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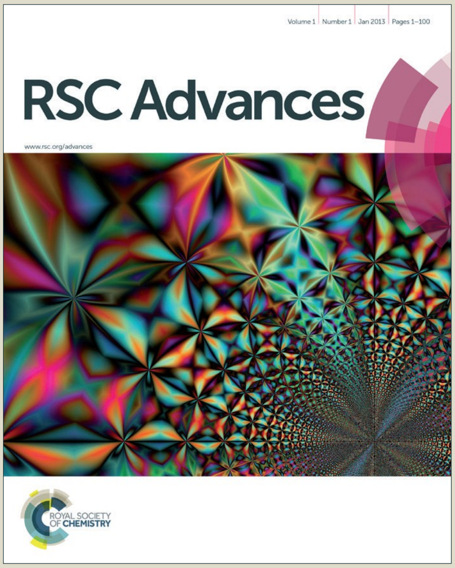

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ARTICLE

Synthesis and studies on forward and reverse reactions of phenol-blocked polyisocyanates: An insight into blocked isocyanates

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Blocked isocyanates are an important class of raw materials used in polyurethane industries. In this work, the synthesis and kinetics of blocking and deblocking reactions of a series of phenol-blocked polyisocyanates have been studied in detail using a hot-stage FT-IR spectrophotometer adapting neat condition. The results were compared with an aim to resolve complex questions on the relationship between the forward and reverse reaction parameters. As a result, double Arrhenius plots for thermally reversible reactions were proposed for the first time and using these plots, most probable equilibrium temperatures for forward and reverse reactions and the equilibrium rate constants of these reactions were assessed. It was found that the trend present in the rate constants of forward and reverse reactions and the same in the equilibrium rate constants was uniform i.e., the rate of these reactions were decreased or increased with respect to acidity of blocking agent. And, a phenol with more acidity and less nucleophilicity, e.g., 2-chlorophenol was found to be a better blocking agent; it blocks the isocyanate quickly and at the same time it cleaved off easily. The most probable temperatures assessed using the double Arrhenius plots were found in accordance with deblocking temperatures. The data like time required for conversion into product, the equilibrium temperature range for forward and reverse reactions and most probable equilibrium temperature in combination with deblocking temperature reported in this work are very attractive at manufacturing and application point.

Introduction

The extreme reactivity of isocyanates with hydroxyl compounds makes them attractive curing agents for making polyurethanes in different forms, such as elastomers, foams, coatings for many purposes, and adhesives. In some of these applications, it is necessary to delay the desired isocyanate–hydroxyl reaction until the final stages of the process. To achieve this objective, blocked isocyanates are used to generate the isocyanate functionality at the final stage. Thus, blocked isocyanates are used to obtain the performance of two package (2K) polyurethane in one package (1K) thermally curable systems. In addition, blocked isocyanates have several advantages like marked reduction of moisture sensitivity and elimination of toxicity associated with the free isocyanates. Blocked isocyanates have prolonged work life, which is particularly important for all heat-curable polyurethane products. Blocked isocyanates are used in a wide range of coating applications such as coil coatings, electro-coatings, powder coatings and eco-friendly water-born coatings. These coatings exhibit good adhesion, high weather resistance and good mechanical properties.[1] The industrial importance of blocked isocyanates can be clearly seen from the number of patents issued on this kind of materials. A very recent Scifinder® search on “blocked isocyanate” returned 7627 patents and this is more than 85% of the related overall literature. This shows the industrial importance of blocked isocyanates.

A blocked isocyanate is an adduct containing a comparatively weak bond formed by the reaction between an isocyanate and a compound containing an active hydrogen atom. At elevated temperatures, the reaction tends to proceed in such a way to regenerate the isocyanate and the blocking agent. The regenerated isocyanate can react with a co-reactant containing a nucleophile (alcohol or amine) to form urethane or urea with thermally more stable bonds. The overall reaction in a typical polyurethane heat-curable system is described in **Figure 1**.

The deblocking temperature of the blocked isocyanates is one of the limiting factors in industrial applications and it should be as low as possible. For example, a blocked isocyanate that can be deblocked at temperatures below 160 ^{o}C is suitable for heat-curable systems such as organic powder coatings.[2] There are certain application areas for which it is necessary to use a blocking agent that should be cleaved off at temperatures less than 80 ^{o}C (e.g., solid rocket propellant, which contains explosive material).[3]

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Electronic Supplementary Information (ESI) available: [^{1}H-NMR spectra of phenol-blocked polyisocyanates(**2-10**), FT-IR spectra of blocked polyisocyanates recorded at dynamic condition, FT-IR spectra of blocked polyisocyanates record at isothermal condition for blocking and deblocking reaction and Arrhenius plots of blocking and deblocking reaction of blocked polyisocyanates]. See DOI: 10.1039/x0xx00000x

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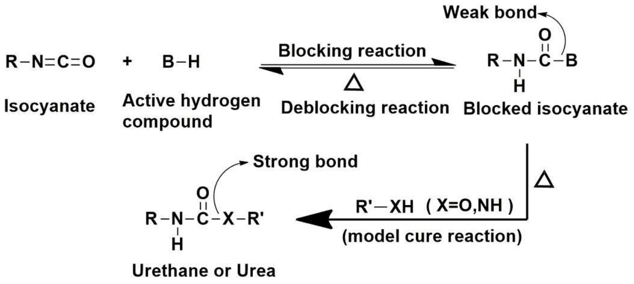

where BH is the blocking agent.

