. The specimens were then removed from the solvent, blotted, and weighed again. The swelling ratio ( $q$ ), which can be defined as the inverse of the equilibrium volume fraction of the polymer ( $V_p$ ) in the swollen networks, was calculated according to the following equations<sup>6,9</sup>:

$$Q = \frac{(w_1 - w_0)\rho_p}{w_0\rho_s} \quad (4)$$

$$q = 1 + Q = \frac{1}{V_p} \quad (5)$$

where  $w_0$  and  $w_1$  are the specimen weights before and after swelling, respectively, and  $\rho_s$  is the density of the solvent.

Under equilibrium-swollen conditions, the average molecular weight between crosslinks ( $M_c$ ) and the crosslink density ( $v_c$ ) of the PUIRS were calculated using the Flory–Rhener equation<sup>6,12,17</sup>:

$$M_c = \frac{\bar{v}_s \rho_p (V_p^{1/3} - V_p/2)}{\ln(1 - V_p) + V_p + \chi V_p^2} \quad (6)$$

and

$$v_c = \frac{\rho_p}{M_c} \quad (7)$$

In these equations,  $\bar{v}_s$  is the molar volume of solvent,  $\chi$  is the interaction parameter for the solvent–network system, which was calculated using the solubility parameters from the following equation<sup>14</sup>:

**TABLE III**  
Calculated Data from FTIR Analysis of Copolyurethanes

Sample	$\frac{A_{1410}}{\Sigma A}$ (mol %)	Theoretical		$\frac{A_{1454}}{A_{930}}$
		Trimer Content <sup>a</sup> (wt %)	$\frac{A_U^b}{\Sigma A}$ (mol %)	
A	0.00	0.00	23.67	1.397
B	5.18	3.51	21.48	1.654
C	7.25	6.55	19.87	1.391
D	5.30	3.51	21.28	1.435
E	5.96	3.51	22.02	1.439
J	0.00	—	22.40	1.319
K	0.00	—	22.28	1.303
L	0.00	6.55	20.94	1.323
M	4.67	3.51	17.35	1.680
N	0.00	6.55	21.39	1.433

<sup>a</sup> % isocyanurate =  $([\text{NCO}] - [\text{OH}]) / \text{total weight} \times 42 \times 100$ , used for  $r \geq 1$ .<sup>8</sup>

<sup>b</sup>  $A_U = A_{3350} + A_{1730} + A_{1530} + A_{1230}$ .

$$\chi = \beta + \frac{\bar{v}_s(\delta_p - \delta_s)^2}{RT} \quad (8)$$

where  $\beta$  is the lattice constant whose value is about 0.34 and  $\delta_p$  and  $\delta_s$  are the solubility parameters of the polymer and solvent, respectively. The value of  $\delta_p$  was considered to be  $9.467 \text{ (cal/cm}^3)^{1/2}$ , as estimated in our previous work for PUs with the base of TDI and PPG.<sup>18</sup>

### Sol fraction determination

The sol fractions of the PUIRs were determined by extraction of the soluble contents in chloroform.<sup>12,17</sup> The weighed amounts of samples were extracted in chloroform at room temperature for 72 h. Finally, they were filtered under a vacuum and the insoluble fraction was dried to constant weight in a vacuum at room temperature. The sol fraction was then calculated from the weight lost during solvent extraction of the network<sup>17</sup>:

$$\text{sol fraction} = \frac{w_i - w_f}{w_i} \quad (9)$$

where  $w_i$  and  $w_f$  are the weights of the specimen before and after extraction, respectively.

## RESULTS AND DISCUSSION

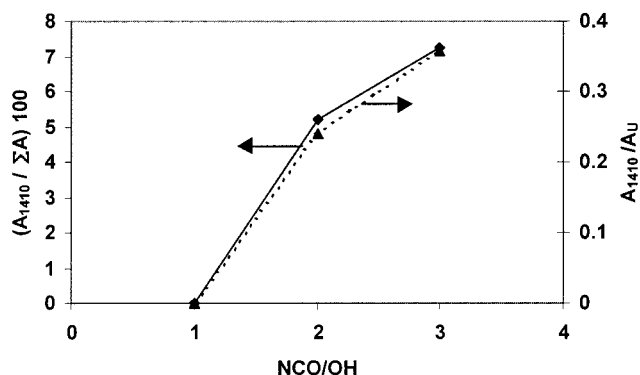
### FTIR analysis

Table III shows the results of the quantitative FTIR measurements of PUIR samples, for which the specifications are explained in Table II. It is revealed from the  $A_{1410}/\Sigma A$  ratios that, at the reaction condition used, the isocyanurate formation did not occur in samples A, J, and K with an  $r$  value equal to or less

