Effect of Urea Groups on Reaction Kinetics of Polyurethane Formation

NING LUO, DE-NING WANG, and SHENG-KANG YING*

Institute of Material Science and Engineering, East China University of Science and Technology, Shanghai 200237, People's Republic of China

SYNOPSIS

Urea-containing polyurethane reaction systems, based on ethylene oxide-capped poly(propylene oxide) polyether diol, 1,4-butyldiol, uretonimine liquefied 4,4'-diphenylmethane diisocyanate, and a biurea compound, were used to investigate the effect of urea groups on polyurethane bulk polymerization by using Fourier transform infrared spectroscopy. The biurea compound was a liquid biurea-capped poly(propylene oxide) polyether, which can mix well with the polyurethane systems. Catalysis of urea groups was observed clearly regardless of whether organotin catalyst was used. A catalytic mechanism was presented in this paper. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Product catalysis in isocyanate-amine reactions were reported by Baker and Bailey,¹⁻³ that is, the urea product is an effective catalyst for the ureaformation reactions. Although a second-order model was used to describe the reaction kinetics of polyurea formation as well,⁴⁻⁶ it is generally accepted that the second-order kinetic behavior was deviated due to the urea product catalysis.^{1-3,7,8} The product-catalytic effect of urethane groups in the reaction between isocyanate and alcohol (as measured by disappearance of isocyanate) was observed previously by Okada and Iwakura⁹ and Sato,¹⁰ but urethane product is a very weak catalyst in the isocyanatealcohol reaction and hardly affects the second-order kinetics of polyurethane formation.

In the preparation process of poly(urethane urea), especially in reaction injection molding of poly-(urethane urea), urea and urethane groups form almost simultaneously, so the information about effect of urea groups on reaction kinetics of polyurethane formation are necessary for thoroughly understanding the poly(urethane urea) polymerization. According to previous studies,¹⁻¹⁰ a catalysis of urea groups on polyurethane formation in poly(urethane urea) polymerization can be inferred reasonably. However, no detailed experimental information is available in the literature. One possible difficulty in experimental design is that almost all the common low-molecular-weight urea compounds are insoluble in commercial polyurethane systems.

In the present work, urea-containing polyurethane reaction systems were designed to investigate the effect of urea groups on polyurethane formation. The urea groups were supplied by a biurea compound containing a long polyether chain that is analogous to the polyether segments in the polyurethane, so the compound can mix well with the polyurethane system throughout the reaction.

EXPERIMENTAL

Raw Materials

Ethylene oxide-capped poly(propylene oxide) diol (PPO, ZS-2185, content of ethylene oxide = 15%, $M_n = 2000$, Jinling Petrochemical Industry Corp.) was dehydrated at 40°C under vacuum for more than 24 h before use. Uretonimine liquefied 4,4'-diphenylmethane diisocyanate (L-MDI, NCO content = 27.89%, functionality = 2.13) was available from Yantai Synthetic Leather General Factory. Butyl-1,4-diol (BDO, M = 90.12, $\rho = 1.015-1.017$ g/mL,

^{*} To whom all correspondence should be addressed. Journal of Applied Polymer Science, Vol. 61, 367-370 (1996) © 1996 John Wiley & Sons, Inc. CCC 0021-8995/96/020367-04



Figure 1 The second-order dependence of polyurethane polymerization in the presence of urea groups without organotin catalyst.

mp > 17°C) was used commercially available. Dibutyltin dilaurate (DBTDL, Kosmos 19, Goldsmidt A.G.) was used as catalyst. The biurea compound, labeled UA2000, was synthesized by reacting a poly-(propylene oxide) diamine (Jeffamine D2000, M_n = 2000, f = 2, Texaco Chemical Company) with phenyl isocyanate (M = 119.3, purity > 98%, d= 1.090-1.096, $n_D = 1.535-1.537$) as described previously.¹¹

Method

A Nicolet 5DXC Fourier transform IR spectrometer was used to follow the reaction. Precisely calculated amounts of PPO, BDO, L-MDI, and UA2000 were mixed and stirred thoroughly. The blend was injected into a sample cell formed by two KBr salt plates in which no spacer was used. IR spectra were recorded by applying a Macro program¹² with 4 cm⁻¹ resolution at a constant temperature of $20 \pm 1^{\circ}$ C. The molar ratio of PPO, BDO, and L-MDI was fixed on to 1.0/2.0/3.0 in the present work. The molar ratio of urea groups (in UA2000) with hydroxyl groups (in both PPO and BDO) was designed as 0.0, 1.0, 2.0, and 3.0.

RESULTS AND DISCUSSION

Absorption band at 2270 cm^{-1} in IR spectra, assigned to stretching vibration of NCO groups, was chosen for monitoring the reaction. To compensate for thickness changes in the sample during polymerization, CH₂ absorption band at 2900 cm⁻¹ was used as an internal standard band. If A_{NCO} is the absorption intensity, area of absorption peak, of NCO groups and A_{ref} is the absorption intensity of the internal standard, then

$$\frac{A_{\rm ref}}{A_{\rm NCO}} = \frac{\alpha_2 [\rm ref]}{\alpha_1 [\rm NCO]} = \frac{\beta}{[\rm NCO]}$$
(1)

where α is the absorption coefficient characteristics of the absorption species and $\beta = \alpha_2 \, [ref]/\alpha_1$ is a constant. If the overall reaction is second order, then its rate expression can be integrated and rearranged to give

$$\frac{1}{[NCO]} = kt + \frac{1}{[NCO]_0}$$
(2)

where subscript zero means initial time, k is the apparent rate constant, and t the reaction time. Combination of eqs. (1) and (2) gives

$$\frac{A_{\text{ref}}}{A_{\text{NCO}}} = \frac{\beta}{[\text{NCO}]} = k\beta t + \frac{\beta}{[\text{NCO}]_0}$$
(3)

The initial concentration of NCO groups, $[NCO]_0$, is a known value for the designed experiment. A plot of $(A_{ref}/A_{NCO}) - (\beta/[NCO]_0)$ versus time will be linear if second-order kinetics is followed.

