A Recycling Model of Excess Toluene Diisocyanate Isomers in the Preparation of Polyurethane Prepolymer

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ABSTRACT: Reaction kinetics of dropwise addition of trimethylolpropane (TMP) to toluene diisocyanate (TDI-80) at various temperatures and initial stoichiometry was studied. The progress of the polymerization reaction was monitored by measuring the concentration of isocyanate groups and TDI isomers by means of backtitration and high performance liquid chromatography (HPLC), respectively. The kinetics of dropwise addition method, compared with the conventional one-shot method, was well described by a second order equation. This procedure was optimized by comparing the deviations between experimental data and theoretically calculated data. The effects of temperature, initial stoichiometry and TDI isomers on the amount of excess 2,4-TDI and 2,6-TDI were investigated. Three commercially available TDI mixtures, 65 : 35, 80 : 20, and 100 : 0 ratio of 2,4-TDI/2,6-TDI, respectively, were used. A recycling model of unreacted TDI isomers and solvent was established to reach a stable process and yield polyurethane prepolymer with good reproducibility. This model has been applied in the chemical plant to prepare polyurethane prepolymer with precisely defined chemical compositions in a continuous process. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Isocyanate terminated polyurethane prepolymer is widely prepared from nonequivalent amounts of toluene diisocyanate (TDI) over alcohols. This method is preferred to control chemical composition and molecular weight.[1–3] Polyurethane prepolymer can be then extended with diols or diamines to prepare polyurethane or polyurea, respectively.[4–7]

The kinetics of the reaction between diisocyanate and alcohols has been extensively studied. Due to the complexity of reactivity arising from two TDI isomers, several authors[8–12] established a two stage kinetic model with only two rate constants corresponding to isocyanate groups in the ortho and para position, respectively, and thus discontinuity was observed in the second order plots. Nevertheless, the reaction of isocyanate groups with hydroxyl compounds should occur simultaneously, and it failed to take into account the substitution effect. Grepinet et al.[13,14] distinguished the isomeric monourethane (MU) and diurethane (DU) using nuclear magnetic resonance (NMR) spectroscopy, and proposed a competitive model for all the isocyanate groups at different positions. However, the differences between the chemical shifts were so small that the attribution could be considered doubtful if more species appeared.[15–17] All the kinetic

researches focused principally on finding kinetic parameters for the reaction of various monoisocyanates and diisocyanates with alcohols by one-shot method. This was not realistic in commercial application since the large reaction enthalpy would result in a runaway reaction. The hydroxyl compound should be added dropwise to the diisocyanate to control the temperature and the chemical composition.

Scheme 1 shows that the reaction of polyols with diisocyanate first produces MU and then DU, however, the DU cannot be favored. To synthesize polyurethane elastomer with high molecular weight, most MU should be reacted with another hydroxyl group arising from polyether or polyester in the succeeding step. With increasing initial ratio of NCO/OH, the content of the DU decreases continuously at the expense of an increase in the amount of unreacted diisocyanate.[18] The unreacted diisocyanate should be removed and recycled for its toxicity and negative impact on the properties of polyurethane prepolymer. This objective could be realized by conservative evaporation in the thin film evaporator[19] and selective extraction.[20,21] The isomeric composition of the unreacted and recycled TDI is different from TDI-80 due to the reactivity difference between 2,4-TDI and 2,6-TDI. In the new stage, isocyanate components consist
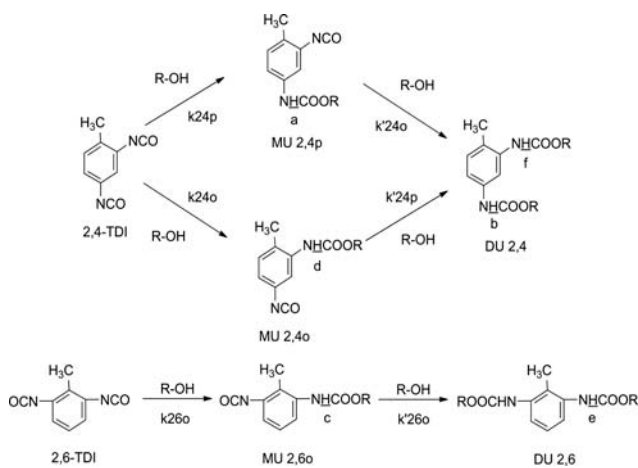
Scheme 1. Formation of isomeric MU and DU.

of recycled TDI and fresh TDI-80, but the TDI isomers ratio *R* is not the same as that in the previous stage although the stoichiometry and temperature remain the same. Moreover, it is well known that 2,6-TDI is more symmetric than 2,4-TDI, and the physical properties of polyurethane are highly dependent on the symmetric structure of hard segments.[22–24] Thus the uncontrollable TDI isomers ratio may give rise to an unstable process and uncontrollable polyurethane products.

