



## Study on the Pyrolytic Behaviors and Kinetics of Rigid Polyurethane Foams

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### Abstract

In order to investigate the pyrolytic behaviors and kinetics of rigid polyurethane foams (PUFs), three samples named PUF01, PUF02 and PUF03 were synthesized with different [NCO]:[OH] ratios of 1.05, 1.1 and 2, respectively. Many techniques including thermogravimetric analysis (TGA), Fourier-transform infrared spectrometry (FTIR) and synchrotron radiation vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) were used to analyze their pyrolytic behaviors. The results show that the process of PUFs pyrolysis can divide into two stages in nitrogen atmosphere: one is from room temperature to 400 °C, and the other is above 400 °C. The pyrolysis of PUFs mainly occurred at temperature between 200 and 400 °C. The activation energies of the copolymers at lower percent conversion ( $\alpha < 0.3$ ) grow with the increase of the isocyanate index. The higher activation energies were obtained at higher isocyanate index. Mass spectra of pyrolytic products evolved at low pressure indicate that the fission of main chain of polyurethane macromolecules leads to the formation of primary product of isocyanate. Along with the increase of temperature, the chief breakage of polyurethane occurs in the bonds of C-O and C-N. Kinds of pyrolysis products reduce with the increase of isocyanate index.

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### Nomenclature

$W_{\text{isocyanate}}$	weights of isocyanate	$W_{\text{polyol}}$	weights of polyol
$W_{\text{water}}$	weights of water	$E_{\text{isocyanate}}$	equivalent weights of isocyanate
$E_{\text{polyol}}$	equivalent weights of polyol	$A$	the initiator
$B$	pyrolytic products	$C$	release gas
$m_0$	the initial mass of the sample	$m_\alpha$	mass correspond to $\alpha$
$m_\infty$	residue quality	$A$	pre-exponential factor
$E$	reaction activation energy	$n$	order of reaction
$v_a$	asymmetric vibration	$v_s$	symmetric vibration
<i>Greek symbols</i>			
$\delta$	scissoring vibration		

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## 1. Introduction

Polyurethane foams (PUFs), containing a closed-cell structure, are rigid foams. They mainly consist of polyurethane and a small amount of additives. The repeating unit in polyurethane is the urethane linkage produced from the reaction between an isocyanate [ $\text{-NCO}$ ] and an alcohol [ $\text{-OH}$ ]<sup>[1]</sup>. Polyurethane material is a new kind of organic polymer materials, which is known as the "fifth big plastic". Because of its excellent properties, it is widely used in many areas of the national economy including light industry, chemical industry, electronics, textiles, medical, construction, defense, aerospace and others. However, PUFs can create dense toxic smoke during combustion and their flame spread quickly, so more and more attentions were paid to the fire risk of polyurethane foams nowadays. The illegal use of inflammable polyurethane foam leads to the rapid fire spreading. Therefore, it is of great importance to study the thermal degradation behaviors and mechanisms of PUFs.

Basic research shows polyurethane foam (PUFs) pyrolysis is a complex process, which includes a number of partial pyrolytic reactions<sup>[2]</sup>. That is to say the PUFs pyrolysis is not controlled by a simple reaction but the result of many physical and chemical phenomena. Generally speaking, covalent bonds of PU chain have experienced a series of complex vibration and rotation in the heating process. As more thermal excitation, these bonds will form a variety of free radical fragments or atoms, which may further restructure or break. Finally, the debris will evaporate and the carbon diffuses. Because of different structures of PUFs, decomposition products are slightly different. The thermal stability of polyurethane has been extensively studied. Pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), Fourier transform infrared spectroscopy (FTIR) and thermogravimetry (TG) are commonly used to investigate the thermal properties of polyurethanes<sup>[3-7]</sup>. Yang Shou-sheng et al.<sup>[8]</sup> studied the thermal decomposition of polyurethanes using TG/DSC. They found that pyrolytic process of PUFs occurred in two ranges of temperature including 200~300 °C and 340~410 °C. The thermal degradation activation energy of polyurethane was calculated according to the analytical method of Friedman:  $n=0$ ,  $E=226.09$  kJ/mol,  $A=3.79 \times 1020$ . M.M. Esperanza et al.<sup>[9]</sup> studied the pyrolysis of Varnish wastes containing polyurethane under 850 °C, the conversion of samples at low and high temperature phases are less than their entire response phase transformation rate. The main products are benzene and naphthalene, which would be progressively broken down into CO, CO<sub>2</sub>, CH<sub>4</sub>. The process of reaction could be divided into three stages, and the maximum decomposition rate was found at 300, 350, 420 °C in each stage. Activation energy and reaction order by TG and DTG curve fitting:  $E_1=89.5$  kJ/mol,  $n_1=2.54$ ;  $E_2=186.6$  kJ/mol,  $n_2=0.82$ ;  $E_3=340.9$  kJ/mol,  $n_3=1.49$ . Jiang et al.<sup>[10-11]</sup> studied thermal decomposition of polyester polyurethane and polyether polyurethanes using FTIR. It was found that the process of polyester polyurethane pyrolysis has two steps, the hard segment was pyrolyzed first following the soft segments pyrolysis. However, for the polyether polyurethanes, the hard and soft segments were pyrolyzed at the same time. So far, isocyanate index has little effect on pyrolysis kinetics, so it is necessary to study the thermal degradation behaviors of isocyanate polyurethane foam materials with different index.