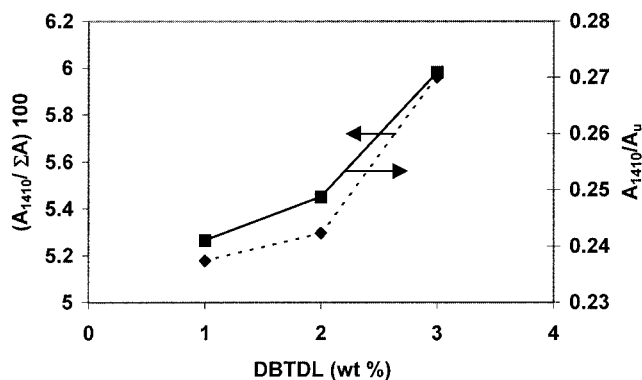
than unity nor in L and N in which no DBTDL was applied as catalyst. The use of 3 wt % FeAA catalyst in sample N did not lead to the formation of a trimer, even though the NCO/OH ratio was as high as 3. This may be explained by the low stability of the transient complexes formed between this catalyst and isocyanate. The theoretical values of the isocyanurate content are also given in Table III, considering the weight percentage of the excess of NCO groups not involved in urethane formation.<sup>8</sup> The contribution of the urethane groups, expressed by  $A_U/\Sigma A$  values, is maximum for sample A, in which a stoichiometric amount of NCO and OH was used in its synthesis. Samples A, J, K, L, and N, which have no trimer content, are in a viscous liquid state rather than an elastic solid (Table II) because no crosslinking is present in these polymers.

The effect of the NCO/OH ratio on trimer formation is shown in Figure 1 for samples A, B, and C with the same DBTDL concentration (1 wt %) but different stoichiometric ratios. The isocyanurate content increases with an increasing NCO/OH ratio, as expected because of the higher extent of cyclotrimerization. Figure 1 also compares the relative amount of isocyanurate rings to urethane groups for specimens A, B, and C, which were synthesized with different ratio values. The trimerization, rather than urethane formation, is enhanced as the NCO/OH ratio increases because of the higher concentration of isocyanate groups.<sup>4,12</sup>

The effect of the catalyst concentration on the trimer content of PUIRs was studied for samples B, D, and E, which were synthesized with an  $r$  value of 2 and with different DBTDL concentrations. As shown in Figure 2, the higher the DBTDL concentration, the higher the isocyanurate content in the PUIR. From this figure one can see that, for these polymers, the relative amount of trimer to urethane in the PUIR structure is also increased with increasing DBTDL concentrations. Hence, we conclude that DBTDL is more favorable to



**Figure 1** The effect of the stoichiometric ratio on the percent of trimer and trimer/urethane ratio for samples A, B, and C with 1 wt % DBTDL.



**Figure 2** The effect of the catalyst concentration on the percent of trimer and trimer/urethane ratio for samples B, D, and E that are synthesized at  $r = 2$ .

promote the trimerization reaction than urethane formation. It is also implied from this figure that the trimerization is more enhanced at a higher concentration of DBTDL.

The formation of allophanate and biuret, which leads to a branched structure, can be followed by the absorption band at  $1460\text{--}1450\text{ cm}^{-1}$ , which is assigned to their carbonyl group.<sup>2</sup> However, this is overlapped with absorbance related to  $\text{CH}_2$  bending of polyol at about  $1454\text{ cm}^{-1}$ . To distinguish these two peaks, we consider the absorption bands at  $1454$  and  $930\text{ cm}^{-1}$ . In a linear PU the former is merely attributed to  $\text{CH}_2$  bending and the latter is related to the etheric group of polyol.<sup>19</sup> For TDI-PPG based linear PUs, the  $A_{1454}/A_{930}$  ratio was shown<sup>20</sup> to be about 1.3–1.4. The excess  $A_{1454}/A_{930}$  ratio over this value in PUIR samples is probably attributed to the contribution of allophanate and/or biuret formation in the structure. Therefore, it can be found from the data in Table III that no allophanate/biuret linkage is formed in linear PUs J and K, which are synthesized with an  $r$  value of 0.85 and in the presence of a low concentration of catalyst, as we