Figure 1. Concept of blocked isocyanate.

Blocked isocyanates have been the subject of thorough and well-updated reviews.[4-9] Several compounds namely phenols,[10-13] oximes,[14,15] amides,[16] imides,[16] imidazoles,[17,18] amidines,[19] lactams,[20-23] mercaptans,[24] amines,[25-27] alcohol,[26-30] sodium bisulphite,[31-34] pyrazoles,[35-37] 1,2,4-triazoles,[38] hydroxamic acid esters,[39] and formyl acrylate[40] have been reported as blocking agents. Among these blocking agents, phenols are widely used and most studied blocking agents because of the possibilities of introducing number of substituents on the benzene ring; substituents seriously influence the synthesis process and deblocking temperature of blocked isocyanates.

The field of blocked isocyanate now has developed well in terms of development of new blocking agents, blocked isocyanate equivalents,[41-43] products and stable and good market potential. However, the complex question on relationship between kinetic and activation parameters of forward and reverse reactions were not resolved yet. These parameters are essential to optimize the production process of blocked polyisocyanates and cure process with coreactant. With this background, we decided to study real systems of phenol-blocked polyisocyanates in detail. In this paper, we report synthesis, deblocking temperatures, kinetic and activation parameters of blocking and deblocking reactions of a series of phenol-blocked polyisocyanates carried out without using solvent. Also we report equilibrium temperature ranges and most probable equilibrium temperatures assessed using double Arrhenius plots for thermally reversible reactions for the first time. All the data reported in this paper will make the design and synthesis of phenol-blocked polyisocyanates and their end application easy.

Experimental

Materials. Phenol (SRL, India), p-cresol (SRL, India), poly(tetrahydrofuran) (Terathane, M_n = 650) (Aldrich), toluene-2,4-diisocyanate (TDI) (Fluka), o-cresol (SRL, India), o-chlorophenol (SRL, India), o-methoxyphenol (Alfa-Aesar), p-methoxyphenol (Alfa-Aesar), methylsalicylate (Alfa-Aesar), p-hydroxy methylbenzoate (Alfa-Aesar), N,N-diethylcyclohexylamine (TCI) and p-chlorophenol (Spectrochem, India) were used as received. The TDI used for the preparation of blocked polyisocyanates was a mixture of isomers containing 94% 2,4-isomer and 6% 2,6-isomer. The solvent, tetrahydrofuran (Merck) was purified by standard procedure.

Measurements. FT-IR spectra of polyurethane prepolymer (polyisocyanate) and blocked polyisocyanates were recorded on a PerkinElmer Spectrum Two model (FT-IR C101375) spectrophotometer by neat thin film method. ^{1}H-NMR spectra were recorded on a Bruker 500 MHz NMR spectrometer using $CDCl_3$ as a solvent.

General procedure for synthesis of phenol-blocked polyisocyanates (2–10). Blocked polyisocyanates were prepared in a two-step process. In the first step, isocyanate-terminated polyurethane prepolymer **1** was prepared. Subsequently, in the second step, the terminal –NCO groups of prepolymer were blocked with phenol. The following general procedure was adopted for the preparation of blocked polyisocyanates. In a typical synthesis, 2.68 g (15.38 mmol) of TDI was taken in a three-neck round bottomed flask fitted with a mechanical stirrer and a nitrogen inlet. 5.0 g (7.69 mmol) of polyol, [poly(tetrahydrofuran); M_n = 650] was added drop wise into the flask using an addition funnel with stirring by mechanical means. The experimental setup was maintained in a temperature controlled oil bath. The addition rate was such that it took one hour for complete transfer. The reaction time was 5 hours; for the first 2 hours the temperature of oil bath was maintained at 50 °C and for the next 3 hours it was maintained at 70 °C. After 5 hours, the reaction temperature was reduced to 40 °C. The –NCO terminated prepolymer was then blocked with an equivalent amount (i.e., 7.69 mmol) of phenol using 1.7194×10^{-2} mmol of N,N-diethylcyclohexylamine as catalyst. After thorough mixing, a very small quantity of sample was taken with the help of a glass-rod for FT-IR measurements towards kinetic analysis and the reaction in the flask was allowed to continue till the complete disappearance of –NCO absorption in the FT-IR spectrum. The structures of the blocked polyurethane prepolymers (blocked polyisocyanates) were confirmed by FTIR and ^{1}H-NMR spectroscopic methods.

