

Reaction Kinetics of Polyureas with Acetylated Diamine Chain Extenders

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ABSTRACT: Diacetyl hexamethylene-diamine (MHAD) and diacetyl m-phenylenediamine (*Mm*-PDA) were synthesized by acetylating hexamethylene-diamine (HAD) and m-phenylenediamine (m-PDA) with glacial acetic acid in presence of phosphoric acid, in order to retard the high reactivity of polyurea. Chemical structures of modified diamine chain extenders were confirmed through FTIR, the determination of the nitrogen content, High resolution ESI-Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry and ¹H-NMR analysis. Polyureas were synthesized via two-step solution process by reaction of 4,4'-diphenyl diisocyanate (MDI), amine terminated polyether (Jeffamine D-2000) with different chain extenders. The influence of

modified diamine chain extenders on gel time of polyurea was investigated. The gel time was prolonged from 11s to 52s and 13s to 65s respectively. The reaction kinetics of synthesizing polyureas were studied by FTIR. The results showed that extending reaction with MHAD was second order kinetic mechanism, its apparent activation energy was 43.99 kJ·mol⁻¹; extending reaction with *Mm*-PDA reaction was first order, its activation energy was 58.95 kJ·mol⁻¹. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 479–484, 2012

Key words: polyurea; diacetyl hexamethylene-diamine; diacetyl m-phenylenediamine; reaction kinetics; activation energy

INTRODUCTION

Polyureas are prepared by the reactions between prepolymers of end-capping isocyanates and amides. Because of the high reactivity of amine-terminated polyethers and diamine chain extenders, polyureas cure within very short time without a catalyst.^{1,2} The reaction rate of aromatic isocyanates with conventional amine-terminated polyethers and liquid amine chain extenders is very high, and the general gel time is as short as 3–5s.^{3,4} The high reactivity is unfavorable for the research of polyurea reaction kinetics, as well as the preparation of polyurea coating with excellent properties, such as substrate wetting ability, adhesion, interlayer combination, coating internal stress, and etc.^{5,6} The molding and operation of spray polyurea^{7,8} are also difficult. Because of the complexity of the amino-isocyanate reaction, previous work involving urea reaction mechanism is limited to the reaction of small molecules ArNCO with aromatic amines.⁹ There is no report on the direct chain extender reaction of end-capped isocyanates prepolymers with amines. The reactions between amino-terminated pol-

yethers and isocyanates were so fast that it is difficult to scale up the polymerisate into actual operation, and the result did not have practical value. Stanford et al.¹⁰ studied the effect of raw materials of polyurea coatings, coating formulas, and spraying process parameters on the physical properties of polyurea coating. The results showed that system gel time could be extended if aromatic amine chain extenders were used, but specific experiments were not conducted. Domestic research reported the effect of chain-extender type and amount on polyurea gel time, which indicated that cyanoethyl modification of primary amine to secondary amine can reduce reactivity.¹¹ Pu et al.^{12,13} studied the effect of different chain extenders on polyurea coating performance, but they put more emphasis on ratios of chain extenders to polyurea properties. However, the kinetic analysis of synthesizing polyurea has not been carried out.

Urea is formed by the reaction of amine and isocyanate. The reactivity is influenced by the structure of isocyanate and amine. Among isocyanates, acylamino has the lowest reactivity when reacting with various active hydrogen compounds. The following work has been introduced in this article. First, novel sterically hindered chain extenders, diacetyl hexamethylene-diamine (MHAD) and diacetyl m-phenylenediamine (*Mm*-PDA) were synthesized by acetylation of hexamethylene diamine (HAD) and m-phenylene diamine

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(*m*-PDA). Second, new polyureas were synthesized via two-step solution process by reaction of 4,4'-diphenyl diisocyanate (MDI), amine terminated polyether with different chain extenders. The influence of modified diamine chain extenders on gel time of polyurea was investigated. In the end, the curing process was monitored with FTIR for which the reaction rate constants at different temperatures were estimated. The reaction orders were determined, and their apparent activation energy were calculated.