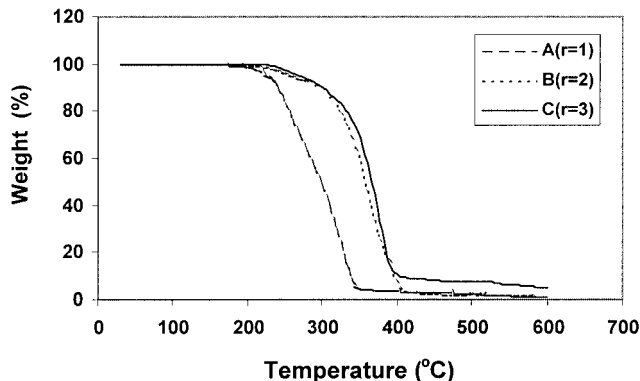
also reported in our earlier work.<sup>20</sup> However, a high level of these linkages is observed in samples B and M, which are both synthesized with the same ratio value and DBTDL concentration. It is thus implied that the maximum amount of allophanate/biuret is formed with an NCO/OH ratio of 2 and 1 wt % DBTDL. Further, the higher reaction temperature in the synthesis of sample M enhances allophanate/biuret formation rather than trimerization.

### TGA study

The thermal degradation behavior of urethane-derived polymers was studied in detail by numerous authors.<sup>3,7,8,10,13,21–24</sup> The mechanism of thermal decomposition of these polymers involves at least three overlapping steps, which are sometimes difficult to distinguish from TGA curves, but become more obvious from DTGA curves. According to this mechanism, the copolyurethane decomposition starts from  $180$  to  $200^\circ\text{C}$ , which is called the temperature of the onset of degradation ( $T_{\text{onset}}$ ). This is a simple depolymerization of the urethane bonds and it is intensified at  $260^\circ\text{C}$  to produce the starting materials (TDI and PPG) or some side products such as amines, olefines, and carbon dioxide.<sup>23</sup> Under an atmospheric pressure of inert gas ( $\text{N}_2$ ), the monomers volatilize slowly from the condensed phase, because of low diffusivity, and undergo a series of further secondary reactions. The PPG chain scission occurs at about  $370\text{--}380^\circ\text{C}$  and produces more volatile chain fragments and rearrangement products such as acetaldehyde and propionaldehyde.<sup>3</sup> The diisocyanate formed during the thermal decomposition may be dimerized to carbodiimide, which can in turn react with urethane groups to form a crosslinked structure. The final stage at about  $400\text{--}600^\circ\text{C}$  may be attributed to thermal decomposition of isocyanurate rings and carbodiimide linkages, which leads to the

**TABLE IV**  
TG Data from TGA and DTGA Curves of Copolyurethanes

Sample	Heating Rate ( $^\circ\text{C}/\text{min}$ )	$T_{\text{onset}}$ ( $^\circ\text{C}$ )	$T_{\text{max}1}$ ( $^\circ\text{C}$ )	$T_{\text{max}}$ ( $^\circ\text{C}$ )	$\left(\frac{dw}{dT}\right)_{\text{max}}$ (%/ $^\circ\text{C}$ )	$T_{\text{final}}$ ( $^\circ\text{C}$ )	Residue (%)
A	10	180	260	325	1.114	380–600	1.38
B	10	200	260	375	1.547	425	1.16
C	10	195	250	370	1.268	420–600	4.25
D	10	200	240	370	1.417	400–550	1.13
E	10	200	260	385	1.629	530	1.01
F	10	200	260	380	1.455	475	3.88
G	5	200	255	355	1.421	450–570	4.17
B	5	200	260	370	1.549	520	2.63
J	5	205	—	370	2.501	—	1.54
K	5	205	—	360	2.826	—	0.00
L	5	100	—	365	2.052	475	0.62
M	5	200	240	370	1.664	425–520	1.68
N	5	80	260	370	1.946	470	2.24



**Figure 3** The effect of the stoichiometric ratio on the thermal stability of samples A, B, and C that are synthesized with 1 wt % DBTDL.