In this work, we used FTIR to study the groups of polyurethane (Isocyanate index is 1.05). Meantime, the pyrolysis process of three different PUFs was studied using synchrotron radiation vacuum ultraviolet photoionization mass spectrometry (SVUV-PIMS) and thermogravimetry analysis (TGA).

## 2. Experimental

### 2.1. Materials

Polyether polyol with a hydroxyl value 454.9 mg KOH/g was produced by China national chemical corporation. Polymeric 4, 4-diphenylmethane diisocyanate (MDI) was obtained from Basf Corp of Germany. Triethylene diamine, as an amine catalyst, was dissolved in diethylene glycol with the concentration of 33 wt %. The triethanolamine was supplied by Reagent storehouse. Dibutyltin dilaurate, as a tin catalyst, was provided by Air Products Corp of China.

### 2.2. Foam synthesis

All the PUF samples were synthesized with a one-shot method. The components used in the preparation of PUFs are presented in Table 1. The mixtures of surfactant, catalyst and water were weighed and poured into a paper cup, followed by adding 59-143 g Polyether polyol ([NCO]: [OH] ratio was in the range of 1.05-2). Then, an appropriate MDI was added to the mixture and vigorously stirred at a fixed speed. After sufficiently mixing, the mixture was poured into a 200 × 200 × 80 mm mold with a detachable lid to produce free-rise foam. After one minute delayed, the foam was put into an incubator and was cured for 12 hours at 70 °C. The [NCO]: [OH] ratios of samples PUF01, PUF02 and PUF03 are 1.05, 1.1 and 2, respectively. The [NCO]:[OH] ratio (Isocyanate index) was calculated as follows:

$$[\text{NCO}]:[\text{OH}] \text{ ratio} = (W_{\text{isocyanate}}/E_{\text{isocyanate}}) / (W_{\text{polyol}}/E_{\text{polyol}} + W_{\text{water}}/9) \quad (1)$$

Where  $W_{\text{isocyanate}}$ ,  $W_{\text{polyol}}$  and  $W_{\text{water}}$  are the weights of isocyanate, polyol and water, respectively.  $E_{\text{isocyanate}}$ ,  $E_{\text{polyol}}$  are the equivalent weights of isocyanate and polyol, respectively.

Table1 The reagent used in the preparation of PUFs

sample	PUF01	PUF02	PUF03
polyether polyol(g)	143	135	59
MDI(g)	150	150	150
Dibutyltin dilaurate(g)	0.5	0.5	0.5
Silicone oil(g)	2	2	2
Water(g)	2	2	2
A-33(g)	1	1	1
Triethanolamine(g)	3	3	3
Isocyanate index	1.05	1.1	2.0

### 2.3. Characterization

#### 2.3.1 Thermogravimetric analysis

The TGA experiments were performed using the DSC-TGA Q600 thermal analyzer under nitrogen atmosphere. The flow rate of nitrogen gas was 100 mL/min. The samples (3-5 mg) were heated from room temperature to 800 °C at the heating rates of 10, 15 and 20 °C /min, respectively.