EXPERIMENTAL

Materials

Amino terminated polyether with molecular weight of 2000 and degree of Functionality 2 (Jeffamine D-2000, from Chenhua Science & Technology Group Co., Ltd., Yangzhou, China) was vacuum dried at 100°C for 3 h. *N,N*-dimethyl formamide (DMF, from Yongda Guangming Chemical Reagent Development Center, Tianjin, China) was dried with anhydrous magnesium sulfate for 24 h, then purified by vacuum distillation and stored in presence of 4A molecular sieve. 1,6-hexamethylene diamine(HAD, from Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) was vacuum dehydrated under 80°C for 3 h. 4,4'-diphenylmethane diisocyanate (MDI, from Yantai Wanhua Polyurethanes Co., Ltd., Yantai, China), *m*-phenylene diamine (*m*-PDA, from Guangfu Institute of Fine Chemical Engineering, Tianjin, China), Glacial acetic acid (from North Tianyi Chemical Reagent Factory, Tianjin, China), and phosphoric acid (from North Tianyi Chemical Reagent Factory, Tianjin, China) were used as received.

Synthesis and characterization of chain extenders

HAD or *m*-PDA was melted firstly in a four-necked flask below 80°C, and the solution of glacial acetic acid and phosphorus acid was dropped into the flask within 50 min for HAD or 30 min for *m*-PDA. The mixture was refluxed and the water was removed off. Then the reaction mixture was cooled and filtrated, then washed by cold water and vacuum dried at 120°C to constant weight. The HAD product was white, the *m*-PDA product was black. The yields of MHAD and *Mm*-PDA were 94 and 74%,¹⁴ and melting point were 127–128°C and 195–196°C, respectively.

Infrared spectra were obtained by KBr pellets and recorded on a WQF-510 FTIR spectrophotometer. High resolution mass spectra (HRMS) were measured on Varian 7.0 high resolution ESI-Fourier transform ion cyclotron resonance (ESI-FTICR) mass spectrometry. ¹H-NMR spectra were recorded on Varian Inova 500M nuclear magnetic resonance spectrometer, deuterated water (D₂O) was served as solution. Nitrogen content was determined by Kjeldahl method using KDT-1000.

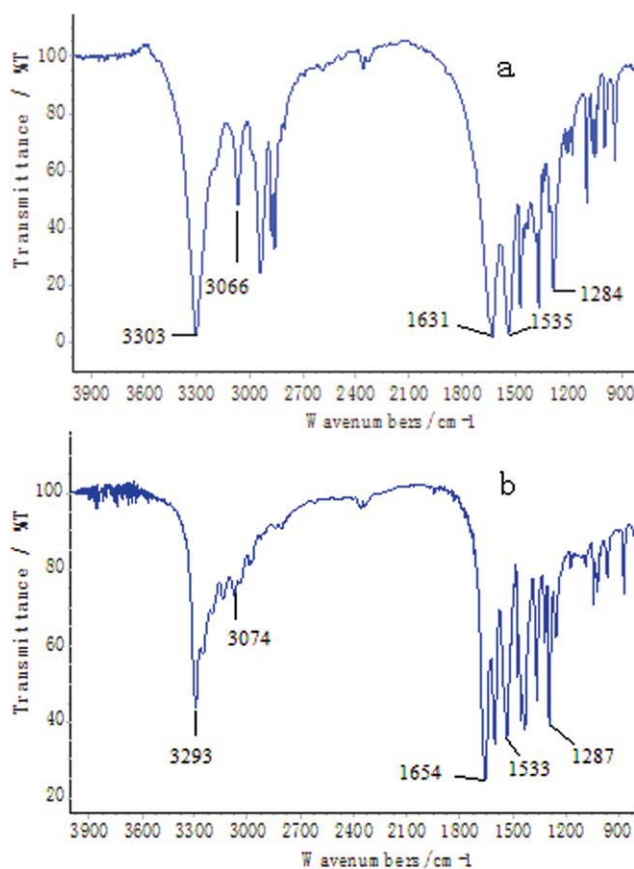


Figure 1 Infrared spectra of MHAD and *Mm*-PDA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Preparation of polyureas and infrared tracking

Determination of gel time

Chain extender, D-2000, and DMF were mixed and heated in hot water bath and kept at 25°C for more than 8 h, and MDI was put into the above solution. The molar ratio of MDI:D-2000:chain extenders was 1.05:0.39:0.61. The mixture was stirred until it did not flow, and the time taken until cessation of motion.¹⁵