In our previous study, we reported the structural investigations of TDI-TMP based polyurethane prepolymer, and the effect of separation process on the side reactions.[25] In this article, a new second order kinetic to this polymerization reaction of TDI over polyols by dropwise addition method was presented. We proposed a recycling mode of isomeric TDI and applied it to the chemical plant. The typical simplification was used as follows: the isocyanate groups only react with hydroxy groups. No side products, such as DU, allophanate and biuret are obtained in the reaction. Excess TDI and solvent could be completely removed in the separation process. The experimental data was compared with that calculated from a mass balance method and any deviations could be detected to optimize this procedure.

EXPERIMENTAL

Materials
TDI-100 (98% 2,4-TDI and 2% 2,6-TDI, Bayer Chemical), TDI-80 (80% 2,4-TDI and 20% 2,6-TDI), and TDI-65 (65% 2,4-TDI and 35% 2,6-TDI) were used as received from BASF Chemical without any purification. Trimethylolpropane (TMP) was purchased from Sigma Aldrich. Prior to the reaction, the residual water content of TMP was checked by Karl Fisher method and controlled to below 0.05%. Reagent grade butyl acetate was supplied by Guangzhou Chemical Reagent (Guangzhou, China). Methanol (chromatographic grade) was supplied by Sigma Aldrich.

Preparation of Polyurethane Prepolymer
Polymerizations were conducted in three-neck Pyrex reaction flasks equipped with an overhead stirrer, addition funnel, and nitrogen inlet. The polyurethane prepolymer was prepared at

three different ratios of NCO/OH = 2.4, 3, and 3.6. The mixture of TDI and butyl acetate was added into the flask under nitrogen atmosphere. TMP was melted and maintained at 120°C. After the reaction mixture was heated to the setting temperature, the melted TMP was added dropwise within 100 min. Further heating continued for 2 h to get complete conversion. The solid content was 50 wt %.

For characterization, samples were collected in a constant interval (20 min) during the addition period. Concentration of isocyanate groups was determined using backtitration method, note that unreacted TDI in the prepolymer also contributed to isocyanate groups. In addition, to determine the concentration of unreacted TDI isomers monomer, the methanol was employed to block all free NCO before employing high performance liquid chromatography (HPLC).

Measurements
Concentration of Isocyanate Groups. The isocyanate concentration was determined indirectly. The isocyanate compound reacted with a known excess of *n*-dibutylamine. Then the excess amine was back-titrated with standard HCl solution. The isocyanate concentration was calculated from the amount of *n*-dibutylamine consumed. The backtitration method could also be used to determine the amount of secondary products, when the obtained values were lower than the theoretical ones as calculated from the main reaction.

Concentration of Unreacted TDI Isomers. The HPLC method was employed to determine unreacted TDI isomers after derivatization with methanol. The diluted samples were analyzed by HPLC using an Agilent 1100 apparatus with an ultraviolet absorbance detector (254 nm). The fast conversion of methanol was used to end the reaction, this allowed more time to precisely determine the concentration of TDI isomers in the sample. The methanol derivatives of TDI were determined using gradient elution with a mobile phase of methanol-water (50 : 50%).

Fourier Transform Infrared Spectroscopy (FTIR) Analysis. The IR absorption spectra of prepolymer were taken after applying thin films on KBr crystals. A Spectrum 2000 from PerkinElmer (USA) was used.

^{1}H-NMR Analysis. ^{1}H-NMR (400 MHz) was recorded on a Bruker AVANCE Digital spectrometer [in DMSO-d_6, tetramethyl silane (TMS) as an internal standard]. Prepolymer (0.1 mL) was diluted with 0.6 mL of deuterated solvent.

