

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 urea-formation 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 isocyanate-alcohol 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.

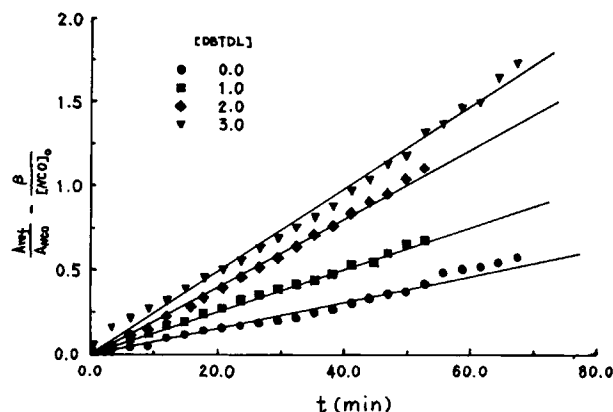


Figure 1 The second-order dependence of polyurethane polymerization in the presence of urea groups without organotin catalyst.

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 $20 \pm 1^\circ\text{C}$. 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, CH_2 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

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

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

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

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

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

The initial concentration of NCO groups, $[\text{NCO}]_0$, is a known value for the designed experiment. A plot of $(A_{\text{ref}}/A_{\text{NCO}}) - (\beta/[\text{NCO}]_0)$ 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

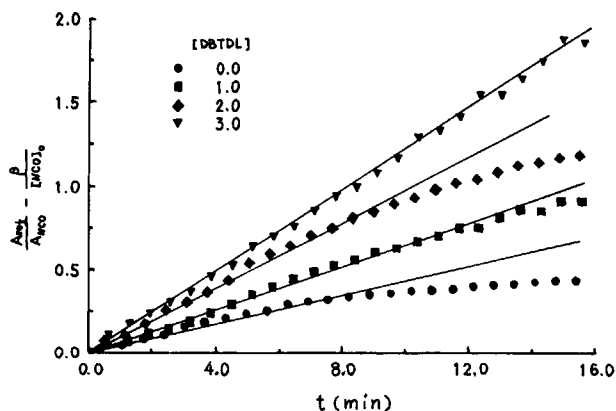


Figure 2 The second-order dependence of polyurethane polymerization in the presence of urea groups with DBTDL content of $1.0 \times 10^{-3} \text{ g/g PPO}$.

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

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