Synthesis of semiprepolymer

D-2000 was vacuum dehydrated for 1–2 h in a three-necked flask at 110°C, and it was cooled to 60°C. MDI was added into the flask, and the temperature was slowly raised up to 85°C and kept for 2.5 h, so the –NCO content reached theoretical value, thus –NCO-terminated prepolymer was obtained.^{16–18}

Curing process of polyurea

The above semi-prepolymer and diamine chain extender MHAD or *Mm*-PDA (The molar ratio $n_{\text{NCO}}/n_{\text{NH}_2} = 1$) were mixed and deposited onto KBr salt pellets in the thermostatic cell of Bio-Rad FTS 6000 FTIR.

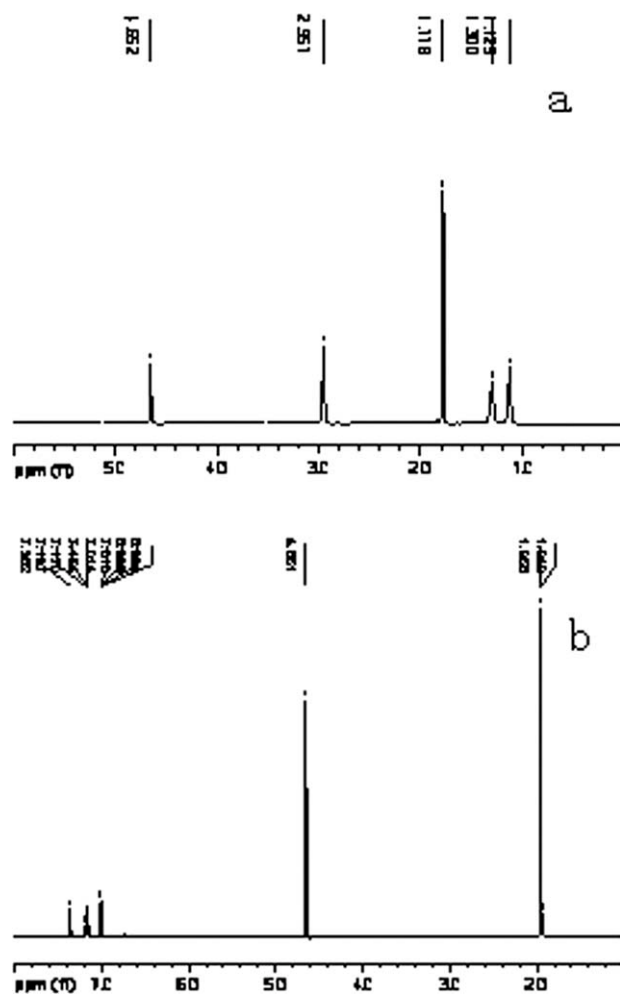


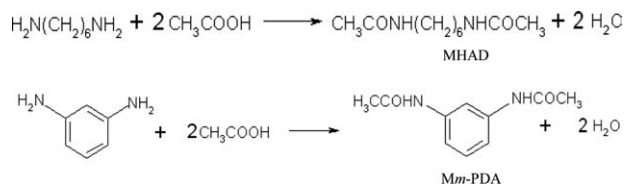
Figure 2 $^1\text{H-NMR}$ of MHAD and Mm-PDA.

The curing process of polyurea was tracked at 26, 36, 42, and 51°C through dynamic infrared technology. During the process, $-\text{NCO}$ group was found to be the most suitable for tracking the reaction, for it showed a strong asymmetric stretching vibration band at 2273 cm^{-1} without interference. Therefore, the variation of the band area in absorption band could be taken to study kinetics of polymerization.^{19,20}

RESULTS AND DISCUSSION

Characterization of the chain extenders

The reaction of HAD or *m*-PDA with glacial acetic acid was as follows:



The infrared spectra of the compounds were shown in Figure 1. The strong absorption bands at 1631(a) and 1654(b) cm^{-1} were the stretching vibrations of

TABLE I
Comparison of Gel Time

Chain extender	Gel time/s
HAD	11
MHAD	52
<i>m</i> -PDA	13
Mm-PDA	65

$\text{C}=\text{O}$, which were amide band. The stretching vibrations for free N-H at 3303(a) and 3293(b) cm^{-1} , and those of associated N-H for hydrogen bonding at 3066(a) and 3074 (b) cm^{-1} were single bands, which indicated that the diethyl amide groups existed. Strong bending vibrations of N-H were found at 1535(a) and 1533(b) cm^{-1} , which were amide band. The stretching vibrations of C-N at 1284(a) and 1287(b) cm^{-1} were amide band. These characteristic bands showed that the samples possessed the structure of diethyl amide, just as expected.