RESULTS AND DISCUSSION
Reaction Kinetics
Polyurethane is generally synthesized by step-growth polymerization, which includes both one-shot method and prepolymer method. In one-shot method, all the reactants are mixed together and reacted in one step. The whole heat of reaction is evolved right away which elevates the temperature of the reaction mixture considerably. This method is simple, yet its applicability is limited as the properties of the products are inferior to polyurethane obtained from prepolymer method.[26,27]
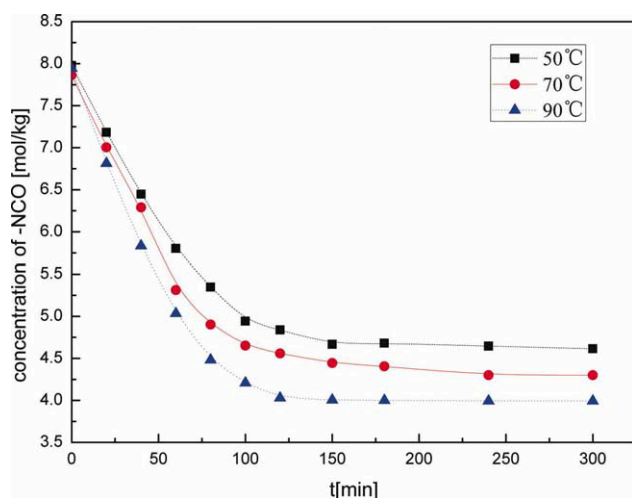
Figure 1. Reaction time dependent changes in the concentration of isocyanate groups at different temperatures, NCO/OH = 3; τ = 100 min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The reaction kinetics of polyurethane prepolymer with dropwise addition method is far more complicated than that with one-shot method. The concentration of all the reactive groups in the flask varies not only due to the consumption during the reaction, but also due to the variation of the total mass in the flask caused by addition of the polyol. It is significantly different from the same reaction with one-shot method that only consumption is responsible for the concentration of the reactive groups. The kinetic model can be described by the following rate equation:

$$-\frac{d[\text{NCO}]}{dt} = k[\text{NCO}][\text{OH}] \qquad (1)$$

where [NCO] is the momentary concentration of free isocyanate groups, [OH] is the momentary concentration of free hydroxyl groups, k is the experimental rate constant for the second order reaction, and t is the reaction time.

The total mass of the reagents in the flask increases continuously during addition polyol, and the momentary mass of the reagents depends on the total mass of the polyol and t.

$$m_r = m_{r0} + \frac{m_{\text{OH}}}{\tau} t \qquad (2)$$

where m_r is the momentary total mass of reagents in the flask, m_{r0} is the initial mass of TDI-80 and solvent charged in the flask, m_{OH} is the total mass of polyols predefined, and τ is the total time predefined to add the polyol, 100 min. It should be noted that the momentary ratio of NCO/OH for the reaction with dropwise addition method is extremely higher than that with one-shot method although the same recipe is employed. Accordingly, we simplified it as follows. All the polyol could react immediately with diisocyanate and be consumed completely after addition. Thus the momentary mass of the polyol in the flask is kept constant. However, the momentary concen-

tration of hydroxyl groups [OH] decreases continuously with increasing mass of the reagents in the flask.

$$[\text{OH}] = \frac{\frac{\alpha m_{\text{OH}}}{\tau M_{\text{polyol}}}}{m_r} = \frac{\alpha m_{\text{OH}}}{M_{\text{polyol}}(\tau m_{r0} + m_{\text{OH}} t)} \qquad (3)$$

where M_{polyol} is the molecular weight of the polyol, and α is the functionality of the polyol. Combining eqs. (1) and (3) to obtain the following equation:

$$-\frac{d[\text{NCO}]}{[\text{NCO}]} = \frac{\alpha k m_{\text{OH}} dt}{M_{\text{polyol}}(\tau m_{r0} + m_{\text{OH}} t)} \qquad (4)$$

which leads to the classical integrated expression, when $t = 0$, $[\text{NCO}] = [\text{NCO}]_0$.

$$\ln \frac{[\text{NCO}]_0}{[\text{NCO}]} = \frac{k\alpha}{M_{\text{polyol}}} \ln\left(1 + \frac{m_{\text{OH}}}{\tau m_{r0}} t\right) \qquad \text{when } t < \tau \qquad (5)$$

After the polyol was added completely, the total mass of reagents would be kept constant, and the kinetics study could be conducted in accordance with the conventional research using one-shot method.

