



Structural investigations of toluene diisocyanate (TDI) and trimethylolpropane (TMP)-based polyurethane prepolymer

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ABSTRACT

Polyurethane prepolymer prepared from nonequivalent amounts of toluene diisocyanate (TDI) over trifunctional trimethylolpropane (TMP) was followed by gel permeation chromatography (GPC). Steric hindrance of TMP was considered as the main factor affecting the molar mass distribution, especially in the higher molecular weight region. An optimum reaction condition was the initial NCO/OH ratio of 3 and the reaction temperature of 50 °C. Then polyurethane prepolymer could be purified through the thin film evaporator with excellent properties. A combination of mass spectrometry (MS) and ¹H nuclear magnetic resonance (NMR) spectroscopy was employed to identify and confirm the individual compounds presented from GPC analysis.

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1. Introduction

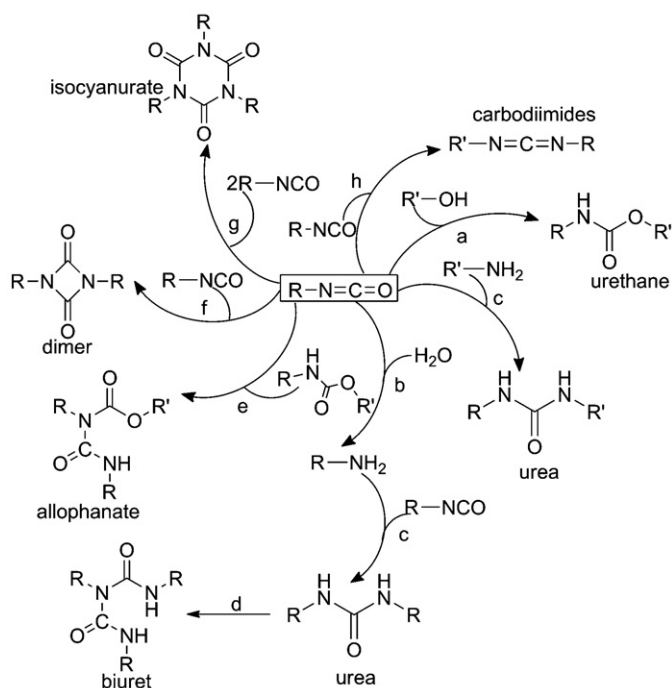
Isocyanate terminated polyurethane prepolymer is widely used in the preparation of high performance coatings [1,2], paints [3], decorative architectural components, sports device and household goods [4,5]. The versatile polyurethane chemistry provides these products with outstanding properties of hot melt adhesives, compatibility with different components, excellent thermal and mechanical properties [6–8].

Polyurethane prepolymer can be synthesized by the reaction between diols or polyols and stoichiometric excess of diisocyanate. Multifunctional polyols are incorporated into the backbone chain as branching and chain extending agents. Several studies have been carried out to understand the reactivity of hydroxyl groups. Typically, secondary hydroxyl group exhibits significant lower reactivity than primary hydroxyl group [9–11]. In addition, the reactivities among three same primary hydroxyl groups of trifunctional polyols are also different, and the reaction constant decreases with a higher substitution degree of polyols [12,13]. Steric hindrance is found to be the main problem associated with the reactivity differences of hydroxyl groups in reactions with isocyanate terminated compounds. This generally yields different polymeric structures and therefore influences the physical properties of the final polyurethane products. Understanding the relationships between steric hindrance and chemical structure is necessary to tailor material performance.

Prepolymer synthesis method is employed at the expense of an increase in the concentration of excess diisocyanate [14]. It should be removed due to its toxicity and negative impact on the properties of polyurethane products [15]. Conservative evaporation in the thin film evaporator under high vacuum and high temperature conditions is considered as an effective technique to tackle this problem [16]. However, side reactions occur seriously at higher temperature in the separating process, consequently, and result in urea, biuret or allophanate. The possible reactions are shown in Scheme 1. These reactions affect the molar mass distribution and final product properties such as curing dynamics and mechanical properties of segmented polyurethane in various ways [17,18]. The chemical structure of polyurethane prepolymer has been extensively studied by several techniques such as gel permeation chromatography (GPC) [19–23], nuclear magnetic resonance (NMR) spectroscopy [14,24,25] and mass spectrometry (MS) [26–28]. It is essential to thoroughly investigate the mechanism of urethane reactions and other side reactions to control the properties of the resulting polyurethane products, and most importantly, to obtain polyurethane prepolymer which could be purified through the thin film evaporator.