production of  $\text{CO}_2$  and the formation of char in the solid state, which remained as residue.<sup>3,22,23</sup>

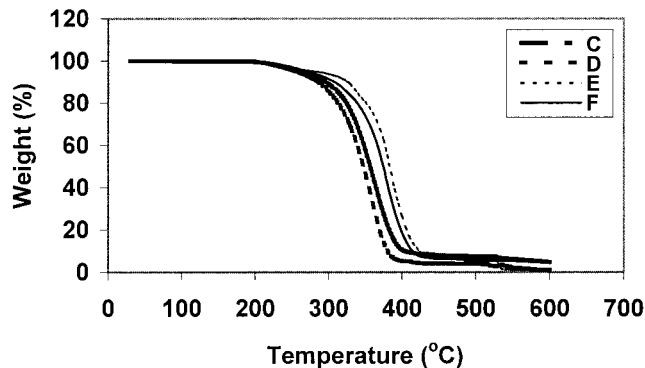
The thermal degradation behaviors of the PUIR samples are summarized in Table IV. In all samples, the  $T_{\text{onset}}$  is observed at about 200°C, where urethane linkages begin to degrade, except in samples L and N in which the weight loss starts at 100 and 80°C, respectively. This is due to the vaporization of unreacted TDI, because its presence was also confirmed through the FTIR spectra at 2270  $\text{cm}^{-1}$ .

No significant peak was observed at about 260°C ( $T_{\text{max1}}$ ) in the DTGA curves of samples J, K, and L (not shown). In samples J and K with a low NCO/OH ratio (high amount of PPG relative to TDI), the decomposition of urethane groups is probably overshadowed by the degradation of the bulk of PPG. In sample L, it seems to be attributed to the low content of urethane groups.

The principal degradation temperature ( $T_{\text{max}}$ ) in all PUIR samples is in the range of 355–385°C, which is related to PPG chain scission. The final degradation step occurs mainly from 400 to 550°C ( $T_{\text{final}}$ ), where isocyanurate rings and carbodiimides decompose.

A larger amount of residue is observed for samples C, F, and G, which were synthesized with an  $r$  value of 3 and in the presence of DBTDL, due to the extent of dimer and trimer formation.<sup>7</sup> The residue of sample K, which is synthesized with an  $r$  value of 0.85 and in the presence of FeAA catalyst, is zero, because of no trimer and/or carbodiimide formation.

The maximum rates of weight loss  $[(dw/dt)_{\text{max}}]$  occurring at  $T_{\text{max}}$  are also compared in Table IV. The liquid specimens J, K, and L, with linear structures, show the highest values, because diffusion of secondary side products, arising from PPG decomposition, can be easily achieved. Although sample A is not solid, however, because of the equal stoichiometry of NCO and OH in this specimen ( $r = 1$ ), which causes higher molecular weight and therefore higher viscosity, the rate of weight loss decelerates.



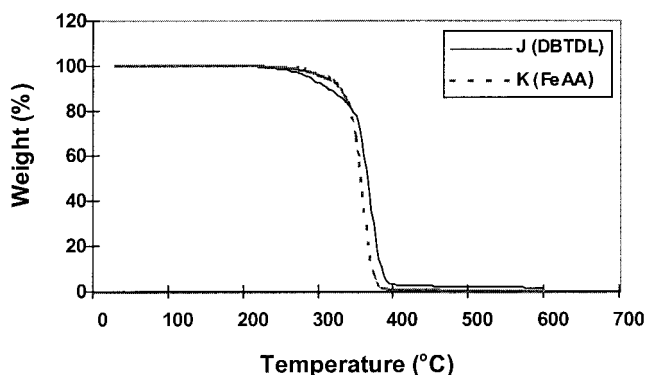
**Figure 4** The effect of the stoichiometric ratio and catalyst concentration on the thermal stability of PUIRs C ( $r = 3$ , 1% DBTDL), D ( $r = 2$ , 2% DBTDL), E ( $r = 2$ , 3% DBTDL), and F ( $r = 3$ , 2% DBTDL).

Figure 3 compares TGA curves of samples A, B, and C, to show the effect of the  $r$  value on the thermal stability of PUIRs. Sample A ( $r = 1$ ) shows lower thermal stability, as expected because of the absence of trimer groups in the structure. At greater ratio values, the thermal stability increases for specimens B and C. This is also confirmed in Figure 4, in which samples D ( $r = 2$ ) and F ( $r = 3$ ) with higher catalyst concentration (2%) are compared. Sample F is more thermally stable than the other, because of the greater extent of crosslinking, and leaves a larger amount of residue.