Determination of blocking kinetic parameters. The blocking kinetics of –NCO terminated prepolymer with a series of phenol was followed by a hot-stage FT-IR spectrophotometer. The experiments were carried out isothermally at 40 ^{0}C, 50 ^{0}C, and 60 ^{0}C. In a typical experiment, as soon as the catalyst was added, a thin film of the reaction mixture of phenol and –NCO terminated prepolymer was cast on two NaCl disc and they were covered with each other with a separation by 0.5 mm lead spacer. Then, the NaCl windows with lead spacer were placed in a heating transmission cell (HT-32, model 0019-200, Thermo Electron Corp., Madison, WI, USA.) connected to a microprocessor-based programmable temperature controller (Omega CT-3251). A program was set in the temperature controller in such a way that once the desired temperature was reached dynamically, then the experiment proceeded isothermally. Eight scans at a resolution of 4 cm^{-1} were co-added to produce a single spectrum in a single run. Spectrum of zero time was recorded within two minutes from the time of addition of catalyst to the reaction mixture and then the spectra were recorded at regular time intervals. As the time increased, the absorption by –NCO group of isocyanate-terminated polyurethane prepolymer at 2270 cm^{-1} decreased due to the blocking of –NCO group by phenol. The peak area under absorption by the –NCO grpup in each spectrum was calculated using PerkinElmer Spectrum software (Version 10.4.4) and considered as equivalent to the

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concentration of the polyisocyanate at time‘t’. The obtained data were treated according to a second-order rate equation in which the two reactants are having equal initial concentration, because it gave a linear fit.

Second order rate equation: $k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$

Where ‘a’ is the initial concentration of the polyisocyanate at time ‘t’ = 0 and (a-x) is the concentration of the polyisocyanate at time ‘t’. The activation energy E_a, for the catalyzed blocking reaction of polyisocyanate with phenol was calculated from the slope of the Arrhenius plot (log k versus 1/T) using the equation E_a = -2.303 x R x slope. The entropy of activation, $\Delta S^{\#}$ was calculated from the well-known Eyring equation,

$$k = \frac{k_B T}{h} \cdot e^{\Delta S^{\#}/R} \cdot e^{-\Delta H^{\#}/RT}$$

where k_B is the Boltzmann constant (1.3806 x 10^{-23} JK^{-1}), h is the planck's constant (6.626 x 10^{-34} J.s), R is the gas constant (8.314 $JK^{-1}mol^{-1}$), T is the reaction temperature in Kelvin, k is the rate constant at T and $\Delta H^{\#}$ is the enthalpy of activation. The $\Delta H^{\#}$ in the above equation was obtained from the energy of activation using the relation $\Delta H^{\#} = E_a - RT$.

Determination of deblocking temperatures of blocked polyisocyanates. In a typical experiment, one drop of a solution of a blocked polyisocyanate in THF was placed at the centre of a NaCl disc and the solvent was evaporated under IR lamp and then the discs were assembled with heating accessory. The sample was heated dynamically; the temperature was increased from ambient to 170 °C with a heating rate of 5 °C/min. Eight scans at resolution of 4 cm^{-1} were co-added to produce a single spectrum in a single run. The lowest temperature at which detectable absorption at 2270 cm^{-1} range due to regeneration of –NCO group was noted as the minimum deblocking temperature.

