

Effects of Solvent Polarity on the Reaction of Phenol with Toluene-2,4-Diisocyanate

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ABSTRACT: Using toluene-2,4-diisocyanate as standard compound, the relationship between —NCO absorbance and concentration was studied with *in situ* FTIR. The linear relationship appeared correct only for concentrations lower than 0.4 mol L^{-1} . Then, the urethane reaction kinetics of phenol with toluene-2,4-diisocyanate were investigated in different solvents, such as dimethyl sulfoxide, cyclohexanone, *n*-butyl acetate, 1,4-dioxane, and xylene. It showed that solvents largely affected reaction rates. The reaction was largely accelerated in polar solvents, following the order of dimethyl sulfoxide > cyclohexanone > *n*-butyl acetate > 1,4-dioxane > xylene. It was

in contrast to the alcohol–diisocyanate reaction. Finally, an appropriate reaction mechanism was proposed. The H—O bond in phenol was polarized under the influence of solvents, which made the combination of hydrogen to nitrogen and alkoxy group to carbenium easier. After that the solvent was dissociated and the carbamate generated. The kinetic equation could be derived as $v = k'K \cdot [S] \cdot [\text{ROH}] \cdot [\text{R}'\text{NCO}]$. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 580–584, 2012

Key words: urethane reaction; kinetics; solvent polarity; phenol

INTRODUCTION

Polyurethanes (PUs) are a very large and varied family of extraordinarily versatile and useful engineering materials.¹ The reaction between isocyanate (—NCO) and alcohol (—OH) is the basis of PU, so its kinetics have been largely investigated at all times.^{2–6} There are several factors affecting the urethane reaction rate, such as the property⁷ and concentration⁸ of each reactant, the catalyst,^{9,10} and the reaction temperature.^{11,12} As far as the effect of solvent was concerned, it was reported that^{13–15} the polarity of solvents greatly affected the reaction of alcohols with isocyanates, and the reaction rate fell down with the increase of solvent polarity in the absence of catalyst. Raspoet¹⁶ and Draye¹⁷ considered that alcohol complexes could accelerate the reaction. Chen¹³ further explained that the “polymeric alcohols” reacted with isocyanates faster than common alcohol due to polarization of the O—H bond in the alcohol; polar solvent was capable of forming hydrogen bonding with the alcohol, which led to a large reduction of

polymeric alcohols and therefore reduced the reaction rate.

However, as for the phenol–isocyanate reaction, namely, the blocking reaction of isocyanate, little attention was focused on the effects of solvent polarity.¹⁸ Kothandaraman et al.¹⁹ investigated the carbamate reaction of phenol with phenyl isocyanate in 1,4-dioxane, benzene, toluene, acetonitrile, and dimethyl formamide. They only studied the reaction with dibutyltin dilaurate as catalyst and found that reaction rate seemed of little relevance to solvent polarity. Yet, Subrayan et al.²⁰ considered that catalyst impacted the reaction mechanism, which could lead to the difference between catalytic and noncatalytic reactions.

In situ FTIR is a powerful tool for the kinetic investigation of homogeneous reactions.^{21–23} The particular advantage of *in situ* FTIR for monitoring PU or polyurea reactions derives from the obvious disappearance of —N=C=O absorption and the visible formation of —C=O absorption. The intensity of that absorbance allows quantitative measurement even at low conversion.²⁴ In this study, the reaction of phenol with toluene-2,4-diisocyanate carries on without catalyst. *In situ* FTIR is used to monitor the reaction in different polar solvents, such as dimethyl sulfoxide, cyclohexanone, *n*-butyl acetate, 1,4-dioxane, and xylene. From that the reaction kinetics is studied, and a possible mechanism is proposed.