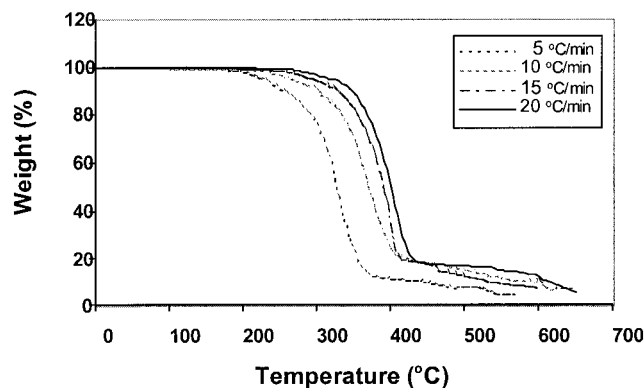
To study the effect of the DBTDL concentration, the TGA curves of samples D and E, and also C and F with the same ratio but different catalyst concentrations, are compared in Figure 4. As the catalyst is increased by 1%, a significant increase in thermal stability is observed.

The TGA curves of the J and K specimens (Fig. 5) are also remarkable. Although the DBTDL-catalyzed sample (J) starts to lose weight faster than the FeAA-catalyzed one, it is generally more thermally stable at a higher temperature and leaves some residue.

Figure 6 illustrates the influence of the rate of heating on the TGA curves of sample G. It can be implied



**Figure 5** The effect of the catalyst type on the thermal stability of samples J and K.



**Figure 6** The effect of the rate of heating on the TG curve of sample G.

that the gradual temperature rise (low heating rate) causes a slightly greater weight loss at a given temperature. This is generally expected as it was also obtained by other authors,<sup>22,24,25</sup> and can be justified from the heat transfer point of view.

The kinetics of the thermal decomposition of copolyurethanes was studied using TGA and DTGA data. The process can be expressed in terms of the degree of conversion, which is the weight loss at a given temperature/initial weight of the sample ( $\alpha$ ), according to following equation<sup>26–28</sup>:

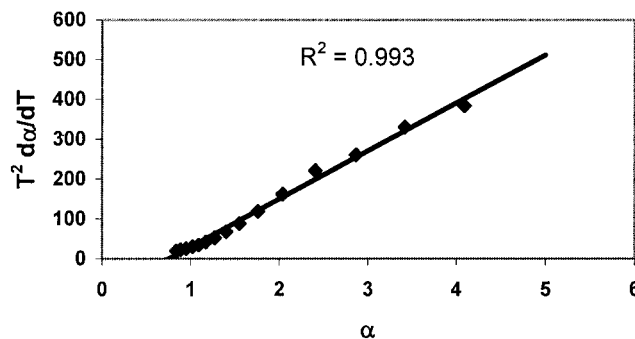
$$\frac{d\alpha}{dT} = \frac{A}{\phi} \exp(-E_a/RT)(1-\alpha)^n \quad (10)$$

where  $A$  is the frequency factor,  $\phi$  is the heating rate,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $n$  is the order of reaction. Several approaches have been developed to calculate the kinetic parameters of thermal degradation.<sup>22–31</sup> The values for the activation energies obtained by fitting the experimental data are dependent on the method of calculation.<sup>22,25,29–31</sup> In the present study, the Flynn–Wall, Kissinger, and Ozawa methods were used to evaluate the activation energy of thermal degradation for samples C, E, G, and N.<sup>26–28</sup>

The Flynn–Wall method gives the activation energy at the beginning of thermal decomposition and is fitted with better linear regression than the methods developed by Yang,<sup>29,30</sup> Coats–Redfern,<sup>26</sup> and Freeman–Carroll.<sup>26,27</sup> Using the Flynn–Wall method, the initial activation energy for decomposition at a heating rate of 10°C/min was calculated, as shown typically for sample G in Figure 7, from the slope of the plot of  $T^2(d\alpha/dT)$  versus  $\alpha$  in the range of  $0 < \alpha \leq 0.05$ . This is shown by the following relationship<sup>30</sup>:

$$E_a = (\text{slope} - 2\bar{T}) \times R \quad (11)$$

where  $T$  is the average temperature over the range in which the slope is measured. Good linear correlations



**Figure 7** The dependence of  $\alpha$  in the Flynn–Wall method for the evaluation of the initial activation energy ( $E_a$ ) for sample G.

were obtained for all four samples. The calculated  $E_a$  values from this method are given in Table V. It is implied from these results that the activation energy at the beginning of degradation is increased as the ratio value or DBTDL concentration in the synthesis of PUIR is increased. In addition, this  $E_a$  value is higher for the copolyurethane synthesized with DBTDL than that with FeAA.