HRMS analysis showed the molecular weights were 200.1526 for MHAD and 192.0893 for Mm-PDA, respectively, which were equal to the

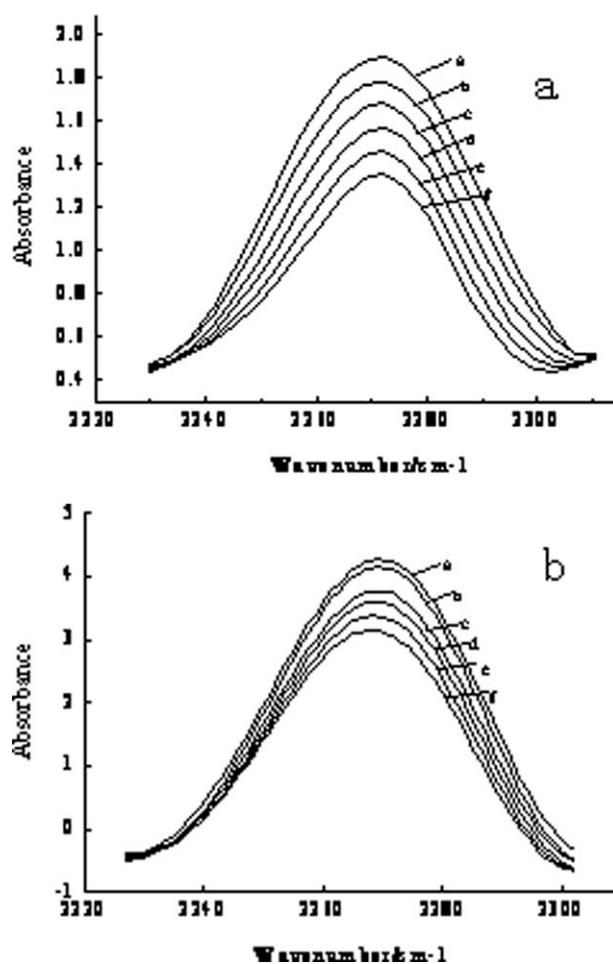


Figure 3 Changes of $-\text{NCO}$ characteristic peak with reaction time. Time/s: a.0; b.30; c.60; d.90; e.120; f.150.

