The effect of reaction conditions on the urethane prepolymer formation

Tzong-Liu Wang[1,*] and Donald J. Lyman[2]

[1]Department of Chemical Engineering, National Tsing-Hua University, Hsinchu, Taiwan 30043, China
[2]Department of Materials Science and Engineering, University of Utah, Salt Lake City, UT 84112, USA
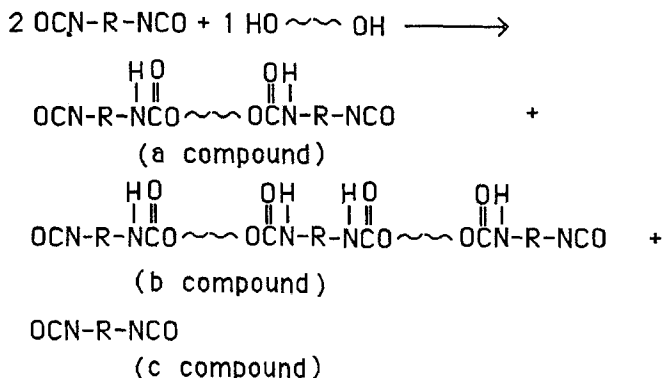
Summary
    In the two step synthesis of urethane copolymers, most statements from the literature assume that all of the diisocyanate will be used up in the formation of the isocyanate-endcapped polyol. However, a computerized simulation indicated the formation of three kinds of product.
    Synthetic experiments were conducted to study the first step of this reaction. It was found that not all of the intermediates reacted in the first step of the synthesis. Some diisocyanate remained unreacted and a polyol dimer was formed. Two different polyols were used in this study. When a polyol has primary hydroxyl groups on each end, more unreacted diisocyanate was present at the completion of the reaction than when the polyol has a primary and a secondary hydroxy end. The investigation of the solvent effect revealed that the solvent used had little effect on the prepolymer formation. The study of the temperature effect showed that more unreacted diisocyanate was obtained at the higher temperature for the 4,4'-diphenylmethane diisocyanate/polytetramethylene glycol reaction.

Introduction
    In the preparation of urethane copolymers by the diisocyanate-diol route the polymerization can be conducted as a one-step or a two-step process (1-4). In the two-step process, the first step is to form a prepolymer by reacting two moles of diisocyanate with one mole of polyol in the presence or absence of solvent. The prepolymer formed by this reaction is called the isocyanate-endcapped polyol. This is then chain extended by reaction with a diol or diamine in the second step.
    The general literature assumes that two moles of diisocyanate will react completely with one mole of macrodiol prepolymer to form an isocyanate-endcapped polyol (3-7). However, computer studies by Peeble indicated that not all of the intermediates should react in the first step of the synthesis (8,9). According to his computer simulated reactions, three kinds of products will be formed in this reaction. The reaction equation is as follows :

$$2\ \text{OCN-R-NCO} + 1\ \text{HO} \sim\!\sim \text{OH} \longrightarrow$$

$$\text{OCN-R-}\overset{H}{\underset{}{N}}\overset{O}{\underset{}{C}}\text{O}\sim\!\sim\text{O}\overset{O}{\underset{}{C}}\overset{H}{\underset{}{N}}\text{-R-NCO} \qquad +$$

(a compound)

$$\text{OCN-R-}\overset{H\ O}{N C}\text{O}\sim\!\sim\text{O}\overset{O\ H}{C N}\text{-R-}\overset{H\ O}{N C}\text{O}\sim\!\sim\text{O}\overset{O\ H}{C N}\text{-R-NCO} \quad +$$

(b compound)

$$\text{OCN-R-NCO}$$

(c compound)

Indeed, depending on the reactivity ratio of the first reaction rate constant of an isocyanate group to the second reaction rate constant for a number of diisocyanate with two aliphatic alcohols, the amount of free diisocyanate (i.e., c compound) could range from 0% to 35.65%. This could lead to complication in the chain extension step and possibly influence the block copolymer morphology.