According to the isocyanate concentration as determined by backtitration at different temperatures, a global reaction scheme is considered: $-\text{NCO} + -\text{OH} \rightarrow -\text{NHCOO}-$. The reaction can proceed for about 90% even at 50°C when the polyol is added completely, as shown in Figure 1. Figure 2 indicates that the kinetics of this system is well described by a second order equation. The most significant deviation is observed at higher reaction temperature (90°C). It could be attributed to an autocatalytic effect induced by the urethane functions or, alternatively, to the consumption of isocyanate groups by side reactions like the formation of urea and allophanates.[28,29] The break in the slope does not occur in this second order reaction system as Kothandaraman and Nasar[8–10] found. In the
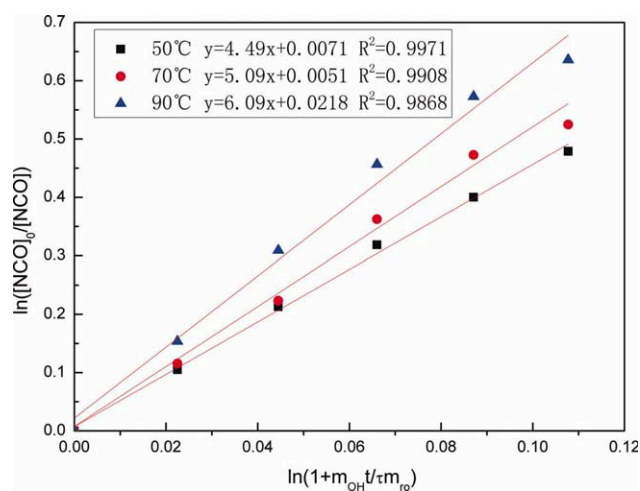
Figure 2. Second order plots for the reaction of TMP with TDI-80 in butyl acetate at different temperatures during addition process, NCO/OH = 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
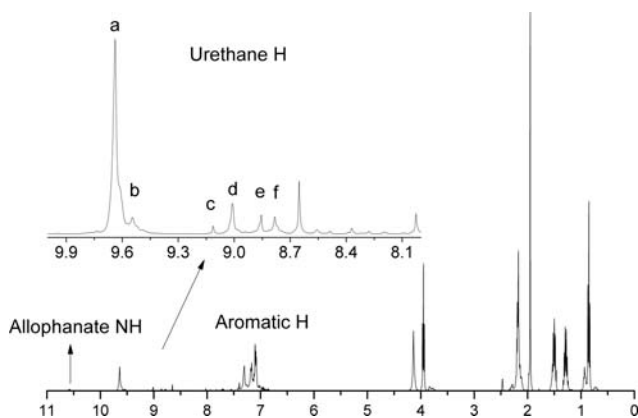
Figure 3. ^{1}H-NMR spectrum of TDI-TMP based polyurethane prepolymer prepared at 50°C, NCO/OH = 3.

Table I. Kinetic Constant of Polyurethane Prepolymer at Different Temperatures, NCO/OH = 3

T (°C)	Kinetic constant k (Kg mol^{-1} s^{-1})	Activation energy E_a (KJ mol^{-1})
50	0.201	7.35
70	0.227	
90	0.272	

nonstoichiometric polymerization reaction of polyol with a considerable excess of TDI, it seems that the para position isocyanate group in 2,4-TDI with high reactivity mainly contributes to the reaction with polyol. This speculation could be verified by NMR (Figure 3), urethane have unique resonances due to the nature of the degree of hydrogen bonding,[15,30] and the highest peak (a) representing MU 2,4p in Scheme 1 plays a dominant role in urethane oligomers.

The rate constants corresponding to eq. (5) are calculated at different temperatures (Table I). The activation energy E_a for the reaction is found graphically based on the Arrhenius equation:

$$\ln k = -\frac{E_a}{R_c T} + \ln A \qquad (6)$$

where T is the temperature, R_c is 8.314 J mol^{-1}K^{-1} the universal gas constant, and A is the frequency factor.

Effects of Temperature and NCO/OH Ratio

The kinetics research focuses on the variation of concentration of the isocyanate group during the global reaction. However,

the different reactivity of isocyanate group in TDI isomers and side reaction are responsible for the deviations from second order kinetics. The experimental data could be studied to minimize the undesirable chain extension and to recycle the excess TDI when compared with theoretically calculated data.