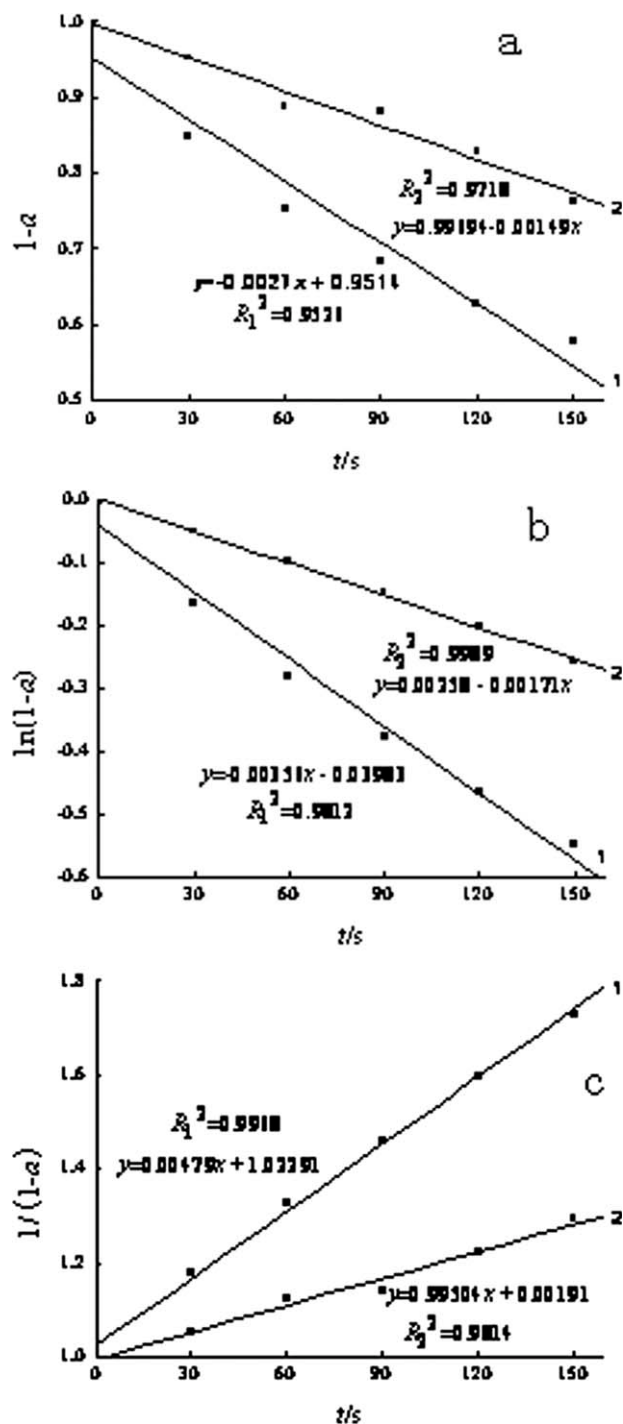


Figure 4 Kinetics curves of zero order, first order and second-order reactions. (1) the synthesis reaction of polyurea with MHAD and (2) the synthesis reaction of polyurea with Mm-PDA.

theoretically calculated values for $C_{10}H_{20}N_2O_2$ and $C_{10}H_{12}N_2O_2$.

1H -NMR of MHAD and Mm-PDA are shown in Figure 2. The $-NH-$ absorption band overlaps with a D_2O band at $\delta = 4.65$. In Figure 2(a), hydrogen adsorption bands of the carbon in original HAD were

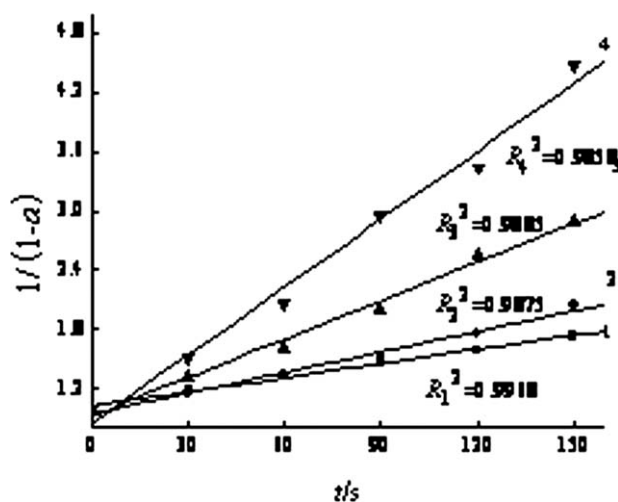


Figure 5 Relations between $1/(1-\alpha)$ and time t at different temperatures T/K : 1. 299; 2. 309; 3. 317; 4. 324.

found at the chemical shift of $\delta = 1.13$ (multiplet, 4H), 1.29 (m, 4H), and 2.96 (triplet, 4H). Two methyl hydrogen absorption bands which were bound to acetyl were observed at $\delta = 1.78$ (singlet, 6H). In Figure 2(b), $\delta = 1.96$ (s, 6H) was the methyl hydrogen of acetyl, and $\delta = 7.01$ (m, 2H), 7.16 (m, 1H), and 7.36 (s, 1H) were from aromatic ring. The results of 1H -NMR indicated that the formulas of MHAD and Mm-PDA were $CH_3COHNCH_2CH_2CH_2CH_2CH_2CH_2NHCOCH_3$ and $CH_3COHNC_6H_4NHCOCH_3$, respectively.

The nitrogen content of MHAD was determined to be 13.86%, close to the theoretically calculated nitrogen value of 14%. The nitrogen content of Mm-PDA was determined to be 14.47%, and its theoretical value was 14.58%. Therefore, it can be inferred that the chemical formula of MHAD was $H_3CCOHN(CH_2)_6NHCOCH_3$ and Mm-PDA was $H_3CCOHN(C_6H_4)NHCOCH_3$.