#### 2.3.2 Infrared spectroscopic analysis

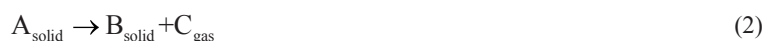
The IR spectrum of the sample was carried out by a Model Nicolet 8700 FT-IR operating in the range 7000-50  $\text{cm}^{-1}$  with a resolution of 0.01  $\text{cm}^{-1}$  (sample: PUF01, heating rate: 10 °C /min, temperature: room temperature, heating atmosphere: air).

#### 2.3.3 Synchrotron radiation photoionization mass spectrometric analysis

Mass spectrometric analysis was carried out at National Synchrotron Radiation Laboratory (NSRL) in Hefei. The detailed information of pyrolysis setup has been described in a previous report [12]. Briefly, sample was put into pyrolysis furnace by stainless steel pole. Pyrolysis products formed supersonic molecular which interacted with synchrotron light to generate ions, which were subsequently detected by commercial triple quadrupole time-of-flight mass spectrometer. In our experiments, PUF01, PUF02, PUF03 were tested, respectively.

### 2.4. Pyrolysis dynamics

General formula of polymer pyrolysis can be described as Eq. (2) [13]:



where A is the initiator, B is the pyrolytic products and C is the release gas. In this paper,  $\alpha$  represents the mass loss ratio of the sample in the process of pyrolysis, and

$$\alpha = (m_0 - m_\alpha) / (m_0 - m_\infty) \quad (3)$$

where  $m_0$  is the initial mass of the sample,  $m_\alpha$  is the mass correspond to  $\alpha$  and  $m_\infty$  is the residue quality. Chemical reaction rate can be deduced from the formula Eq. (4):

$$d\alpha / dt = A \exp(-E / RT) f(\alpha) \tag{4}$$

where  $T$  is the pyrolysis temperature (K),  $R$  is the perfect gas constant (8.314J/(mol·K)),  $A$  is the pre-exponential factor ( $s^{-1}$ ) and  $E$  is reaction activation energy (kJ/mol). In the process of polymer pyrolysis, the change of the conversion rates is normally assumed to be proportional to the concentration of reactant, then:

$$f(\alpha) = (1 - \alpha)^n \tag{5}$$

where  $n$  is order of reaction. Chemical reaction rate can also be obtained by the Eq. (6)

$$d\alpha / dt = A(1 - \alpha)^n \exp(-E / RT) \tag{6}$$

Friedman [14] calculated activation energy using data from TGA at different heating rates. In his study, the mathematical expression is Eq. (7):

$$\ln(d\alpha / dt) = \ln[A(1 - \alpha)^n] - E / RT \tag{7}$$

A straight line can be created by setting  $1/T$  as  $x$  axis and  $\ln(d\alpha / dt)$  as  $y$  axis. As a result, the activation energy can be derived from the gradient of the straight line  $E / R$ .

### 3. Results and discussion

#### 3.1. Identification of characteristic IR frequencies of polyurethane

First, in our analysis, we identify relevant spectral features responsible for PUR film formation. Table 2 summarizes FTIR active bands observed in individual urethane components. Fig.1 illustrates transmission FTIR spectra of waterborne polyurethane. The wide absorption band at  $3380\text{cm}^{-1}$  represents stretching vibration of N-H urethane hydrogen bonded. The band at  $2265\text{cm}^{-1}$  is attributed to the out-of-phase stretching vibrations of NCO. This band is of particular interest because the NCO dictates the crosslinking reactions of waterborne PURs. In the polyurethane spectrum, the band at  $3380\text{cm}^{-1}$  results from N-H stretching vibration modes. The asymmetric stretching band of  $\text{CH}_2$  at  $2930\text{cm}^{-1}$  was used as the normalized band. Other  $\text{CH}_2$  deformation modes are detected at  $1456\text{cm}^{-1}$ . The C=O stretching modes are detected at  $1720\text{cm}^{-1}$ . Another band of interest is detected at  $1520\text{cm}^{-1}$ , which is caused by amide II stretching modes of polyurethane and polyurea. As shown in Figure 2, overtone of amide II at  $3080\text{cm}^{-1}$  are detected in polyurethane.