The spectrum in Figure 4 exhibits the chemical structure of TDI-TMP based polyurethane prepolymer. The characteristic bands at 1714 and 3319 cm^{-1}, arising from stretching vibration of carbonyl and imine groups, respectively, confirm the presence of urethane group.[31,32] The band at 2293 cm^{-1} that represents asymmetrical stretching vibrations of isocyanate groups is the most specific band for isocyanate terminated oligomers. The extra band at 3412 cm^{-1} represents unreacted hydroxyl group, even in the presence of excess TDI. This result could be attributed to the presence of steric hindrance in TMP.[33]

To put considerable limitations to molecular weight and monodispersity of polyurethane prepolymer, we chose the initial NCO/OH ratio ranging from 2.4 to 3.6 for experiments. The isocyanate concentration mainly contains two parts. One is provided by the isocyanate groups in the polyurethane oligomers, another one is provided by the unreacted TDI isomers, and the amounts of unreacted TDI isomers could be determined by HPLC method. Thus the concentration of isocyanate groups in the polyurethane oligomers could be calculated by combining HPLC and backtitration method together. The effects of NCO/OH and temperature on the composition of the prepolymer are
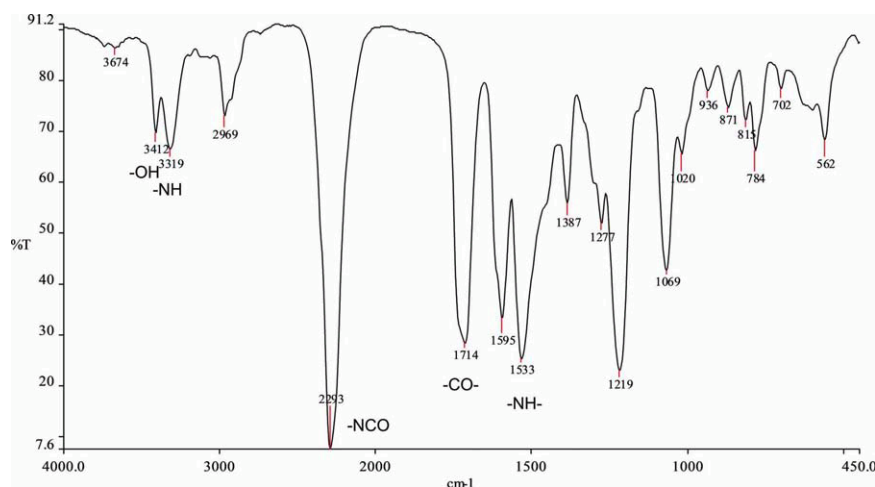
Figure 4. FTIR spectrum of TDI-TMP based polyurethane prepolymer prepared at 50°C, NCO/OH = 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Effect of NCO/OH on the Composition of Polyurethane Prepolymer at 50°C

NCO/OH	2.4	3	3.6
Concentration of total —NCO groups as experimented (%)	14.74	19.18	24.72
Concentration of total —NCO groups as calculated (%)	13.41	19.24	24.99
Unreacted TDI concentration as experimented (%)	11.39	20.01	31.45
Unreacted TDI concentration as calculated (%)	7.87	19.96	31.87
Concentration of —NCO groups in MU as experimented (%)	9.24	9.51	9.53
Concentration of —NCO groups in MU as calculated (%)	9.60	9.60	9.60
Isomers reaction constant β	8.74	9.63	12.22

presented in Tables II and III, respectively. We introduce three parameters, one is isomers reaction constant $\beta = \frac{m_{2,4-TDI_0} - m_{2,4-TDI}}{m_{2,6-TDI_0} - m_{2,6-TDI}}$, which reflects the reactivity difference between 2,4-TDI and 2,6-TDI, where $m_{2,4-TDI_0}$ and $m_{2,6-TDI_0}$ are the mass of 2,4-TDI and 2,6-TDI in the initial diisocyanate components comprising TDI-80 and recycled TDI (if used), respectively. $m_{2,4-TDI}$ and $m_{2,6-TDI}$ are the mass of excess 2,4-TDI and 2,6-TDI in polyurethane prepolymer, respectively. The higher this value is, the more significantly reactivity difference between TDI isomers displays. Another two $R = \frac{m_{2,4-TDI_0}}{m_{2,6-TDI_0}}$ and $r = \frac{m_{2,4-TDI}}{m_{2,6-TDI}}$ represent the TDI isomers ratio of initial diisocyanate components and of excess TDI in polyurethane prepolymer, respectively. When NCO/OH ratio is 2.4, the concentration of isocyanate groups in MU (only MU is considered in polyurethane prepolymer) determined is lower than that calculated theoretically due to steric hindrance of TMP. It also could be confirmed by a higher concentration of unreacted TDI determined compared with that calculated theoretically. With increasing initial ratio of NCO/OH, the concentration of isocyanate groups in MU increases at the expense of an increase in the content of unreacted TDI. The quantitative results agree with that reported in previous study.[18] In addition, the concentration of isocyanate groups in MU and unreacted TDI decreases rapidly at higher temperature, confirming the formation of side products, such as urea and allophanate. The reactivity difference between 2,4-TDI and 2,6-TDI reduces with increasing temperature as β decreases. The optimal condition we choose is NCO/OH = 3 at 50°C by comparing the deviations between experimental data and theoretically calculated data. The subsequent experiments were carried out at the same temperature and initial NCO/OH, but different R was employed using different types of commercial TDI.