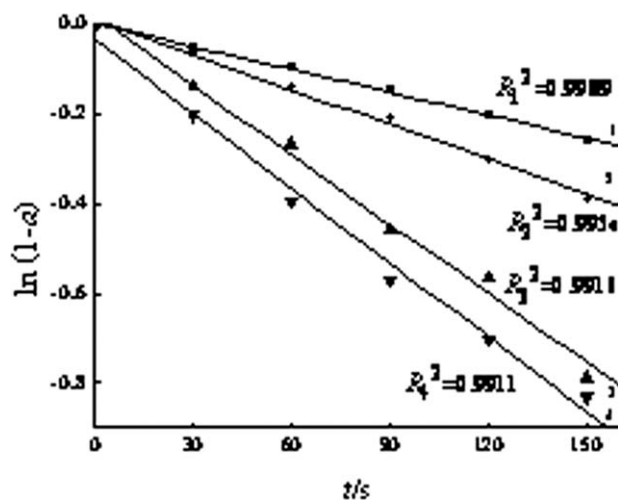


Figure 6 Relations between $\ln(1-\alpha)$ and time t at different temperatures T/K : 1. 299; 2. 309; 3. 315; 4. 324.

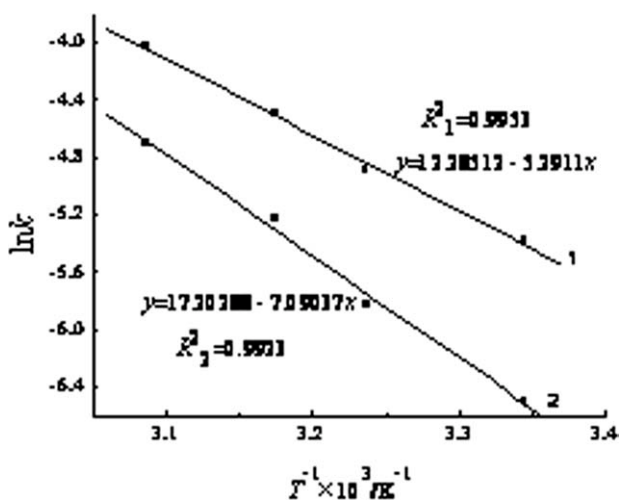
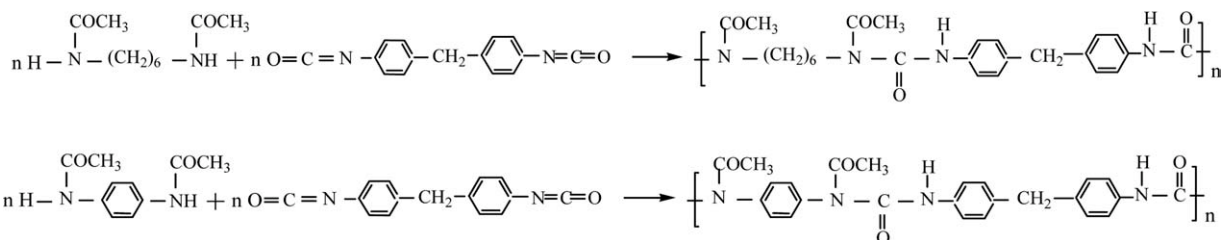


Figure 7 Relations between reaction rate constant and temperature.

Reaction kinetics of synthesizing polyureas

Effect of acetylating on gel time

The reaction activity of chain extenders is influenced by the molecular structure and steric hindrance of diamines, so the gel time can be controlled by selecting appropriate chain extenders. The gel time of different chain extenders is presented in Table 1. The



The kinetics model of curing process can be expressed as: $-dC_{\text{NCO}}/dt = kC_{\text{NCO}}^{n_1} \cdot C_{\text{NH}_2}^{n_2}$ (C represents concentration; n_1 and n_2 are the reaction orders of $-\text{NCO}$ and $-\text{NH}_2$ functional groups, respectively).

The reaction proceeded at 26°C , and $n_{\text{NCO}}/n_{\text{NH}_2} = 1$, so we are assuming that $-dC_{\text{NCO}}/dt = kC_{\text{NCO}}^{(n_1+n_2)}$. During the process, infrared spectroscopy was used to track the characteristic peak variations with time.²¹ The interrelation between the absorbance of $-\text{NCO}$ at 2273 cm^{-1} and time was shown in Figure 3. The characteristic peak became smaller as the reaction progressed over time.