Similarly, for a reaction with other integer and semiinteger order, the rate expression can be obtained also. A TURBO BASIC computer program for linear least-square fitting was compiled and used to try these reaction orders step by step for fitting experimental data.

When second order was selected, the best linearity of kinetic relationship was found (Figs. 1 and 2). The second-order rate coefficients of the reactions are shown in Table I. The results indicate that a



Figure 2 The second-order dependence of polyurethane polymerization in the presence of urea groups with DBTDL content of 1.0×10^{-3} g/g PPO.

catalysis of urea groups on polyurethane polymerization occurs and the catalysis affects the polyurethane formation whether the organotin catalyst was used or not.

The presence both of basic tertiary nitrogen and of acidic hydrogen atom in one urea group makes it theoretically possible for them to function as either acid or base catalysts. Baker and Bailey² suggested an acid-catalyzed mechanism for the urea product catalyzed reaction as follows:

$$-NCO + -HN - C - NH - =$$

$$\downarrow \\ O \\ -N = C^{+} = O \rightarrow NHCNH - (Complex)$$

$$\downarrow \\ O \\ -NH_2 + Complex \rightarrow 2 - HNCNH -$$

$$\downarrow \\ O \\ 0 \\ -NH_2 + Complex \rightarrow 2 - HNCNH -$$

Baker and Bailey indicated that the reaction was facilitated by association (complex) of the acidic hydrogen in urea group with the carbonyl-oxygen atom in isocyanate group, and thus the requisite polarization of the carbonyl group in isocyanate group toward nucleophilic attach by the reactant amine was increased.

Figure 3 is the IR C=O bands of UA2000 in alcohol solution. The bands at 1695 and 1666 cm⁻¹ are the free and the hydrogen-bonded urea carbonyl groups, respectively, and the band located at 1683 cm⁻¹ can be assigned the hydrogen bonding between a urea carbonyl group and a hydroxyl group (H-bond complex).

H-N
C=0...
$$\dot{H}$$
-O-R (H-Bond Complex)
H-N

Figure 3 implies that the catalysis of urea groups may be conducted by way of the hydrogen bonding



Figure 3 Carbonyl region in the IR spectra of (a) UA2000 and (b) UA2000/alcohol solution.

and thus the following mechanism was suggested here:

$$-OH + -HN - C - NH - \implies H-Bond Complex$$

$$0$$

$$-NCO + H-Bond Complex \rightarrow$$

$$-HNCNH - + -HNCO -$$

$$0$$

$$0$$

The hydrogen bonding promotes nucleophilic capacity of the hydroxyl-oxygen toward isocyanate groups and therefore increases the rate of isocyanate-hydroxyl. In this mechanism, the urea group acts like a base instead of an acid.

The catalysis of urea groups on polyurethane polymerization was observed and explained in terms of a possible mechanism that proposed according to the hydrogen bonding property between the urea carbonyl groups and the hydroxyl groups. From the preliminary result in this work, one can infer that urethane formation in poly(urethane urea) polymerization must be affected by the urea formation in the same polymerization process, so paying at-

[UA]/[OH]	0.0	1.0	2.0	3.0
[DBTDL] = 0.0 k (mL/mol s)	0.0691	0.126	0.170	0.186
$[DBTDL] = 1.0 \times 10^{-3} \text{ g/gPPO}$ k (mL/mol s)	0.483	0.772	0.979	0.992

tention to the product catalysis is necessary to the kinetic studies of poly(urethane urea) polymerization.

Financially supported by the National Natural Science Foundation of China.

REFERENCES

- J. W. Baker and D. N. Bailey, J. Amer. Chem. Soc., 79, 4649 (1957).
- J. W. Baker and D. N. Bailey, J. Amer. Chem. Soc., 79, 4652 (1957).
- 3. J. W. Baker and D. N. Bailey, J. Amer. Chem. Soc., **79**, 4663 (1957).
- 4. T. J. Hsu and L. J. Lee, Polym. Eng. Sci., 28(15), 955 (1988).

- K. J. Wang, Y. J. Huang, and L. J. Lee, *Polym. Eng. Sci.*, **30**, 654 (1990).
- N. Vespoli and C. Markon, Urethanes Tech., Feb/ Mar, 22 (1989).
- M. C. Pannone and C. W. Macosko, J. Appl. Polym. Sci., 34, 2409 (1987).
- M. C. Pannone and C. W. Macosko, *Polym. Eng. Sci.*, 28, 660 (1988).
- H. Okada and Y. Iwakura, Macromol. Chem., 64, 91 (1963).
- 10. M. Sato, J. Org. Chem., 27, 819 (1962).
- 11. Ning Luo, De-Ning Wang, and Sheng-Kang Ying, *Polymer*, to appear.
- Ning Luo, Rao-Mei Miao, Zhi-Ping Zhang, and Shang-Kang Ying, Guang Pu Xue Yu Guang Pu Fen Xi, 14(4), 37 (1994).

Received October 23, 1995 Accepted January 17, 1996