In addition, if the segments vary in length because of the irregularities in the synthesis suggested by the computer simulation, i.e., soft segments of both a and b compounds being present and the hard segment having a broad length distribution, phase separation will also be greatly affected.

It is important to study the reaction conditions of diisocyanate with the polyol and find the degree of variation from the pure compound (i.e., a compound) that researchers have assumed formed in the first step of the synthesis. The purpose of this research work was to determine how the reaction conditions (solvent, temperature, etc.) affects the prepolymer formation. In this study, solvent and temperature effects were investigated and two kinds of polyether diols, polypropylene glycol (PPG) and polytetramethylene glycol (PTMG), were used.

Experimental

Isocyanate-endcapped polyol prepolymers were synthesized by the reaction of two moles of diisocyanate with one mole of the macrodiol. The procedure for the synthesis of prepolymer #1 are described below.

1000 MW polypropylene glycol (PPG) polyol (0.02 mole) and 70 ml of a 50/50 mixture of dimethyl sulfoxide (DMSO) and methyl isobutyl ketone (MIBK) were placed in a dry, 250 ml two-necked, round-bottomed flask equipped with a stirrer, condenser fitted with drying tube and thermometer. To this stirred solution was added 0.04 mole of 4,4'-diphenylmethane diisocyanate (MDI). The flask was flushed with a slow stream of nitrogen during the addition. The reaction was then heated and stirred at 85°C for 3 hours. The reaction mixture was then cooled to room temperature in preparation for the quenching step.

To study the effect of reaction conditions (polyol, solvent, temperature) on the prepolymer formation, different prepolymers were synthesized in a similar way except for the conditions listed below.

	Reaction Conditions		
Prepolymer	Polyol	Solvent	Temperature
#2		No	
#3			100-105 °C
#4	PTMG (MW 1000)		
#5	PTMG (MW 1000)	No	
#6	PTMG (MW 1000)		100-105 °C

The model compound of N,N'-(methylene di-4,4'-phenylene) bis (N"-diphenyl urea) was prepared by reacting MDI with an excess of aniline in a 50/50 mixture of DMSO/MIBK. The precipitate was recrystallized from DMSO to give a white crystalline powder, melting with degradation at 303-305 °C.

To assist in the isolation of products formed in the endcapped prepolymer preparation, the reaction was quenched with an excess of a monoamine (aniline) to form the corresponding urea compounds. To the above cooled and stirred prepolymer solutions, a solution of 0.08 mole (the actual reacted amount was 0.04 mole) aniline (AN) in 20 ml of a 50/50 mixture of DMSO and MIBK was added. The reaction was continued for 1 hour at room temperature with stirring. The urea-endcapped polyethers were formed during this step. Excess solvent and aniline were then removed by rotary evaporation at 40°C and 2.5 mmHg .

The pot residue from the MDI/PPG reaction with AN formed a yellow solid after removal of the solvent. The pot residue from the MDI/PTMG reaction with AN formed a light brown solid. The residual aniline in the pot residue was removed by washing with 150 ml , 40 °C warm water several times. The pot residues were then extracted with diethyl ether using soxhlet extractors. The resulting precipitates from the thimbles were recrystallized from DMSO. Infrared studies and melting point measurements indicate that these precipitates were similar to the model compound. Two ether layers formed in the flask and were separated. Each gave a brownish viscous oil on evaporation of the ether. Analysis of the infrared spectra showed that the lower layer material had a stronger urethane amide I absorption peak relative to the urea Amide I absorption peak than did the upper layer material. This would indicate that the upper layer material was the dimeric end-capped diol; the lower layer was the monomeric end-capped diol. Thus, after quenching with aniline, the major products were:

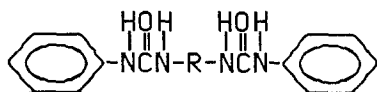(1) the end-capped mono-soft segment (A compound)
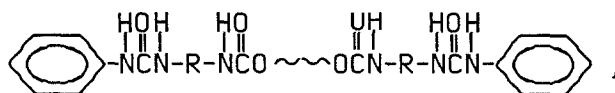
(2) the end-capped dimeric soft segment (B compound)
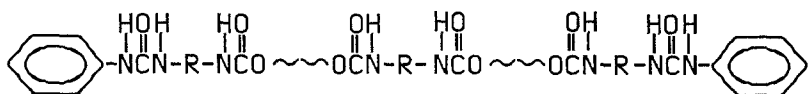
and
(3) the diurea formed from unreacted diisocyanate (C compound)

<u>Results and Discussion</u>
1. Polyol Effect (Prepolymer #1 and #4)
   From the experiments, diurea aniline derivatives of the diisocyanate were obtained, indicating that not all of the diisocyanate was consumed in the first step synthesis. Indeed, products other than the endcapped polyol were found, i.e., unreacted diisocyanate and an endcapped " dimer " of the polyol. This lack of purity will result in the copolymer having non-uniform hard and soft segments after the chain extending stage of the copolymerization. The product distribution for the MDI/PPG and the MDI/PTMG reactions with AN are shown in Tables I and II, respectively.
   In addition, based on the two moles of MDI and one mole of polyol, the molar percentage of A, B and C type compounds can be obtained. Thus, the first step reaction can be rewritten as follows:

Table I: The Product Distribution of Urea-Endcapped Polyethers
for MDI + PPG with AN after Normalization

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)		Molar Percent of Sample (%)	
A Compound	1674.58	(1)[a]	11.29	(1)	56.45
		(2)	11.17	(2)	55.85
B Compound	2912.64	(1)	4.35	(1)	21.75
		(2)	4.41	(2)	22.05
C Compound	436.52	(1)	4.35	(1)	21.75
		(2)	4.41	(2)	22.05

a. (1) and (2) indicate reactions run in duplicate.

Table II: The Product Distribution of Urea-Endcapped Polyethers
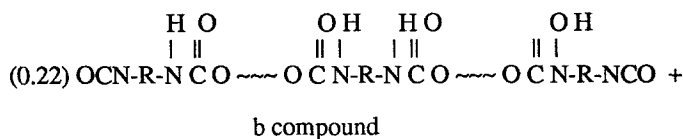for MDI + PTMG with AN after Normalization

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)		Molar Percent of Sample (%)	
A Compound	1717.18	(1)[a]	10.29	(1)	51.45
		(2)	10.25	(2)	51.25
B Compound	2997.84	(1)	4.86	(1)	24.30
		(2)	4.88	(2)	24.40
C Compound	436.52	(1)	4.86	(1)	24.30
		(2)	4.88	(2)	24.40

a. (1) and (2) indicate reactions run in duplicate.

(1) MDI with PPG:

2 OCN-R-NCO + 1 HO ~~ OH ------------>

<pre>
                   H O   O H
                   | || || |
(0.56 ~ 0.57) OCN-R-N C O ~~~ O C N-R-NCO   +
</pre>

           a compound

```
            H O          O H   H O          O H
            |  ||         || |   |  ||        || |
(0.22) OCN-R-N C O ~~~ O C N-R-N C O ~~~ O C N-R-NCO  +
```

b compound

(0.22) OCN-R-NCO

c compound

(2) MDI with PTMG:

2 OCN-R-NCO + 1 HO ~~ OH ------------>

```
               H O          O H
               |  ||         || |
(0.51~0.52) OCN-R-N C O ~~~ O C N-R-NCO   +
```

a compound

```
            H O          O H   H O          O H
            |  ||         || |   |  ||        || |
(0.24) OCN-R-N C O ~~~ O C N-R-N C O ~~~ O C N-R-NCO  +
```
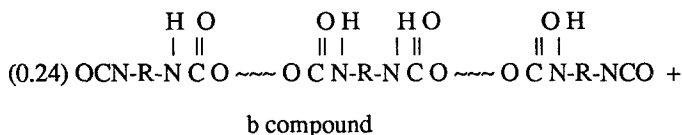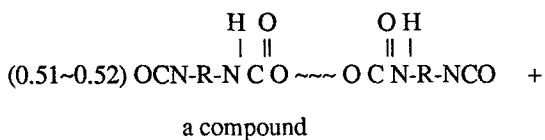
b compound

