

Cure-Reaction Kinetics of Amine-Blocked Polyisocyanates with Alcohol Using Hot-Stage Fourier Transform Infrared Spectroscopy

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ABSTRACT: Cure reaction between a series of *N*-methyl-aniline-blocked polyisocyanates, based on 4,4'-methylene-bis(phenyl isocyanate), poly(tetrahydrofuran) and several substituted *N*-methylanilines, and *n*-decanol has been studied. The solid-state isothermal cure reaction was carried out using hot-stage FTIR spectroscopy, in the temperature range of 125–145°C. The urea carbonyl absorption band of blocked polyisocyanate moiety was used to monitor the conversion of blocked polyisocyanate into polyurethane. Kinetic and thermodynamic parameters were calculated using normalized conversion curves. The overall order of cure reaction, for each of the blocked polyisocyanates was found to be first order. Based on the results of kinetics and reaction conditions used in this study, the elimination-addition (S_N^1) mechanism was suggested for

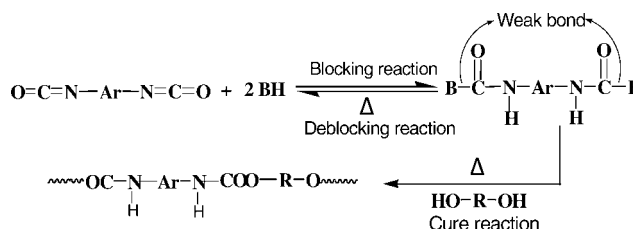
the cure reaction between *N*-methyl-aniline-blocked polyisocyanates and *n*-decanol. The effect of substituents present in the blocking agents on the cure reaction of *N*-methyl-aniline-blocked polyisocyanates was investigated and found that the cure reaction of *N*-methyl-aniline-blocked polyisocyanates was retarded by electron-donating substituents and facilitated by electron withdrawing substituents. The observed high negative entropy of activation value supports the formation of a four-centered, intramolecularly hydrogen-bonded ring structure during transition state of the cure reaction. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1168–1176, 2008

Key words: *N*-methyl-aniline-blocked polyisocyanates; polyurethanes; FTIR; cure kinetics; cure reaction mechanism

INTRODUCTION

Many polyurethanes are manufactured with polyols containing a terminal secondary hydroxyl group.¹ The reactivity of the secondary hydroxyl group with isocyanate is relatively lower than that of the primary hydroxyl group.² Some polyols [e.g., poly(oxypropylene)-poly(oxymethylene) copolymers, poly(oxytetramethylene) glycols, and hydroxyl-terminated polybutadienes] with primary hydroxyl groups are also used in large quantity in the polyurethane industries. In some applications (e.g., single package blocked adduct urethane coatings, solid propellants, etc.) they suffer from a lower pot life due to their higher reactivity with isocyanates. The use of blocked isocyanate instead of isocyanate as crosslinker improves pot life and extends the scope of applications.

The concept of blocked isocyanates is illustrated by



where BH is the blocking agent that is a thermally removable active hydrogen compound. Phenol is classical example. The blocked isocyanate is stable in presence of alcohols and water at ambient temperature, but dissociates to regenerate the isocyanate functionality at elevated temperatures and can react with hydroxyl compounds to form urethane linkages with thermally more stable bonds.^{3,4}

There are extensive patent literatures on the applications of blocked isocyanates, but little has been published about their cure chemistry.^{5–8} The understanding of the cure reaction chemistry is very imperative, because the commercial coatings, adhesive and other polyurethane products are often designed with multiple crosslinking chemistries. These formulations are typically designed based on overall knowledge of the cure chemistry; the optimization of these formulations requires better understanding of cure reaction pathway.

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A hot-stage FTIR spectrophotometer is the best analytical tool for studying the deblocking and cure reaction of blocked isocyanates as this tool directly measures the regeneration of the —NCO functional group and the formation of urethane group. Taking advantage of the rapid scanning ability of the FTIR, it is possible to monitor the chemical changes which occur when a sample is cured in a heated cell. Conversion curves for different reactions involved in the cure process as a function of time and temperature can be generated from the infrared absorbance. This helps to gain a fundamental understanding of the cure chemistry of blocked isocyanates.

In our previous article we reported the preparation, deblocking studies, and potentiality of a series of *N*-methylaniline-blocked polyisocyanates.⁹ The objective of this work is to study the cure kinetics of aromatic secondary amine-blocked isocyanate-alcohol systems, by which we can gain a better understanding of how cure reaction conditions and structure of reactant influence the cure process. This article illustrates the utility of hot-stage FTIR spectroscopy to determine the kinetic parameters and reaction pathway of amine-blocked polyisocyanate-alcohol systems.