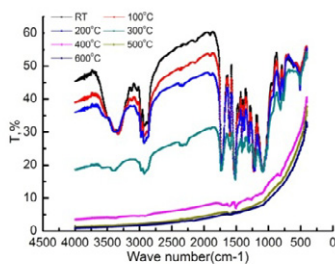


Fig.1 FT-IR spectrum of PUF01

Table2 Identification of characteristic IR frequencies of polyurethane

Wavenumber(cm-1)	Assignment	Relative intensity
3300-3500	N-H free	s
3050	Overtone of amide II	w
2980	$\nu_s\text{CH}_3$	s

2930	$\nu_s$ CH <sub>2</sub>	s
2265	NCO out-of-phase	w
1720	C=O in ester	vs
1600	C=C vinyl ether	s
1520	$\delta$ N-H& $\nu_s$ C-N amideII(urea)	vs
1456	$\delta$ CH <sub>2</sub>	m
1410	C-H	s
1380	$\delta$ -C(CH <sub>3</sub> )	m
1310	N-H associated with aryl	s
1230	(O=)C-O-C	vs
1080	$\nu_s$ C-O-C in ether	vs
816	$\nu_s$ C-O-C	w
768	C-C-O in phase	w

Note: s-strong, w-weak, vs-very strong, m-middle.

It also can be seen that the stretching vibration peak of NH at 3330  $\text{cm}^{-1}$  moved to high band number with the increase of temperature, meantime, the intensity of peak became weak gradually and finally disappeared. That's because polyurethane decomposes continuously with heating, the effect of hydrogen bond was weakening, so the mixability of microfacies in cross-linked PU increases. It has been found that samples are aromatic polyurethane due to the existence of wide and strong peak between 1700  $\text{cm}^{-1}$  and 1740  $\text{cm}^{-1}$ , the stretching vibration peaks of C=O do not split into smaller peaks indicate that they are not aliphatic urethanes. FTIR spectra obtained at room temperature and 100 °C have nothing to change, this illustrate that polyurethane cannot react below 100 °C. Temperature in the range of 200- 300 °C, the stretching vibration of N-H (3320  $\text{cm}^{-1}$ ), CH<sub>3</sub> (2930, 2980  $\text{cm}^{-1}$ ) weakened obviously and amide II (3050  $\text{cm}^{-1}$ ) disappeared, while NCO (2265  $\text{cm}^{-1}$ ) enhanced continuously, this is the decomposition of hard segment. Isocyanate, alcohols, primary amine correspond to decomposition products. Temperature in the range of 300- 400 °C, C-O-C (1080  $\text{cm}^{-1}$ ), C-O-C (1230  $\text{cm}^{-1}$ ) and C=O in ester (1720  $\text{cm}^{-1}$ ) weakened continuously and finally disappeared at 400 °C. So far the sample decomposition has been finished and CO and CO<sub>2</sub> are the main gas products during this period.