The other two methods discussed here for calculation of the  $E_a$  value require several TGA curves at different heating rates. According to the Kissinger method,<sup>27</sup> the plot of  $\ln(\phi/T_{\max}^2)$  versus  $1/T_{\max}$  gave straight lines, as shown in Figure 8. The activation energies were calculated from the slope of straight lines ( $-E_a/R$ ) and are given in Table V.

The isoconversional method proposed by Ozawa is a more reliable method to evaluate the activation energy. Using this method,  $\log \phi$  was plotted versus  $1/T$  for various  $\alpha$  values between 0.1 and 0.9, and the  $E_a$  value at each value of conversion was calculated from the following equation<sup>22,25</sup>:

$$E_a = -\text{slope} \times R/0.4567 \quad (12)$$

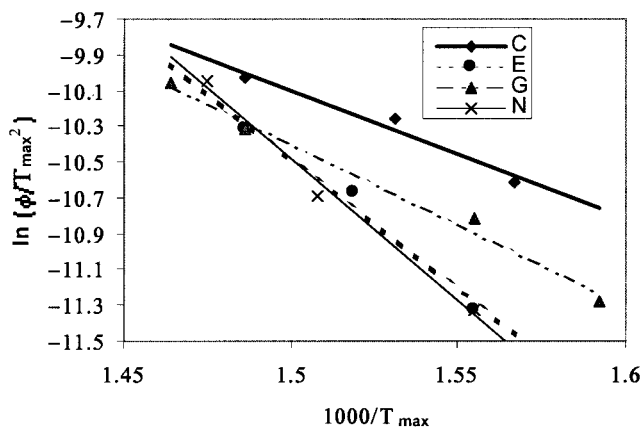
A representative result is shown in Figure 9 for the thermal decomposition of sample G. The changes of the activation energies of samples C, E, G, and N with the degree of conversion are shown in Figure 10. The

**TABLE V**  
Activation Energies ( $E_a$ ) Calculated from Different Methods for Thermal Decomposition of Copolyurethanes

Sample	$E_a$ (kJ/mol)		
	Flynn–Wall <sup>a</sup>	Kissinger	Ozawa <sup>b</sup>
C	71	59	51
E	81	144	127
G	92	71	87
N	56	87	88

<sup>a</sup> For 0–5% degradation at a heating rate of 10°C/min.

<sup>b</sup> Average value for 0–90% degradation.

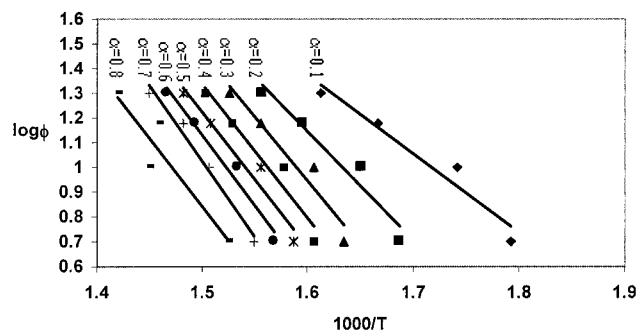


**Figure 8** The linear dependence of  $\ln(\phi/T_{\max}^2)$  on  $1/T_{\max}$  in the Kissinger method used for copolyurethanes.