EXPERIMENTAL

Materials and measurements

The preparative methods and characterization of *N*-methylaniline-blocked polyisocyanates^{1–10} and the model compound **11** were described in our previous report.⁹ *n*-Decanol (Aldrich, Bangalore, India) was used as received.

Determination of the kinetics parameters for the cure reaction of blocked polyisocyanates (1–10)

The cure reaction kinetics of the blocked polyisocyanates^{1–10} with *n*-decanol was followed using a Thermo Mattson FTIR spectrophotometer, equipped with hot-stage accessories and programmable temperature controller. The experiments were carried out isothermally at 125, 135, and 145°C. Initially, the sample was heated from ambient to 100°C for which the time set was 6 min and then the temperature was raised to 125, 135, or 145°C for which the time set was only 2 min. In a typical experiment, equimolar amount of blocked polyisocyanate and *n*-decanol was mixed thoroughly. A thin film of blocked polyisocyanate and *n*-decanol mixture was cast onto a NaCl disc and was covered with an uncoated disc. Both discs were separated by 0.5-mm lead spacer and placed in a heated transmission cell (HT-32, model 0019-200, Thermo Electron Corp., Madison, WI). The heated transmission cell was connected to a microprocessor-based programmable temperature

controller (Omega CT-3251), which provided a constant heating rate for isothermal experiments. The program was performed in the heating device in such a way that once the desired temperature was reached, the experiment proceeded isothermally. Spectra were recorded for zero time, immediately when the sample reached the desired temperature and then recorded for every 5 min for each case. To monitor the cure reaction of blocked polyisocyanates, the urea carbonyl absorption band at 1685 cm⁻¹ was chosen. As reaction time increased, the absorption of the urea carbonyl of blocked isocyanate group decreased. The peak area of the urea carbonyl in each spectrum was calculated with OMNIC software (Thermo Nicolet) and considered equivalent to the concentration factor at a particular time *t*. Difference in film thickness was compensated by normalizing the urea absorbance band at 1685 cm⁻¹, to an absorbance band that remains constant during the course of the cure reaction. In our case, the absorbance band at 1108 cm⁻¹ was used as reference band. The normalized degree of conversion for the cure reaction was calculated by the following equation.

$$x = 1 - \left[\frac{(\text{Peak area at } 1685/\text{Peak area at } 1108)_t}{(\text{Peak area at } 1685/\text{Peak area at } 1108)_{t=0}} \right] \rightarrow \quad (1)$$

where *t* is the time of the cure reaction and *x* = degree of conversion of cure reaction.

The normalized data were used to calculate the kinetic and thermodynamic parameters for the cure reaction of blocked polyisocyanates.

Deblocking reaction of *N*-methylaniline-blocked polyisocyanate **1**

The deblocking reaction of *N*-methylaniline-blocked polyisocyanate **1** was carried out using hot-stage FTIR spectrophotometer attached to hot-stage accessories as described in the preceding section. The experiment was carried out isothermally at 135°C. The sampling technique was similar to that for the determination of cure kinetic parameters except, for the fact that the sample used for the deblocking reaction was blocked polyisocyanate **1** alone and for cure reaction the sample was blocked isocyanate-*n*-decanol mixture.

RESULTS AND DISCUSSION

The reaction mechanism of polyol and blocked isocyanate on the chain extension and crosslinking of polyurethane formation reaction at elevated temperature is complex, because many variables affect the reactivity of the systems. Moreover, most of the effects, such as influence of the environment and the

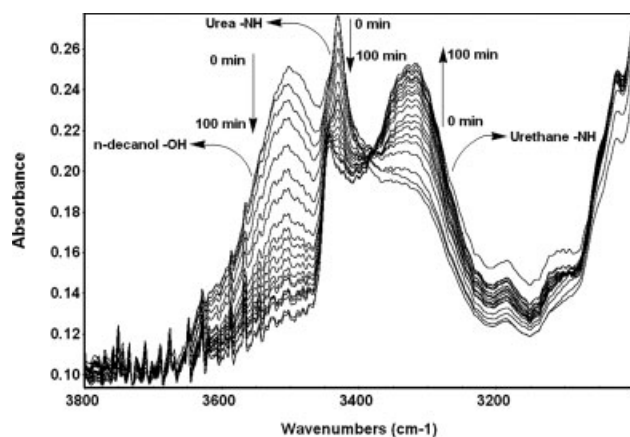


Figure 1 —NH and —OH stretching frequency regions of FTIR spectra of the blocked polyisocyanate **1** recorded during cure reaction with *n*-decanol at 135°C for different time intervals.