### 3.2. The influence of isocyanate index on pyrolysis behavior of the copolymer

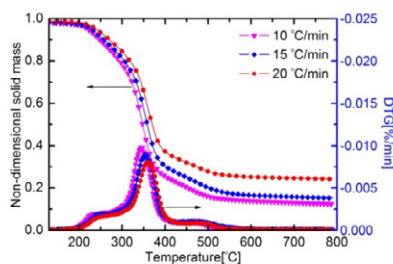


Fig.2 TGA and DTG curves of PUF01 at different heating rates

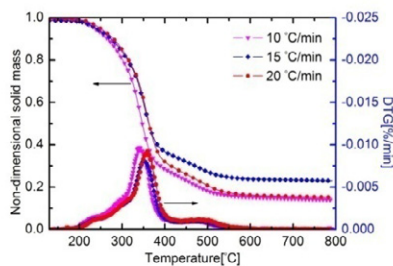


Fig.3 TGA and DTG curves of PUF02 at different heating rates

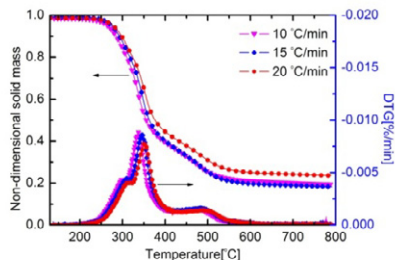


Fig.4 TGA and DTG curves of PUF03 at different heating rates

Based on the experiments, the pyrolytic processes were occurred in the following temperature ranges: PUF01:160~250 °C (stage 1), 250~440 °C (stage 2), above 440 °C (stage 3); PUF02: 150~440 °C ( stage 1), above 440 °C (stage 2); PUF03:180~300 °C ( stage 1), 300~420 °C (stage 2), above 420 °C (stage 3). Comparing the TGA plots of PUF01, PUF02 and PUF03 (see Fig. 2, 3, and 4), it can be seen that the retention rate of quality grows gradually with the increase of heating rate. It takes a long time for polymer to be fully pyrolyzed in the low-temperature area, because the compositions of polyurethane that is much easier to be pyrolyzed are dominated in the low-temperature area. At lower heating rate, for example 10°C/min, quality retention rate increases gradually along with the increase of isocyanate index. The reason is that the increase of dosage produce surplus isocyanate polymerize to stable cyclic compound and its pyrolysis composition decreases. It can also be seen from the DTG plots in the two temperature ranges ( see Fig. 2, 3, and 4 ).Their qualities largely lose at the first stage along with the increase of isocyanate index. The thermal degradation activation energies of polyurethanes with three different isocyanate indexes were calculated according to the Friedman method (Friedman fitting curve of PUF03 is shown in Fig. 5). The calculation results are listed in Table 3. When  $\alpha < 0.3$ , it can be concluded that activation energy presents a growth trend as the isocyanate index increases. When  $0.3 \leq \alpha \leq 0.55$ , the activation energy is oscillated between 126 and 177 kJ/mol and the energy increases rapidly at the latter inorganic stage. The high correlation coefficient  $R_c$  of various systems demonstrates that the experimental results are reliable.

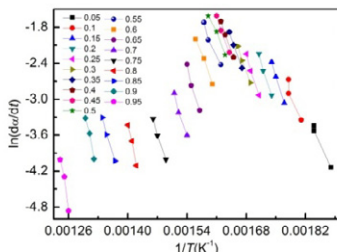


Fig.5 Friedman plots of  $\ln(da/dt)$  versus  $1/T$  for the calculation of E at varying heating rates

Table 3 Calculated activation energies of PUFs by Friedman method.

Conversion, $\alpha$	PUF01		PUF02		PUF03	
	$E$ (kJ/mol)	$R_c$	$E$ (kJ/mol)	$R_c$	$E$ (kJ/mol)	$R_c$
0.05	146.5	0.9924	-	-	136.1	0.9944
0.1	119.3	0.9998	89.8	0.8829	154.7	0.9396
0.15	121.7	0.9983	131.6	0.9663	188.7	0.9994
0.2	155.9	0.9950	188.6	0.9882	188.2	0.9964
0.25	144.9	0.9967	142.7	0.9998	187.0	0.9966
0.3	141.6	0.9928	134.9	0.9998	167.1	0.9983
0.35	175.8	0.9941	166.7	0.9875	165.8	0.9995
0.4	153.1	0.9810	126.9	0.9999	165.1	0.9992

0.45	177.5	0.9945	168.9	0.9878	168.7	0.9975
0.5	137.0	0.9976	136.4	0.9971	134.8	0.9935
0.55	130.0	0.9754	138.4	0.9974	138.8	0.9836
0.6	184.7	0.9890	135.9	0.9929	155.5	0.9968
0.65	187.5	0.9865	179.3	0.9986	206.7	0.9894
0.7	135.6	0.9477	137.9	0.9878	189.3	0.9891
0.75	193.7	0.9459	140.7	0.9791	184.6	0.9958
0.8	-	-	135.7	0.9675	280.1	0.9929
0.85	-	-	165.0	0.9748	197.7	0.9982
0.9	-	-	225.2	0.9758	282.3	0.9896
0.95	-	-	-	-	355.9	0.9828

### 3.3. Mass spectrometry spectrometric analysis of polyurethane copolymer

We have mentioned above, the repeating unit in polyurethane is the urethane linkage produced from the reaction between isocyanate [ $-\text{NCO}$ ] and an alcohol [ $-\text{OH}$ ]. The process of polyurethane pyrolysis contains fracture and recombination of urethane, which were demonstrated by SVUV-PIMS. Fig.6 shows the mass spectra of pyrolysis products of PUF01 at different temperatures. As is shown in Fig.6, the relative intensity of fragments increases as the temperature rises. At 350 °C, the relative intensity of main fragments can reach 9000, which is much higher than other fragments. Peak at  $m/z$  250 represents isocyanate. Above 350 °C, isocyanate decay obviously. The main products are isocyanate and alcohol in vacuum, which eventually were broken down into hydrocarbon. It also can be seen that the discrepancy of pyrolysis products disappeared with the increase of temperature. During this stage, the broken of C-O and C-N dominated in the process of pyrolysis, which leads to the huge isocyanate and parts of pyrolytic products cannot be detected.