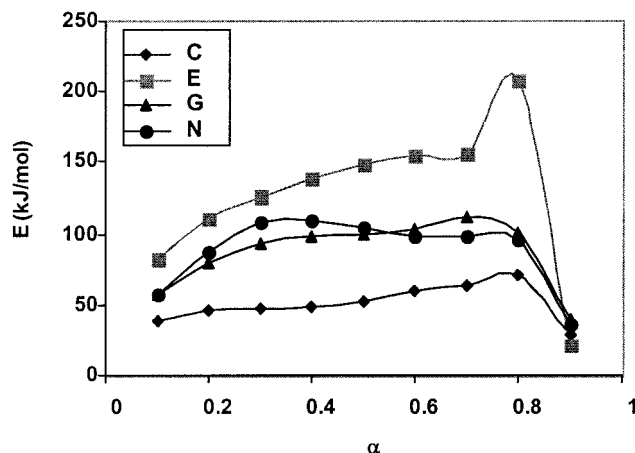
wide variation of  $E_a$  with  $\alpha$  is expected to be due to the continuous change of the degradation mechanism.<sup>22,25</sup> The average value of the activation energy calculated from the Ozawa method for the whole range of conversions (90%) are given in Table V. The results show that the  $E_a$  values calculated by the Kissinger and Ozawa methods are comparatively close to each other. However, this is not generally dependent on the thermal stability of the copolyurethane, suggesting the complexity of the thermal degradation of these polymers. This was concluded also by Chang et al.<sup>25</sup> and Ronaldo et al.<sup>31</sup> for other PU systems.

### Swelling studies

The swelling behavior of the solid PUIRs (samples B, D, E, C, F, and G, Table II) with NCO/OH ratios of 2 and 3 and with different DBTDL concentrations was investigated in toluene at room temperature. The measured values of the polymer densities were in the range of 0.907–0.927 g/cm<sup>3</sup>. The swelling ratios were then calculated using eqs. (4) and (5). Figure 11 indicates that the swelling ratio decreases with increasing catalyst concentration or with increasing ratio value, which is attributable to the higher degree of crosslink-



**Figure 9** The linear dependence of  $\log \phi$  on  $1000/T$  at different  $\alpha$  values in the Ozawa method used for sample G.

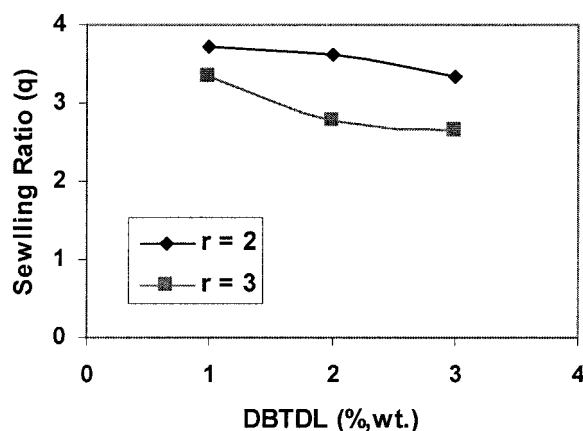


**Figure 10** The dependence of the activation energy calculated by the Ozawa method on the conversion for samples C, E, G, and N.

ing that restricts the swelling of the PUIR. Figure 12 shows the effect of the ratio value and catalyst concentration on the  $M_c$  value. The  $M_c$  values of the samples decrease as the percentage of DBTDL increases for a given NCO/OH ratio. The crosslink density that is inversely proportional to  $M_c$  is plotted against the catalyst concentration in Figure 13. It is observed that the crosslink density increases as the NCO/OH ratio or catalyst concentration are increased. This is attributed to the presence of more reactive NCO groups, which are promoted to participate into crosslinking reactions.<sup>6,12,30</sup>

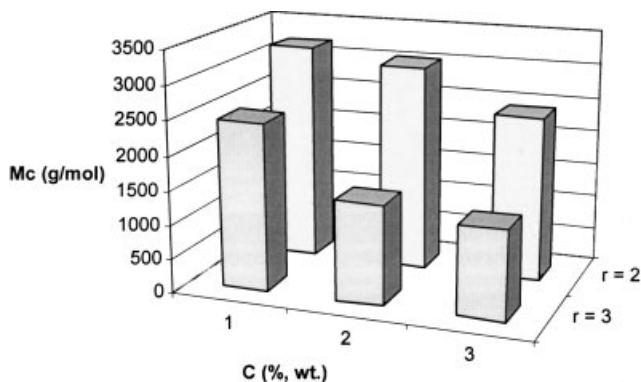
### Sol fraction

The soluble fractions of different PUIRs were extracted with chloroform. As shown in Figure 14, the percentage of sol gradually decreases with the increase of catalyst concentration or with the increase of the NCO/OH ratio. These results also agree with those obtained from swelling experiments. The solu-