gress of the cure reaction from maximum to zero. This is due to the cleavage of the urea group. A thorough evaluation of Figures 1 and 2 clearly show decrease of urea carbonyl absorption band at 1685 cm^{-1} is due to deblocking reaction of *N*-methylaniline-blocked polyisocyanate and increase in the urethane —NH absorption band at 3318 cm^{-1} is due to the cure reaction between *N*-methylaniline-blocked polyisocyanate and *n*-decanol leads to the formation of urethane moiety. The graphical representation of the changes in the intensities of the functional groups, which involved in the cure reaction are given in Figure 3. In our previous reports,^{9,14} we followed urea carbonyl absorption at 1685 cm^{-1} to calculate kinetic and thermodynamic parameters for the deblocking reaction. Since the urea carbonyl band intensity decreased gradually from maximum to zero, we decided to monitor disappearance of this band at

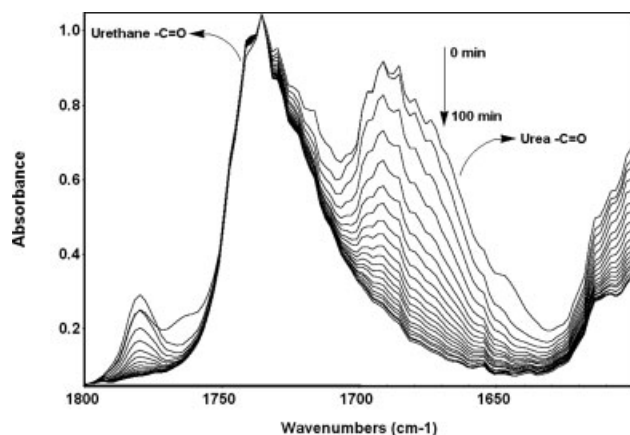


Figure 2 Urea carbonyl stretching frequency region of FTIR spectra of the blocked polyisocyanate **1** recorded during cure reaction with *n*-decanol at 135°C for different time intervals.

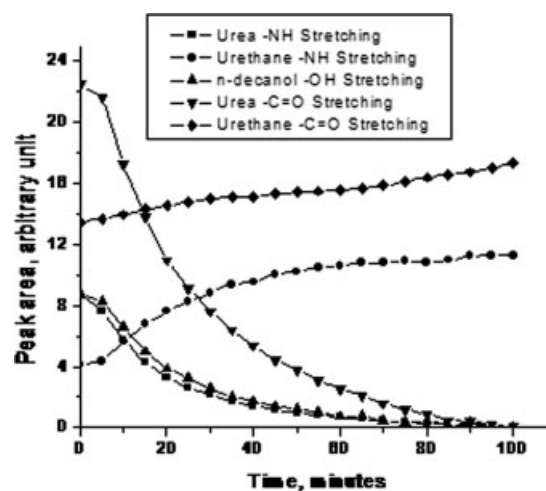
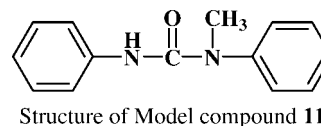


Figure 3 Absorbance of different functional groups during cure reaction between blocked polyisocyanate **1** and *n*-decanol at 135°C with respect to time.

1685 cm^{-1} for kinetic studies. However, the substituted *N*-methylaniline-blocked polyisocyanates have two absorptions bands at 1685 and 1735 cm^{-1} corresponding to urea and urethane carbonyl respectively. To avoid any ambiguity in the peak assignment for the urea carbonyl group, we prepared *N*-methyl-aniline-blocked phenyl isocyanate **11** as a model compound, which has only urea carbonyl and absorbs at 1685 cm^{-1} . During the progress of the cure reaction, the urea



carbonyl alone undergoes cleavage and the urethane carbonyl remains intact under the experimental conditions employed. This can evidently be seen from the FTIR spectra given in Figure 4. Therefore,