According to Lambert-Beer law, the conversion rate of $-\text{NCO}$ was calculated with the net area change of its characteristic peak,²² $\alpha = (c_{i0} - c_{it})/c_{i0} = (A_{i0} - A_{it})/A_{i0} = 1 - A_{it}/A_{i0}$. The squared correla-

test results indicated that acetylated chain extenders greatly decelerated the reaction activity and prolonged gel time.

Comparison of gel time

The chemistry of amine has much to do with the lone pair electrons of nitrogen atom. The lone pair electrons makes amine more nucleophilic. The nucleophilic hydrogen atom attacks the carbonium ion of isocyanate and reaction proceed in the active group $\text{N}=\text{C}=\text{O}$, so the hydrogen atom of the active hydrogen functional groups transfers to the nitrogen atom of $-\text{NCO}$. Modified chain extenders by acetylating become less active because two $-\text{COCH}_3$ functional groups take place of the original two hydrogen atoms, Then, $-\text{COCH}_3$ generate sterically large hindrance, which also make them less likely to react so fast and prolongs gel time.

Kinetics of synthesizing polyurea

The reactions of MHAD or *Mm*-PDA with MDI are as follows:

tion coefficient R^2 was obtained through the least squares method and simple linear regression. Considering the reaction as zero order, first order or second order, respectively, the curves were drawn with $1-\alpha$, $\ln(1-\alpha)$ and $1/(1-\alpha)$ versus time t , as displayed in Figure 4. Straight line 1 in (c) exhibited a nearly linear relationship, given that the R^2 was high, which revealed the synthesis reaction of polyurea with MHAD at 26°C was of second order. Straight line 2 in (b) also exhibited a nearly linear relationship, given that the R^2 was high, which indicated the synthesis reaction of polyurea with *Mm*-PDA at 26°C was of first order.

Figure 5 displayed the change of $1/(1-\alpha)$ with time during the reaction process of preparing polyurea with MHAD at different temperatures. These straight lines revealed the chain extending reaction

followed the rule of second order at the early stage. Figure 6 showed the change of $\ln(1-\alpha)$ with time during the reaction process of preparing polyurea with *Mm*-PDA. The results indicated this chain-extending reaction followed the rule of first order at the early stage. As shown in Figures 5 and 6, linear correlation coefficient R^2 were better at 26°C. When the temperature increased, the value of R^2 decreased. So we conclude that only a simple chain extending reaction has taken place at the lower temperature, whereas at the higher temperatures, branching and crosslinking reaction are taking place.^{23,24} The reaction rate constant k can be obtained from the slope. The curves of $\ln k$ versus $1/T$ are shown in Figure 7 and the slope of the line is E_a/R . The activation energy E_a is calculated to be 43.99 kJ·mol⁻¹ from line 1 and 58.95 kJ·mol⁻¹ from line 2.

CONCLUSIONS

1. Novel sterically hindered chain extenders, diacetyl-hexamethylene-diamine (MHAD) and diacetyl *m*-phenylenediamine (*Mm*-PDA), were synthesized from hexamethylene-diamine (HAD) and *m*-phenylenediamine (*m*-PDA) by acetylating with glacial acetic acid in presence of phosphoric acid. Their structures were confirmed by Infrared spectrographic analysis, high resolution ESI-FTICR mass spectrometry, the determination of the nitrogen content, and ¹H-NMR analysis.
2. Compared with unacetylated chain extenders, the sterically hindered chain extenders greatly decelerate the reaction activity and prolong gel time. Their low reactivity is beneficial to controlling the molding or operation of spray polyurea and improved the performance of polyurea products.
3. At normal temperatures, the curing process of polyureas was monitored with FTIR and reaction rate constants at different temperatures were estimated. Results of infrared tracking showed that the chain extending reaction of preparing polyurea with MHAD followed the rule of second order at the early stage; its

apparent activation energy was calculated to be 43.99 kJ·mol⁻¹; and the reaction with *Mm*-PDA displayed the characteristics of first order reaction kinetics at the early stage; its apparent activation energy was 58.95 kJ·mol⁻¹.

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