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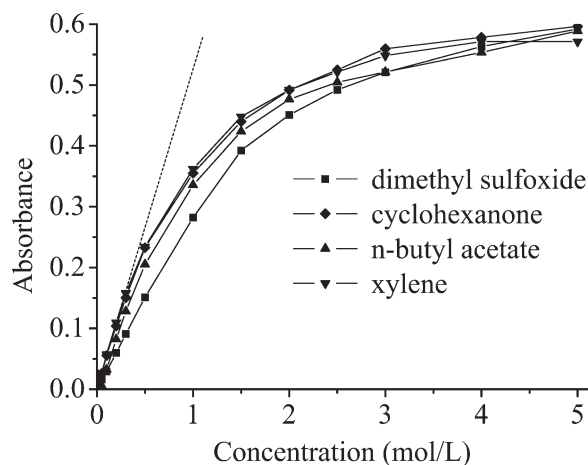


Figure 1 Calibration for $-\text{NCO}$ absorbance (2273 cm^{-1}) from concentration in different solvents. The linear range varies in different solutions and $0\sim 0.4\text{ mol L}^{-1}$ is proper for kinetic studies.

EXPERIMENTAL

Materials and instruments

Tolylene-2,4-diisocyanate was purchased from Sigma Aldrich (Saint Louis, MO) and used as received. Phenol was purchased from Sinopharm Chemical Reagent (Shanghai, China) and purified by vacuum distillation in the presence of Al powder. Dimethyl sulfoxide, cyclohexanone, *n*-butyl acetate, 1,4-dioxane, and xylene were purchased from Sinopharm Chemical Reagent and purified by vacuum distillation in the presence of CaH_2 . The purities of all the reagents were of analytical grade (A.R.).

The IR spectrometer, React IR IC10, was manufactured by Mettler Toledo (Columbia, MD). Air-purification system, XYA-5000G, was manufactured by Shanghai XiYou Analytical Instrument (Shanghai, China).

Calibration for concentration from absorbance

A series of solutions with different $-\text{NCO}$ concentration in dimethyl sulfoxide, cyclohexanone, *n*-butyl acetate, 1,4-dioxane, and xylene were prepared. FTIR was used to measure their absorbance. Thus, the relationship between absorbance and concentration was obtained in highly concentrated solutions.

Kinetic studies

Clean and dry air was flowed into the instrument continuously until the absorbance of all impurities was constant. Thus, the background spectra were recorded to eliminate interference by air.

After that phenol (0.265 g) and solvent (7 mL) were poured into the flask and heated to the preset temperature under a nitrogen atmosphere. Then, the stoichiometric amount of tolylene-2,4-diisocyanate (0.2 mL) was added to begin the reaction.

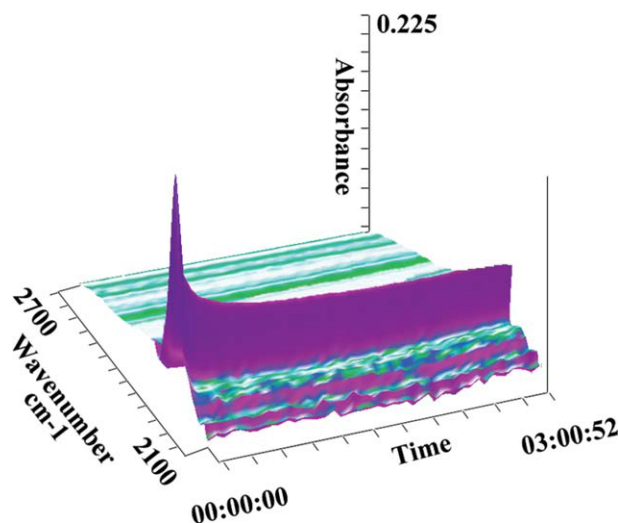


Figure 2 3D *in situ* FTIR spectra for the phenol–tolylene-2,4-diisocyanate reaction (cyclohexanone, 70°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Data were continuously collected until reaction was terminated. The resolution was 8 cm^{-1} , and the scan region was $4000\text{--}650\text{ cm}^{-1}$. Sampling intervals were as follows: dimethyl sulfoxide, every 10 s; cyclohexanone, every 2 min; *n*-butyl acetate, every 3 min; 1,4-dioxane, every 5 min; xylene, every 10 min.