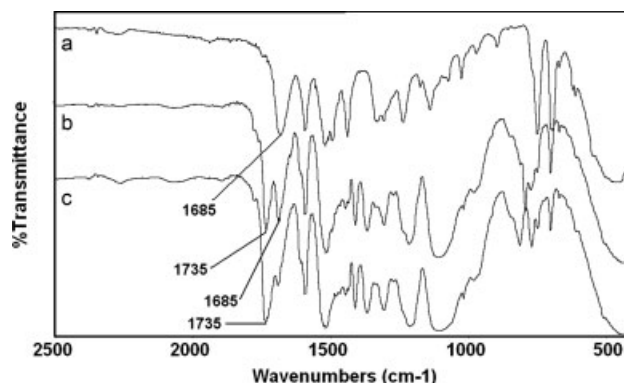


Figure 4 FTIR spectrum of (a) blocked isocyanate **11**, (b) blocked polyisocyanate **1** recorded at 125°C, and (c) blocked polyisocyanate **1** recorded after 100 min at 125°C.

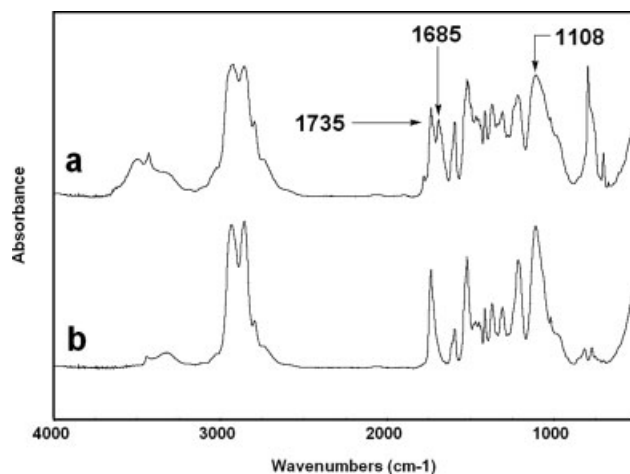


Figure 5 (a) Initial and (b) final FTIR absorption spectrum recorded during curing of blocked polyisocyanate 1 with *n*-decanol.

we followed the disappearance urea absorption band at 1685 cm^{-1} for the cure reaction studies.

The changes that occurred in the film thickness during the cure reaction were compensated by normalizing the urea stretching band at 1685 cm^{-1} . Figure 5 shows the spectra of the cured and uncured material, emphasizing the disappearance of the absorbance band at 1685 cm^{-1} during the cure reaction. The absorbance band at 1108 cm^{-1} associated with stretching vibration of the $-\text{C}-\text{O}-\text{C}-$ linkage of the blocked polyisocyanate, which remains unchanged during the course of the cure reaction. Thus we used the absorbance band at 1108 cm^{-1} as a reference band, to correct, if any changes occurred in film thickness during the progress of the isothermal cure reaction. The normalized conversion of urea group, x , has been calculated according to Eq. (1).

The normalized conversion curves were treated according to first-order rate equation, because the plots of $a/(a-x)$ versus time found to be linear (a = initial concentration and $(a-x)$ = concentration at time " t "). The intensity of absorbance band at 1685 cm^{-1} at time " t " was taken as equivalent to the concentration of the reactant at a particular time " t ," and used to calculate the conversion curves and rates of the cure reaction. The normalized conversion (x) and rate (dx/dt) curve with respect to time for the cure reaction of *N*-methylaniline-blocked polyisocyanates 1 at 125°C is given in the Figure 6.

Inspection of the mechanism for the reaction between *N*-methylaniline-blocked isocyanate and *n*-decanol also reveals that the cure reaction follows first-order kinetics. There are two mechanisms hypothetically proposed for this type of reaction. One is elimination-addition (S_N^1) mechanism and the other one is addition-elimination (S_N^2) mechanism. According to elimination-addition mechanism the blocked isocyanate decomposes to the free isocyanate and *N*-

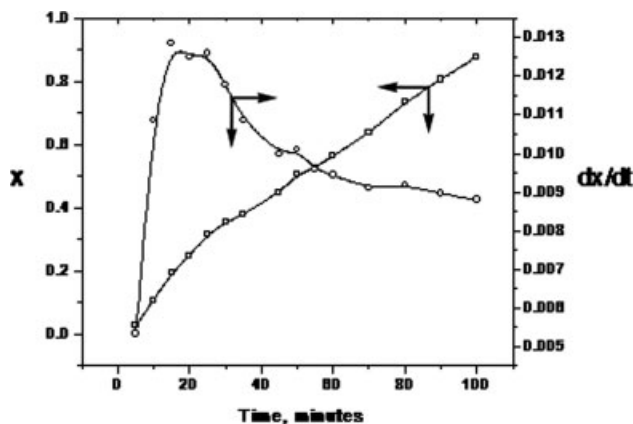
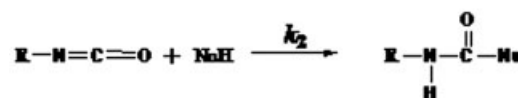
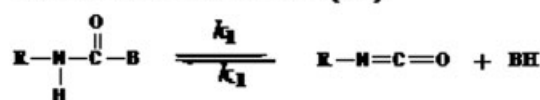


Figure 6 Reaction rate (dx/dt), degree of cure (x) versus time curves for blocked polyisocyanate 1 at 125°C with respect to time.