Effect of TDI Isomeric Ratio R

The isomers ratio R of TDI-80 is 80/20 = 4 according to the definition. The isomers ratio r of excess TDI is < 4 since the reactivity of 2,4-TDI is significantly higher than 2,6-TDI. If the excess TDI are reused completely, R would be also < 4 in the new stage. Three standard commercial TDI with different R were used to study the effect of R on the composition of the prepolymer. It is interesting to see that the concentration of isocyanate groups and unreacted TDI are almost the same for three commercial TDI, as shown in Table IV. Obviously, there is a competitive reaction between 2,4-TDI and 2,6-TDI. Consequently, the amount of total unreacted TDI is independent of R and remains constant to be recycled. However, the TDI isomers ratio varies, for example, when TDI-80 ($R = 4$) is replaced by TDI-65 ($R = 1.86$), the content of 2,6-TDI with low reactivity increases, and then β decreases from 9.63 to 3.52. We can indicate that if β could be kept constant at 4, R and r also could be constant. In other words, hydroxyl groups could completely react with isocyanate groups provided by fresh TDI 80, and excess TDI acts as a "catalyst." This "catalyst" is recycled continuously in the stable stage. Finally, the properties of polyurethane prepolymer and amounts of TDI isomers could be stable.

When TDI-65 is employed in the reaction, β is equal to 3.52. To obtain β of 4, R should be predefined between TDI-80 and TDI-65, that is, 4 and 1.86. It could be realized through mixing different amounts of TDI-80 and TDI-65. Figure 5 represents the effect of R on β in the same optimal condition (NCO/OH = 3; 50°C). We find that when $R = 2.07$; $\beta = 4$, and then excess TDI isomers could be recycled steadily. In this stable stage, the competitive reaction between 2,4-TDI and 2,6-TDI with polyols was followed by determining the amounts of 2,4-

Table III. Effect of Temperature on the Composition of Polyurethane Prepolymer, NCO/OH = 3

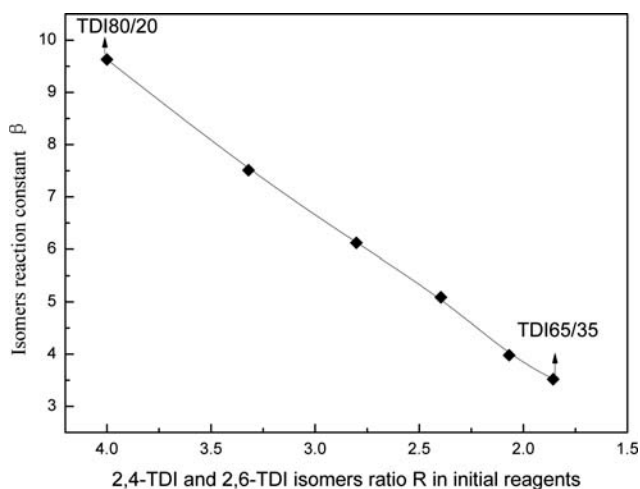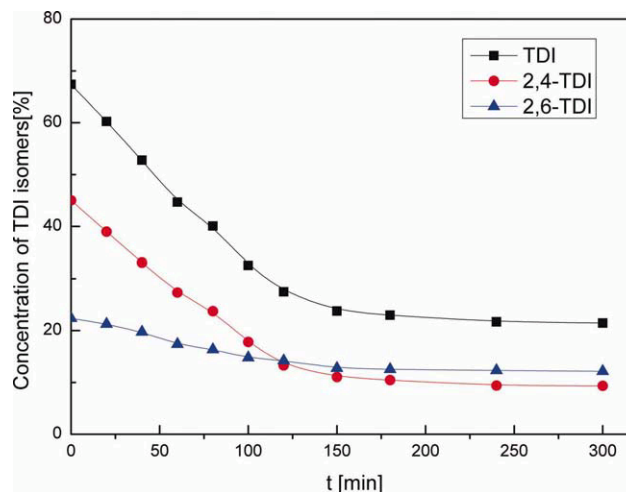| Temperature (°C)	50	70	90
Concentration of total —NCO groups as experimented (%)	19.18	18.06	16.77
Concentration of total —NCO groups as calculated (%)	19.24	19.24	19.24
Unreacted TDI concentration as experimented (%)	20.01	18.17	17.21
Unreacted TDI concentration as calculated (%)	19.96	19.96	19.96
Concentration of —NCO groups in MU as experimented (%)	9.51	9.28	8.46
Concentration of —NCO groups in MU as calculated (%)	9.60	9.60	9.60
Isomers reaction constant β	9.63	7.98	7.33