RESULTS AND DISCUSSION

Absorbance–concentration relationship

It is well known that Beer–Lambert law only holds true at low concentration. When highly concentrated solutions are treated, it is necessary to examine the relationship between absorbance (A) and concentration

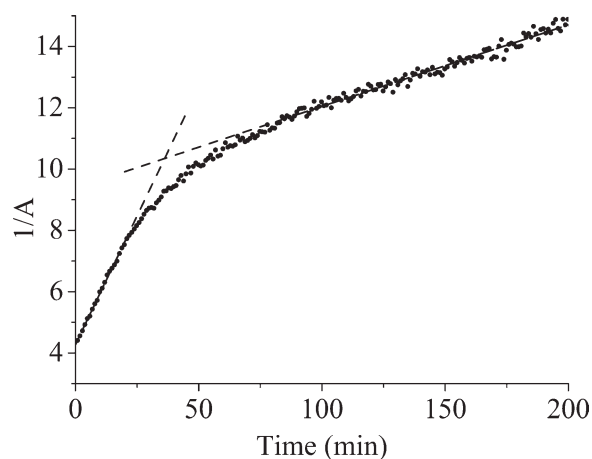


Figure 3 $1/A$ versus t curve for the phenol–tolylene-2,4-diisocyanate reaction in cyclohexanone at 70°C . There are two isocyanate groups in tolylene-2,4-diisocyanate, so the reaction is divided into two stages. A reasonable linear fit of the reaction is achieved with the proposed model.