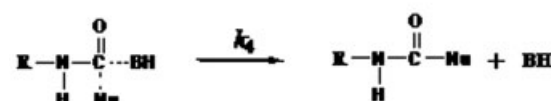
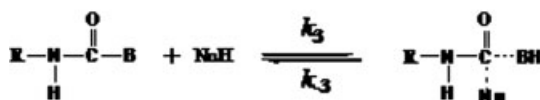
methylaniline. The regenerated polyisocyanate will react with *n*-decanol to form the urethane. According to addition-elimination mechanism, the *n*-decanol reacts directly with the blocked polyisocyanate to yield a tetrahedral intermediate followed by elimination of the *N*-methylaniline. The schematic representations of these mechanisms are given in the Figure 7.

Path way of the cure reaction has not been exclusively studied. Generally it has been assumed and in few cases it has been proven, that the reaction proceeds by elimination-addition (S_N^1) path way. However, in some other cases, addition-elimination reaction (S_N^2) mechanism has been proposed. For some

Elimination-Addition Mechanism (S_N^1)



Addition-Elimination Mechanism (S_N^2)



Where,
BH = Blocking agent
NuH = Nucleophile

Figure 7 Possible reaction mechanisms for blocked isocyanate-reactive nucleophile system.

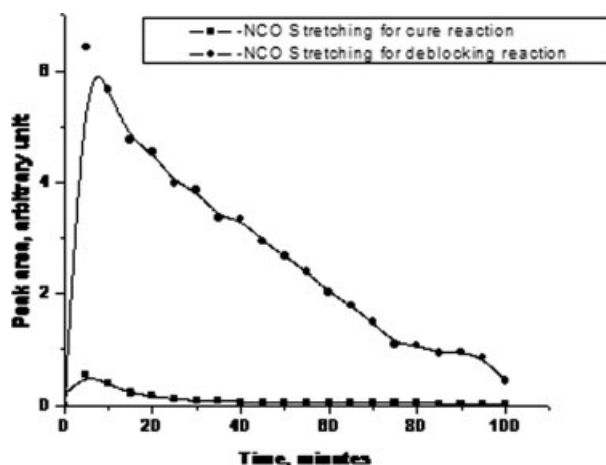


Figure 8 —NCO absorbance band intensity of blocked polyisocyanate **1** during cure and deblocking reaction at 135°C with respect to time.

cases both the S_N^1 and S_N^2 mechanisms are possible.⁷ The type of mechanism depends on the reaction condition such as temperature, structure of isocyanate, blocking agent, and nucleophile.

Here, based on the results of cure-time and deblocking studies, we believe that, the cure reaction of *N*-methylaniline-blocked polyisocyanate with *n*-decanol undergoes the elimination-addition pathway. First step of this mechanism is regeneration of the isocyanate moiety, and subsequently in the second step the regenerated isocyanate reacts with the *n*-decanol.

The rate equation for the elimination-addition pathway is given below

$$\text{Rate} = k_1[\text{BI}] \frac{k_2[n\text{-decanol}]}{k_2[n\text{-decanol}] + k_{-1}[\text{BI}]} \rightarrow \quad (2)$$

where [BI] is the concentration of the blocked polyisocyanate.

Since the temperature fixed for the cure reaction is substantially higher than the deblocking reaction, only forward deblocking reaction will take place and reversible blocking reaction will not take place. Thus, the rate of reversible reaction is negligible and the term for the reversible blocking reaction $k_{-1}[\text{BI}]$ approaches zero. So, the rate equation for cure reaction can be written as follows;

$$\text{Rate} = k_1[\text{BI}] \rightarrow \quad (3)$$

The rate approaches first order. The rate of the cure reaction depends only on the concentration of the blocked polyisocyanate and independent of concentration of *n*-decanol. This conclusion is consistent with the straight line first-order plot of $a/(a-x)$

versus time. Further evidence for this elimination-addition mechanism comes by comparing the intensities of the —NCO absorbance band at 2270 cm^{-1} of cure and deblocking reactions carried out separately. In deblocking reaction, the appreciable amount of —NCO group is regenerated. At first, the intensity of —NCO absorbance band increases with time and then decreases steadily because of the reaction between the regenerated isocyanate and —NH group of urethane moiety present in the prepolymer, which leads to the formation of allophanate groups. Whereas, in the case of cure reaction the intensity of the regenerated —NCO absorbance band at 2270 cm^{-1} is negligible. The changes in the intensities of —NCO absorbance band for deblocking reaction of