(0.24) OCN-R-NCO

c compound

The computer simulation studies by Peeble would suggest that in the reaction of two moles of MDI with one mole of PTMG, about 0.306 mole of unreacted MDI would be present at the end of the first step of the synthesis (8). From actual experiments, it was found that the amount of unreacted MDI was about 0.240 mole. When PPG was substituted for PTMG, less B and C type compounds were formed. Dyer and co-workers investigated the reaction of primary and secondary butanols with phenyl isocyanate and found that the primary alcohol reacted three times as fast as the secondary alcohol (10), and Wissman reported that the rate of the uncatalyzed reactions for the poly (oxyethylene) glycol containing primary hydroxyl groups was found to be twice that of the polyethers containing predominantly secondary hydroxyl groups (e.g., propylene glycol) (11). Thus, primary hydroxyl groups of the polyether react more rapidly with diisocyanate than do secondary hydroxyl groups and therefore would affect the distribution of product (12). In both systems, it was found that the monomeric A-type compounds were present in larger amounts and thus in higher molar concentrations than the dimeric B-type compounds. Furthermore, when the polyol was PTMG, a higher molar percent of B-type compounds was formed.

2. Solvent effect (Prepolymer #2 and #5)

To determine the effect of solvent, the synthesis of the isocyanate-endcapped polyol (the first step) was conducted at 85-90 °C without solvent present. The product distribution for the MDI/PPG and the MDI/PTMG reactions with AN are shown in Tables III and IV, respectively. The results indicated that elimination of the solvent had little effect on the prepolymer formation in either the PPG or the PTMG end-capping reactions.

Table III : The Product Distribution of Urea-Endcapped Polyethers
for MDI + PPG with AN after Normalization (No Solvent)

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)	Molar Percent of Sample (%)
A Compound	1674.58	11.52	57.60
B Compound	2912.64	4.24	21.19
C Compound	436.52	4.24	21.19

Table IV : The Product Distribution of Urea-Endcapped Polyethers
for MDI + PTMG with AN after Normalization (No Solvent)

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)	Molar Percent of Sample (%)
A Compound	1717.18	10.38	51.90
B Compound	2997.84	4.81	24.05
C Compound	436.52	4.81	24.05

3. Temperature effect (Prepolymer #5 and #6)

To determine the effect of temperature on the prepolymer formation, the reactions were conducted at both 85-90 °C and at 100-105 °C. The results are tabulated in Tables V and VI. In the case of MDI/PPG reactions, the results show that no distinct difference was observed for the product distribution at the two reaction temperatures (Tables I and V). In contrast, the MDI/PTMG reactions, the results show that more unreacted diisocyanate was obtained at the higher temperature as compared to the result from the normal temperature synthesis (Tables II and VI).

Thus, if PPG is reacted with MDI, the product distribution is similar up to a reaction temperature of 105 °C. However, when PTMG is the polyol, a higher amount of unreacted diisocyanate and dimer soft segment will be present at the higher reaction temperature. This would lead to a more polydisperse structure for the PTMG urethane copolymers synthesized at higher temperatures.

Table V : The Product Distribution of Urea-Endcapped Polyethers
for MDI + PPG with AN after Normalization (High Temp.)

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)	Molar Percent of Sample (%)
A Compound	1674.58	11.42	57.10
B Compound	2912.64	4.29	21.45
C Compound	436.52	4.29	21.45

Table VI : The Product Distribution of Urea-Endcapped Polyethers
for MDI + PTMG with AN after Normalization (High Temp.)

Sample	Molecular Weight (g)	No. of Moles of Sample (x 10^3)	Molar Percent of Sample (%)
A Compound	1717.18	7.19	35.95
B Compound	2997.84	6.41	32.03
C Compound	436.52	6.41	32.03

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