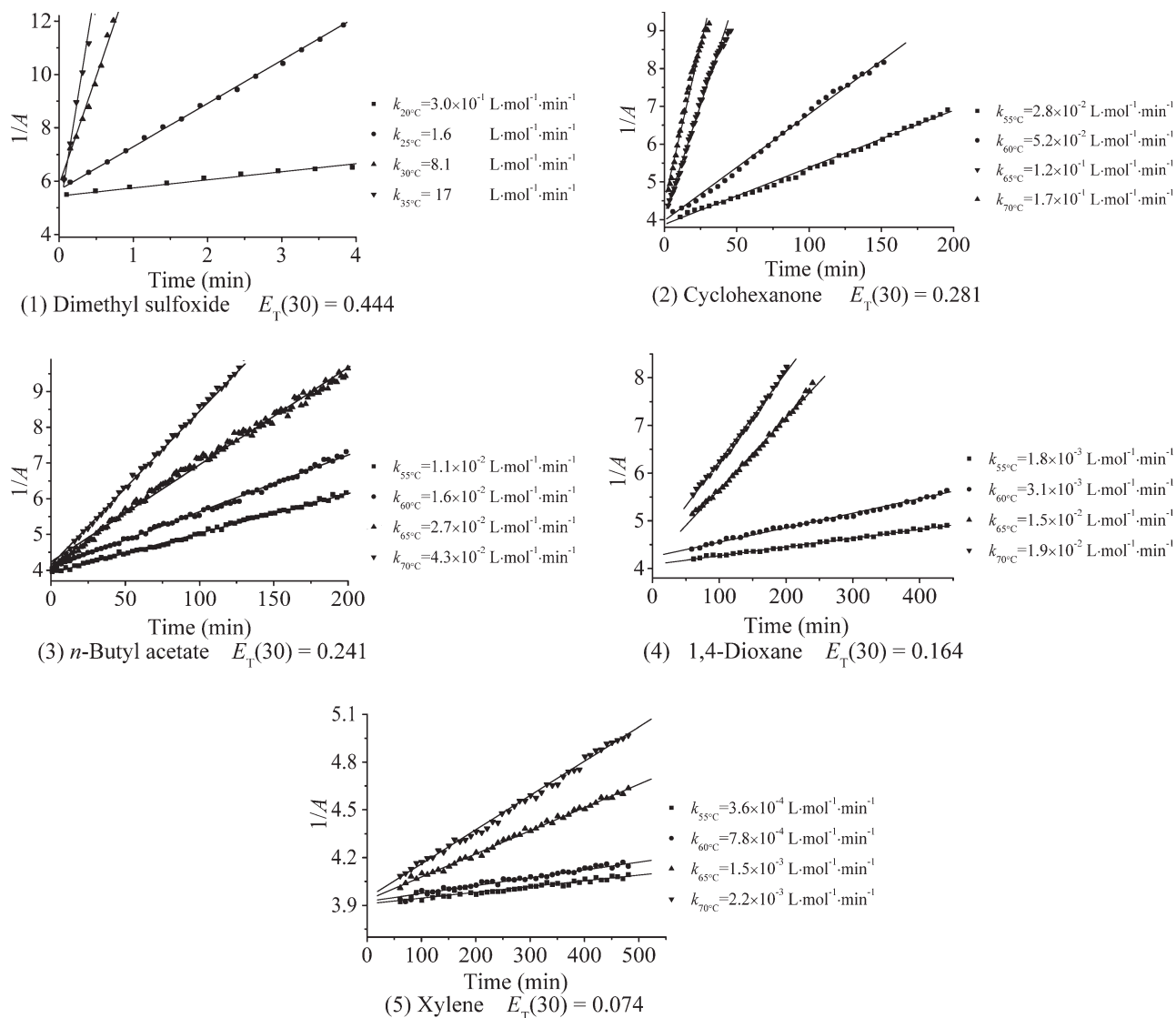


Figure 4 $1/A$ versus t curve for the reaction in various solvents at different temperatures. The initial reaction stage is used to work out the rate constants. $E_T(30)$ value are also laid out.

(C). In our former article,⁶ linear relationship appeared correct only for concentration lower than 0.67 mol L^{-1} in 1,4-dioxane. However, after carefully examining the relationship between $-\text{NCO}$ absorbance (2273 cm^{-1}) and concentration in other four solvents (Fig. 1), we find that the linear range varies in different solutions and $0 \sim 0.4 \text{ mol L}^{-1}$ for kinetic studies is better.

Kinetics for the phenol-tolylene-2,4-diisocyanate reaction

Kinetic studies are based on the reduction of isocyanate. One of the 3D *in situ* FTIR spectra is shown in Figure 2 (cyclohexanone, 70°C).

To obtain the kinetic constants, it is assumed that there is no side reaction. When the stoichiometric ratio is used, the total isocyanate concentration can be given by the general n th-order expression as a

relationship of time dependence.⁶ Assuming it is a second-order process,²⁵ we can use the n th-order approach to model the reaction kinetics as follows:

$$\frac{1}{A} = k \cdot t + \frac{1}{A_0} \quad (1)$$

A_0 is the initial absorbance of isocyanate groups; k is the apparent reaction rate constant (hereinafter as "reaction rate constant"). Thus, $1/A$ versus t curve can be plotted as Figure 3. A reasonable linear fit of the reaction is achieved with the proposed model if the reaction is divided into two phases, and both phases fit well.

There are two isocyanate groups in tolylene-2,4-diisocyanate. The isocyanate group in *para*-position of $-\text{CH}_3$ reacts much faster than that in *ortho*-position of $-\text{CH}_3$. When reacting with phenol, the

para-NCO reacts first, and then follows with the *ortho*-NCO.²⁶ Thus, the reaction is divided into two stages, so that $1/A$ versus t curve behaves as a fold line.

To conveniently investigate the effect of solvent polarity on the reaction rate, only the initial reaction stage is used to work out the rate constants. That is, the reaction of phenol with the *para*-NCO is picked up. The experimental points for the relationship between $1/A$ and t in various solvents at different temperatures are shown in Figure 4.