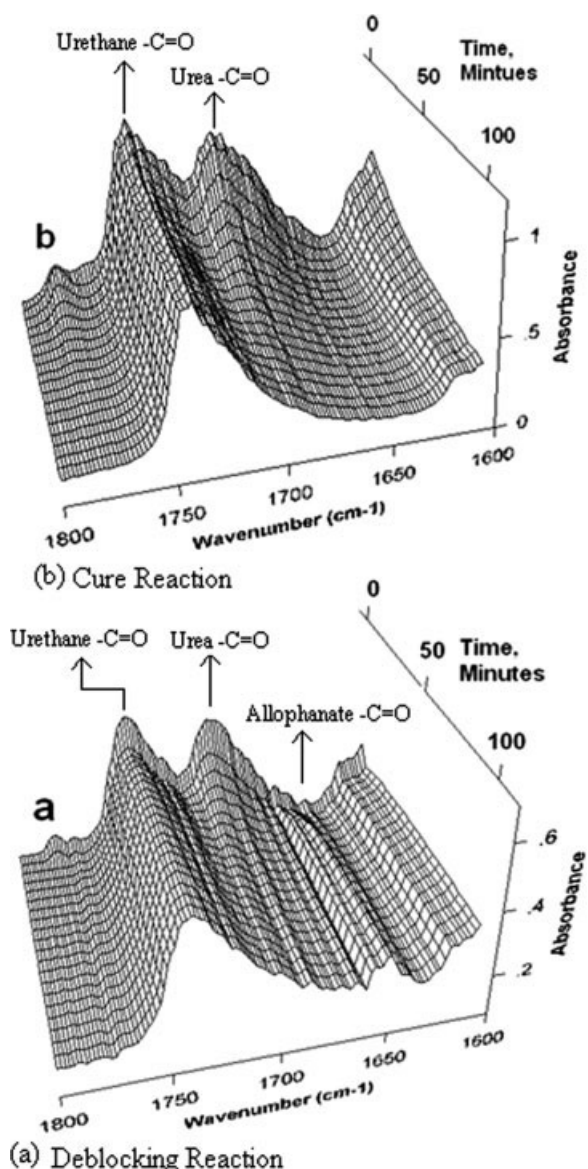


Figure 9 Carbonyl regions FTIR spectra of blocked polyisocyanate **1** during (a) deblocking and (b) cure reaction at 135°C with respect to time.

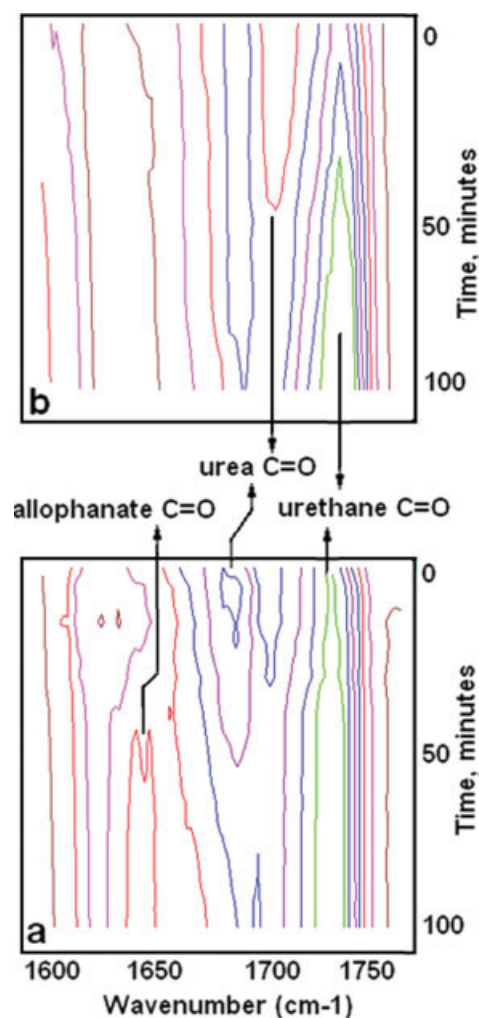


Figure 10 Contour map for FTIR spectra of Carbonyl regions of blocked polyisocyanate **1** during (a) deblocking and (b) cure reaction at 135°C with respect to time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

N-methyl-aniline-blocked polyisocyanate **1** and cure reaction of *N*-methylaniline-blocked polyisocyanate **1** with alcohol with respect to time at 135°C are given in the Figure 8. This result also reinforces our proposed elimination-addition mechanism.