Table IV. Effect of TDI Isomer Ratio on the Composition of Polyurethane Prepolymer with Three Commercial TDI

Isomers ratio R in initial reagents	TDI 100	4 (TDI 80)	1.86 (TDI 65)
Concentration of total —NCO groups as experimented (%)	19.14	19.18	19.35
Concentration of total —NCO groups as calculated (%)	19.24	19.24	19.24
Unreacted TDI concentration as experimented (%)	19.95	20.01	20.58
Unreacted TDI concentration as calculated (%)	19.96	19.96	19.96
Concentration of —NCO groups in MU as experimented (%)	9.50	9.51	9.41
Concentration of —NCO groups in MU as calculated (%)	9.60	9.60	9.60
Isomers reaction constant β		9.63	3.52

TDI and 2,6-TDI in polyurethane prepolymer, as shown in Figure 6, and r could be calculated ($r = 0.74$). The calculation of mass balance in the stable stage is shown (Figure 7), the unreacted TDI ($r_m = 0.74$) generated in the stage m is recycled and mixed with fresh TDI-80 to constitute the TDI components in the stage $m + 1$, and its isomer ratio R_{m+1} of 2.07 is the same as R_m in the previous stage, thus the polyurethane prepolymer synthesized is stable.

**Recycling Model of Excess TDI Isomers in the Chemical Plant**
The raw materials used in the chemical plant to synthesis polyurethane prepolymer consist of TDI-80, TMP, and solvent. The idea of such a process to recycle excess TDI isomers is presented in Scheme 2. In the first stage, all the raw materials are employed and $R_1 = 4$. The value of β and r could be calculated according to the curve given in Figure 5. It is assumed that unreacted TDI ($r_1 = 1.43$) and solvent could be completely separated by means of extraction or distillation to be recycled for the next stage. Polyurethane prepolymer could then be further reacted, that is, extended to form linear polyurethanes with narrow molecular weight distribution and subjected to yield elastomers or foamed plastics. In the following stage, no extra solvent is required to add but polyols and fresh TDI-80. In the stage II, TDI components consist of recycled TDI generated in the stage I and fresh TDI-80, and the value of $R_2 = 2.70$. After several reaction processes, the concentration of 2,4-TDI and 2,6-TDI are kept constant at the Stage V, the stable stage as discussed in


Figure 6. Variation of 2,4-TDI and 2,6-TDI concentration in the stable stage at optimal condition. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the previous section. In the global loop, the polyols and TDI-80 react continuously, while polyurethane prepolymer are synthesized without extra solvent and diisocyanate monomer simultaneously. An environment friendly process to recycle excess TDI isomers has been developed and all the chemicals are effectively used.