**Figure 11** The effect of the catalyst concentration on the swelling ratio of solid PUIRs.





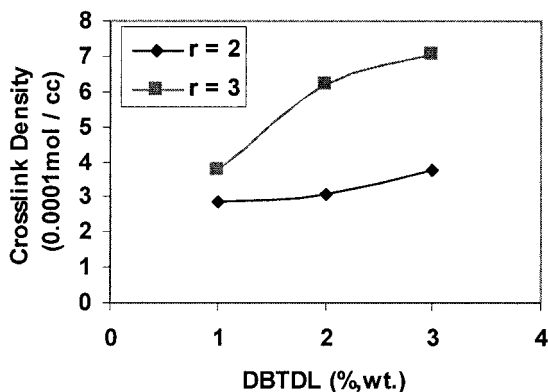
**Figure 12** The effect of the catalyst concentration and ratio value on the average molecular weight between crosslink points ( $M_c$ ) of solid PUIRS.

ble fractions may consist of the unreacted initial components or some low molecular weight chains entrapped in the network.<sup>9</sup> The presence of unreacted PPG in these samples was confirmed by absorption of OH groups at  $3440\text{ cm}^{-1}$ .

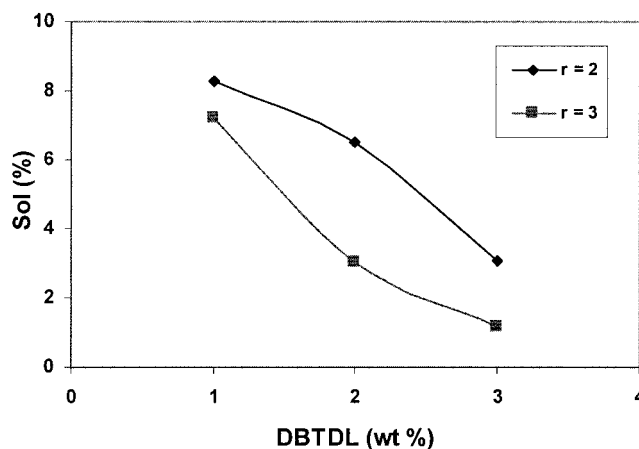
### CONCLUSIONS

The stoichiometric ratio and catalyst type and concentration have significant effects on the structure, thermal stability, swelling behavior, and crosslink density of PUIRS. FTIR analysis showed that, at the reaction conditions used, first, the trimer formation does not occur in the absence of catalyst or in the presence of FeAA, even though there is an excess amount of NCO. Second, in the presence of DBTDL, trimer is not formed if the  $r$  value is  $\leq 1$ . It is also found that the trimer content is increased with increasing NCO/OH ratio and/or DBTDL concentration, and trimerization is more enhanced at a higher concentration of DBTDL. The maximum amount of allophanate/biuret is formed with an NCO/OH ratio of 2 and a DBTDL concentration of 1 wt %.

The mechanism of thermal decomposition of copolyurethanes involves three steps at 260 (urethane



**Figure 13** The effect of the catalyst concentration and ratio value on the crosslink density of solid PUIRS.



**Figure 14** The effect of the catalyst concentration and ratio value on the sol percent of solid PUIRS.

degradation), 355–385 (PPG chain scission), and 400–550°C (isocyanurate/carbodiimide decomposition). The TGA curves of the copolyurethanes indicated that the more thermally stable polymer is produced with a greater  $r$  value or higher catalyst concentration. The copolyurethanes synthesized with DBTDL are generally more thermally stable than those synthesized with FeAA. It was also concluded that the PUIRS synthesized with an  $r$  value of 3 have a greater amount of residue at the end of the degradation process.

The results of the kinetic analysis of the thermal decomposition of copolyurethanes indicated the complexity of this process. The activation energy was calculated from three different methods. Only the value of  $E_a$  at the beginning of decomposition, as calculated from the Flynn-Wall method, was dependent on the thermal stability of the copolyurethanes. The methods of Kissinger and Ozawa gave values that were closer to each other.

Finally, we concluded from the swelling and sol fraction experiments that, with an increasing ratio value and/or percentage of DBTDL, the swelling ratio, average molecular weight between crosslink points, and sol fraction are decreased whereas the crosslink density is increased because of a higher extent of trimerization.

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