In the elimination-addition (S_N^1) cure reaction mechanism for the *N*-methylaniline-blocked polyisocyanate with *n*-decanol system, the first step of the mechanism is slow and rate determining step, whereas the second step is very fast. Hence regenerated $-NCO$ reacts faster with *n*-decanol and forms urethane. The regenerated isocyanate group could react with the *n*-decanol and not with the urethane $-NH$ group in the prepolymer moiety, because, the $-COO-$ group present in the urethane moiety reduces the nucleophilicity of the nitrogen atom of $-NH$ group. Hence, the nucleophilic attack of the urethane nitrogen atom toward carbonyl carbon of regenerated $-NCO$ group is very less compare to the *n*-decanol. This argument is strengthened by comparing FTIR spectra for deblocking and cure reaction of *N*-methylaniline-blocked polyisocyanate **1** recorded at 135°C for every 5 min. Spectra for deblocking and cure reactions involving blocked polyisocyanate **1** are given in Figure 9(a,b) respectively. Figure 9(a) clearly shows the formation of the allophanate group whereas in Figure 9(b) it is clear that there is no formation of the allophanate group during the cure reaction of *N*-methylaniline-blocked polyisocyanate **1** with *n*-decanol. Contour map for the FTIR spectra, given in Figure 9(a,b) are shown in Figure 10(a,b) respectively. Contour map for the deblocking reaction [Fig. 10(a)] clearly indicates the formation of allophanate group and there is no change in the urethane absorption band. Whereas contour map for cure reaction [Fig. 10(b)] clearly shows that there is no allophanate formation and there is an increase in the intensity of urethane absorption band. These

TABLE I
First-Order Rate Constants and Activation Parameters for the Cure Reaction of *N*-methylaniline-Blocked Polyisocyanate with *n*-Decanol

Compound No.	Blocking agents	k (10^2 min^{-1}) ^a			E_a (kJ/mol) ^b	ΔG^\ddagger (kJ/mol) ^c	ΔS^\ddagger (J/K/mol) ^d
		125°C	135°C	145°C			
1	<i>N</i> -methylaniline	2.22	7.02	14.55	14.22	119	-271
2	<i>N</i> -methyl- <i>o</i> -toluidine	0.57	2.34	7.43	19.38	123	-269
3	<i>N</i> -methyl- <i>p</i> -toluidine	0.83	4.19	8.49	17.62	122	-270
4	<i>N</i> -methyl- <i>o</i> -anisidine	1.82	3.74	13.17	14.79	119	-271
5	<i>N</i> -methyl- <i>p</i> -anisidine	0.21	1.87	4.52	23.18	126	-268
6	2-Chloro- <i>N</i> -methylaniline	2.02	9.53	13.84	14.66	118	-270
7	4-Chloro- <i>N</i> -methylaniline	1.76	7.30	12.28	14.76	119	-271
8	Methyl 2-methylamino benzoate	0.67	2.13	8.65	19.22	123	-268
9	Methyl 4-methylamino benzoate	6.85	9.63	15.86	6.28	115	-281
10	<i>N</i> -methyl-4-nitroaniline	8.96	10.99	17.68	5.06	114	-282

^a Apparent rate constant.

^b Energy of activation.

^c Free energy of activation.

^d Entropy of activation.