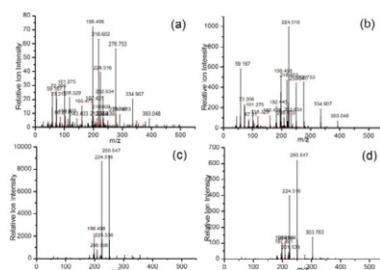


Fig.6 The pyrolysis of PUF01 at different temperature (a-200 °C, b-250 °C, c-350 °C, d-500 °C)

Fig.7 shows two urethane fragments of polyurethane. According to the different  $m/z$  at different temperatures, we can analyze the type of fragments, so as to infer the fracture bond of polyurethane.

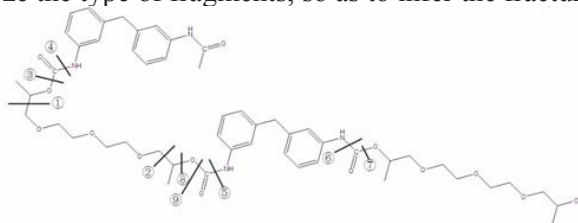


Fig.7 The scheme of carbamate

At 200 and 250 °C, the fragment of  $m/z$  276 formed by the fission of 4 and 5 bonds, the fragment of  $m/z$  224 formed by the broken of 4 bond single, the fragment of  $m/z$  252 formed by the broken of 7 and 9 bond, the fragment of  $m/z$  218 formed by the broken of 3 and 8 bond, the fragment of  $m/z$  198 formed by the cracking of 5 and 6 bond, the fragment of  $m/z$  59,  $m/z$  118 formed by the fission of 1 and 2 bond, respectively.

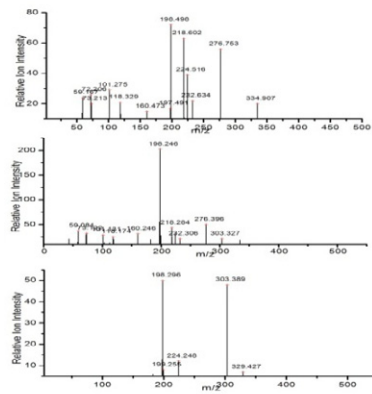


Fig.8 The pyrolysis of three different foams at 200 °C

To study the thermal degradation behaviors for different index of isocyanate polyurethane foam materials, we carried out some experiments for different PUFs at 200 °C. It can be seen from Fig.8, different kinds of pyrolysis products reduced with the increasing index of isocyanate (PUF01 > PUF02 > PUF03). It can be explained that all isocyanates can polymerize itself and form more stability polymer, it cannot be pyrolyzed easily, for example, peak at  $m/z$  303 correspond to the pyrolysis product after polymerizing itself.

#### 4. Conclusions

(1) Under the temperature of 300 °C, The pyrolysis products of polyurethane foams made by ourselves mainly are isocyanate (poisonous gas), alcohol, primary amine and etc. Between the temperature of 300 °C and 400 °C, they are carbon monoxide, carbon dioxide .etc .

(2) The pyrolysis of PUFs can be occurred in two ranges of temperature: One is from room temperature to 400 °C, the other is above 400 °C. The pyrolysis of PUFs mainly concentrated between 200 and 400 °C. The activation energies of the copolymers at lower percent conversion ( $\alpha < 0.3$ ) grow with the increase of the isocyanate index. The higher activation energies were obtained at higher isocyanate index.

(3) Mass spectra of pyrolytic products evolved at low pressure indicate that the fission of main chain of polyurethane macromolecules leads to the formation of primary product of isocyanate. Along with the increase of temperature, the chief breakage of polyurethane occurs in the bonds of C-O and C-N. Kinds of pyrolysis products reduce with the increase of isocyanate index.

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