CONCLUSIONS

The reaction between TDI and polyols agreed with a second order equation by means of dropwise addition method. The chemical structure of the polyurethane prepolymer could be tailored with an increase in the initial ratio of NCO/OH. The NCO/OH ratio of 3 and the reaction temperature of 50°C were chose as the optimal condition. The reactivity difference between 2,4-TDI and 2,6-TDI was responsible for the composition of excess isomeric TDI. The results indicated that when R

Figure 5. Effect of isomers ratio R of 2,4-TDI and 2,6-TDI on isomers reaction constant β at optimal condition.
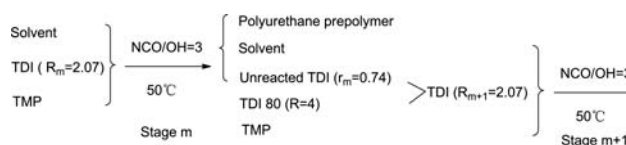
Figure 7. Calculation of mass balance in the preparation of polyurethane prepolymer in the stable stage at optimal condition.
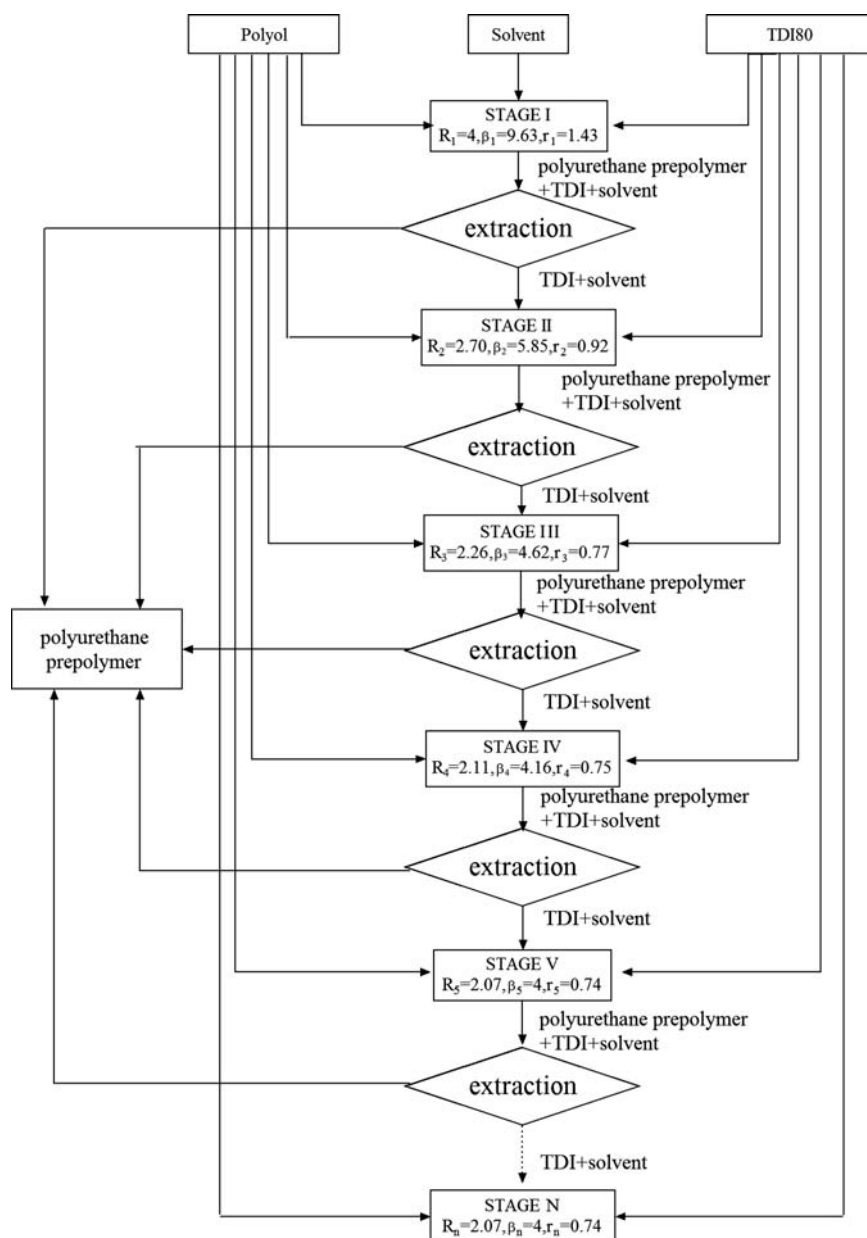
Scheme 2. Recycling model of isomeric TDI for preparing polyurethane prepolymer.

was 2.07, the TDI isomers could be recycled steadily and r was 0.74. The recycling model was established for chemical plant to produce polyurethane prepolymer with excellent properties. However, low levels of residual TDI would be contained in polyurethane prepolymer using extraction or distillation method. The composition of TDI isomers may be fluctuated in the process. Then the recipe should be modified according to the curve in Figure 5.

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