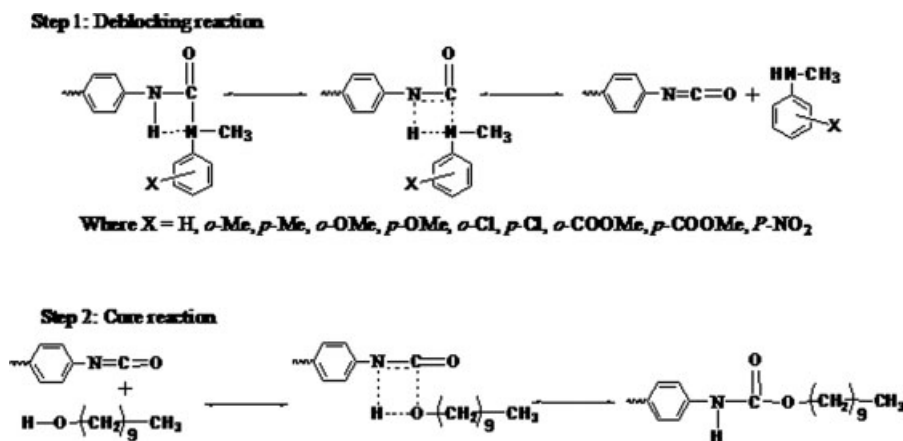


Figure 11 Formation of four-centered transition states during deblocking (Step 1) and cure (Step 2) reaction.

results were much helpful in suggesting mechanism for cure reaction of the *N*-methylaniline-blocked polyisocyanate-*n*-decanol system.

The normalized conversion curves were used to calculate the first-order kinetic and thermodynamic parameters for the cure reaction of *N*-methylaniline-blocked polyisocyanates. The rate constants and the activation parameters are given in Table I. Both the slow rate determining deblocking reaction in the first step and the fast cure reaction in the second step occurred via the formation of four-centered transition state (Fig. 11). In our previous report we proved that the deblocking reaction occurs via formation of four-centered transition state by taking variable temperature ¹H-NMR.⁹ Considering effect of substituent, the trend observed in the results of cure reaction kinetics is similar to that in the results of deblocking studies.⁹ Substituents present in the *N*-methylaniline strongly affect the strength of the labile bond and hence the cure reaction. If the electron withdrawing substituents are present in the *N*-methylaniline, it

reduces the nucleophilicity of the nitrogen atom. Thus, the bond formed between the isocyanate and the *N*-methylaniline will be more labile and the *vice versa* also true. This is reflected in the results obtained, that is, the blocking agent with electron withdrawing substituent increases the cure reaction rate compared to the unsubstituted *N*-methyl-aniline. The high cure reaction rate of the blocked polyisocyanate **9** and **10** is due to the presence of the electron withdrawing substituents in the blocking agent, which drain the electron density of the nitrogen atom of the blocking agent. The low cure reaction rate of the blocked polyisocyanate **8** is due to the presence of a polarizable substituent at the ortho position; possibly this substituent will have association with the urea proton. So the urea proton is not available for the deblocking reaction there by, it reduces the cure reaction rate. The observed high cure reaction rate of blocked polyisocyanate **4** is due to the steric constraint exerted by the bulky methoxy group. Activation energies, entropies of activation, and free energies of activation were calculated from the slopes of the Arrhenius plots (Fig. 12) and included in Table I. The results of activation parameters are consistent with electronic and steric effect operational in the blocked polyisocyanate moiety. The higher entropies of activation of the cure reaction indicates the formation of rigid complex in the four-centered transition state during deblocking and cure reaction (Fig. 11).^{9,14}

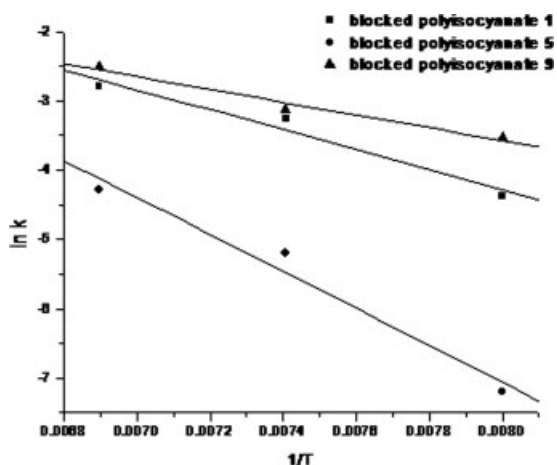


Figure 12 Arrhenius plots for blocked polyisocyanate-*n*-decanol cure reaction.

SUMMARY AND CONCLUSIONS

The cure reaction of *N*-methylaniline-blocked polyisocyanates with *n*-decanol was followed by hot-stage FTIR spectroscopy, and found that the cure reaction follows first-order rate law. The results reveal that the cure reaction rate is increased by electron-withdrawing substituents and decreased by the electron-

donating substituents. Based on the kinetics and thermodynamic results obtained and the reaction conditions, the elimination-addition mechanism (S_N^1) was suggested for *N*-methylaniline-blocked polyisocyanate and *n*-decanol system.

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