In this study, the solution polymerization between toluene diisocyanate (TDI) and TMP was carried out at temperatures ranging from 50 to 90 °C, these temperatures were chosen since they corresponded to the range generally used in polyurethane synthesis without catalyst as well as having considerably reactivity difference for diisocyanate. To prepare polyurethane prepolymer with a narrower distribution of molecular weight [15,29,30], the nonequivalent initial ratio of NCO/OH varied from 2.4 to 3.6. We first optimized the reaction conditions to yield any appreciable

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Scheme 1. Possible reactions of isocyanate with different reactants.

amounts of side reactions in a prepolymer system which could be purified successfully in the thin film evaporator. GPC was then used to identify different components in the polyurethane prepolymer system and obtain quantitative results. Finally, a combination of MS and ^1H NMR was utilized to verify the results from GPC to make a good understanding of the mechanism of urethane reactions and side reactions.

2. Experimental

2.1. Materials

TDI-80 (80% 2,4-TDI and 20% 2,6-TDI) was kindly provided by BASF Chemical without any purification. 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 and methanol were supplied by Sigma–Aldrich and used as received.

2.2. Synthesis of polyurethane prepolymer

The polyaddition process was initiated by a reaction which proceeded in the presence of excess TDI-80. The reaction was carried out at three different ratios of $\text{NCO}/\text{OH} = 2.4, 3$ and 3.6 . The reaction was performed under nitrogen atmosphere to avoid any moisture. TDI-80 and butyl acetate were charged into a four-necked flask equipped with a mechanical stirrer and reflux condenser. TMP was melted and maintained at $120\text{ }^\circ\text{C}$. 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 about 50 wt%.

For characterization, the mixture was stored under inert atmosphere. The methanol was employed to block all free NCO preventing further chemical reactions in the solutions for high performance liquid chromatography (HPLC), GPC and MS analysis.

2.3. Analytical methods

2.3.1. Concentration of unreacted isomeric TDI

The HPLC method was utilized to determine unreacted TDI after derivatization with methanol. The diluted samples were analyzed 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 unreacted TDI in the sample. The methanol derivatives of TDI were determined using gradient elution with a mobile phase of methanol–water (50%:50%).

2.3.2. Gel permeation chromatography analysis

GPC analysis was performed on a Waters Breeze system equipped with a 515 pump, a Refractive Index Detector and Styragel HMW2 columns ($20\text{ }\mu\text{m}$, $300\text{ mm} \times 7.8\text{ mm}$) with THF as solvent at a flow rate of 1 mL/min at $35\text{ }^\circ\text{C}$. The chromatograph operation was controlled by Chromatography Software Version 3.30, which was also used for the interpretation of the elution curves obtained and for converting them into differential molecular weight distribution curves. The calibration function was used for that purpose: $\log M = -0.2005t + 8.2517$. All samples were prepared with a concentration of 30 mg prepolymer/10 mL THF.

2.3.3. MS analysis

Applied Biosystems–MDS SCIEX API 3200TM—triple quadrupole system equipped with a Turbo VTM Ion SprayTM source under the following operational parameters: source temperature, $590\text{ }^\circ\text{C}$; polarity, positive ion mode; Curtain GasTM, 10.0 psi; ion spray voltage, 5500 V; declustering potential, 50 V; entrance potential, 10 V. The electrospray ionization (ESI) technique was used. The flow rate of the mobile phase methanol was 1 mL/min. Only the positive ion mode was employed within the range of 100–2000 M/z. The samples were diluted with methanol to the concentrations of 10 mg/mL.

2.3.4. 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.

2.3.5. ^1H -NMR analysis

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

3. Results and discussion

3.1. Effect of different amounts of TMP on TDI–TMP based polyurethane prepolymer

Following the idea of Scheme 2, TDI–TMP based polyurethane prepolymer obtained by step growth polymerization should initially be mixtures of excess TDI, TMP–TDI, TMP–2TDI, TMP–3TDI, 2TMP–5TDI and 3TMP–7TDI. And after passing through the thin film evaporator, they should be mixtures of predominately urethane oligomers without TDI. Therefore, it is necessary to identify every individual component with GPC.

From the GPC chromatogram (Fig. 1), during the step growth polymerization different TDI–TMP based oligomers are formed. The main product is TMP–3TDI at 25.9 min, and the peaks at 26.5 and 27.6 min correspond to TMP–2TDI and TMP–TDI, respectively. In addition, higher molar mass oligomers are presented, such as 2TMP–5TDI at 24.7 min and 3TMP–7TDI at 24 min. As expected,

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