Dimroth–Reichardt parameter, $E_T(30)$, is an official measure of the ionizing power (loosely polarity) of a solvent.²⁷ It is based on the long-wavelength UV/vis charge-transfer absorption band of the negatively solvatochromic pyridinium *N*-phenolate betaine dyes.²⁸ The value $E_T(30)$ for elected solvents is taken from reference²⁸ and shown in Figure 4. It is obvious that the reaction rate varied greatly in different polar solvents. The order is as follows: dimethyl sulfoxide > cyclohexanone > *n*-butyl acetate > 1,4-dioxane > xylene. The carbamate reaction rate appears very fast in highly polar solvent (DMSO), which has been reported by Dabi et al.^{29–31} They suggested that isocyanate could form a complex with DMSO, which made the reaction carried on easier. Czaja et al.^{32–33} also agreed with that opinion. However, the reaction of phenol with tolylene-2,4-diisocyanate accelerates in common polar solvents. It is quite opposite to the reaction of alcohol with isocyanate proposed by Ephraim³⁴ and Oberth.³⁵

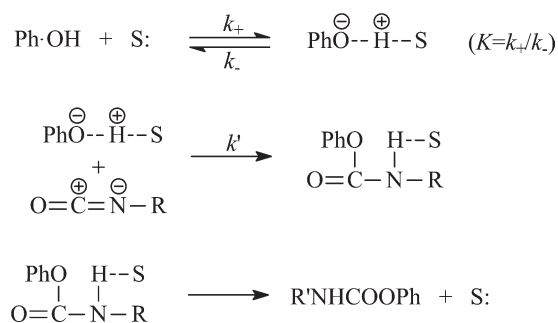
Mechanism of urethane reaction for phenol

When reacting with isocyanate, phenols and alcohols appear very different in reaction rate. It derives from the molecular structure of phenols and alcohols. Phenol is a kind of weak acid ($pK_a = 9.89$); its O=H bond maybe partly ionizes in polar solvent,^{36,37} which is also confirmed by the parameter $E_T(30)$. First, the solvation of phenol generates loose ion-pair and the homeostasis comes into being rapidly.³⁸ Second, the loose ion-pair attacks the nitrogen atom in $-NCO$ easily,³⁹ follows by the combination between alkoxy group and carbon atom in $-NCO$. Thus, the nucleophilic reaction happens more easily. Finally, solvent combines carbamate dissociates, releases solvent, and generates carbamate⁴⁰ (Scheme 1).

The second step is the bottleneck of the reaction.⁴¹ According to the hypothesis of equilibrium state, kinetic equation of the phenol–isocyanate reaction can be calculated as this.

$$v = k'K \cdot [S:] \cdot [ROH] \cdot [R'NCO] \quad (2)$$

where k' is the reaction rate constant, and K is the reaction equilibrium constant in Scheme 1.



Scheme 1 Mechanism of the reaction between phenol and isocyanate. It is divided into three steps and the second step is the bottleneck of the reaction.

The stronger the polarity of solvent is, the larger the value of K is. The larger the value of K is, the faster the reaction carries on.

When the reaction carries on in dilute solution, $[S:]$ is a constant because the solvent is largely excess contrast to reactant. Thus, the reaction rate is only dependent on the concentration of hydroxyl and isocyanate. It follows second-order kinetics (eq. 2), which agrees with the experimental data.

CONCLUSIONS

In situ FTIR is used to monitor the reaction of phenol with tolylene-2,4-diisocyanate, and the reaction rate constants in various solvents at different temperatures are calculated out. It shows that the reaction follows second order. Furthermore, solvent polarity largely affects reaction rate. The reaction accelerates in polar solvents. The order is as follows: dimethyl sulfoxide > cyclohexanone > *n*-butyl acetate > 1,4-dioxane > xylene. It is quite opposite to the reaction law of alcohol with isocyanate.

A likely mechanism of the reaction of phenol with tolylene-2,4-diisocyanate is proposed. First, the solvation of phenol generates loose ion-pair and the homeostasis comes into being rapidly. Second, the loose ion-pair attacks the nitrogen atom in $-NCO$ easily, follows by the combination between alkoxy group and carbon atom in $-NCO$. Finally, solvent combines carbamate dissociates, releases solvent, and generates carbamate. The kinetic equation is as follows: $v = k'K \cdot [S:] \cdot [ROH] \cdot [R'NCO]$. The stronger the polarity of solvent is, the larger the value of K is, the faster the reaction carries on.

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