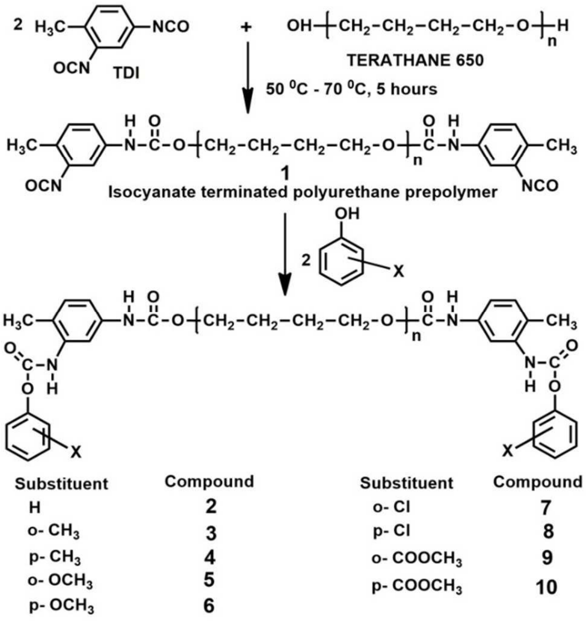
Determination of deblocking kinetic parameters. In a typical quantitative experiment, 7.5 µl of 5.0 X 10^{-4} molar solution of un-blocked polyisocyanate (i.e., –NCO terminated prepolymer) in dry THF was placed on the centre of one of the NaCl discs. The solvent was evaporated under IR lamp and then the discs were assembled and fitted with heating accessory. The spectrum was recorded immediately. The peak area under the –NCO absorption was calculated and considered as “a” appearing in the first order equation. Then, the solution of same concentration of a blocked polyisocyanate was used for deblocking kinetic studies. The deblocking experiments were carried out isothermally at 120 °C, 130 °C and 140 °C. Here, the time set to reach the desired temperature from ambient was 7 minutes in the case of phenol-, o-cresol-, p-cresol- and p-methoxyphenol-blocked polyisocyanates, whereas the time set was only 4 minutes in the case of p-esterphenol-, o- and p-chlorophenol-blocked polyisocyanates. Programme was made in the heating device in such a way that once the desired temperature reached, then the experiment proceeded isothermally. Spectrum was recorded for zero time immediately when the sample reached the desired temperature and then recorded at regular time intervals. At the zero time (in all the cases), there was no isocyanate absorption at 2270 cm^{-1} and as time increased, the absorption by –NCO group at 2270 cm^{-1} was also increased due to the deblocking of blocked polyisocyanates. The peak area of the –NCO group in each spectrum was calculated using PerkinElmer Spectrum software and considered as ‘x’ appearing in the first order rate equation. From the ‘a’ and ‘x’, a-x was calculated and the data obtained were treated according to the first order rate equation, since it gave a linear fit.

First order rate equation: $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

The energy of activation E_a , enthalpy of activation $\Delta H^{\#}$, and entropy of activation $\Delta S^{\#}$ for the amine-catalyzed deblocking reactions were calculated as described in the preceding section.

Results and Discussion

Synthesis of phenol-blocked polyisocyanates (2-10). The polyisocyanate was prepared separately for each entry given in **Table 1** by the reaction of two equivalents of TDI with one equivalent of poly(tetrahydrofuran) diol (**Scheme-1**). The reaction was monitored using FT-IR spectrophotometer. To ensure the completion of the prepolymer formation, the spectrum of the reaction mixture was recorded at regular time intervals after 3 hours from the starting of the reaction until to attain constant ratio of peak area of –NCO group to urethane carbonyl group formed. The FT-IR spectrum of prepolymer is given in **Figure 2(a)**. The strong absorption band appeared at 2270 cm^{-1} indicates the presence of free –NCO groups in the prepolymer. In the 2,4-TDI, the –NCO group adjacent to $–CH_3$ group is less reactive due to the electron donating nature of the $–CH_3$ group, which reduces the positive charge on the carbon atom of –NCO group. Moreover, this methyl group impede the incoming nucleophile to –NCO group.



Scheme 1. Synthesis of phenol-blocked polyisocyanates(**2-10**).

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Table 1. Synthesis of phenol-blocked polyisocyanates.

Compd. No.	Blocking agents	Time (min) required for 75% completion of blocking reaction at		
		60 ^{0}C	50 ^{0}C	40 ^{0}C
2	Phenol	9	14	28
3	o-Cresol	23	36	45
4	p-Cresol	25	36	50
5	o-Methoxyphenol	37	44	50
6	p-Methoxyphenol	10	17	22
7	o-Chlorophenol	5	7	12
8	p-Chlorophenol	6	12	17
9	Methyl 2-hydroxybenzoate	Incomplete for ever	Incomplete for ever	Incomplete for ever
10	Methyl 4-hydroxybenzoate	270 + 5 days at room temp.	270 + 5 days at room temp.	270 + 5 days at room temp.

As a result, the isocyanate group at 2-position of TDI is approximately four times less reactive than the isocyanate group present at 4-position.[44] Thus, the –NCO group present at the 4-position of TDI is converted to urethane during the formation of polyisocyanate. To block the terminal –NCO group of prepolymer, phenol and several substituted phenols were used as blocking agents. The relative reactivity of phenolic hydroxyl towards isocyanate is 1000 times lesser than that of aliphatic primary hydroxyl group,[9] because phenols are poor nucleophiles for isocyanates due to its size and resonance-stabilized planar configuration. Thus, all the blocking reactions were catalyzed using a tertiary amine. Diethylcyclohexylamine was chosen as a catalyst because its boiling point is high enough for reverse reaction to be studied and also it was found to be mixing thoroughly with the reaction mixture. The blocking reaction was stopped when the complete disappearance of –NCO absorption at 2270 cm^{-1} in the FT-IR spectrum. The time required to complete 75% of the reaction at three different temperatures are given in **Table 1**.

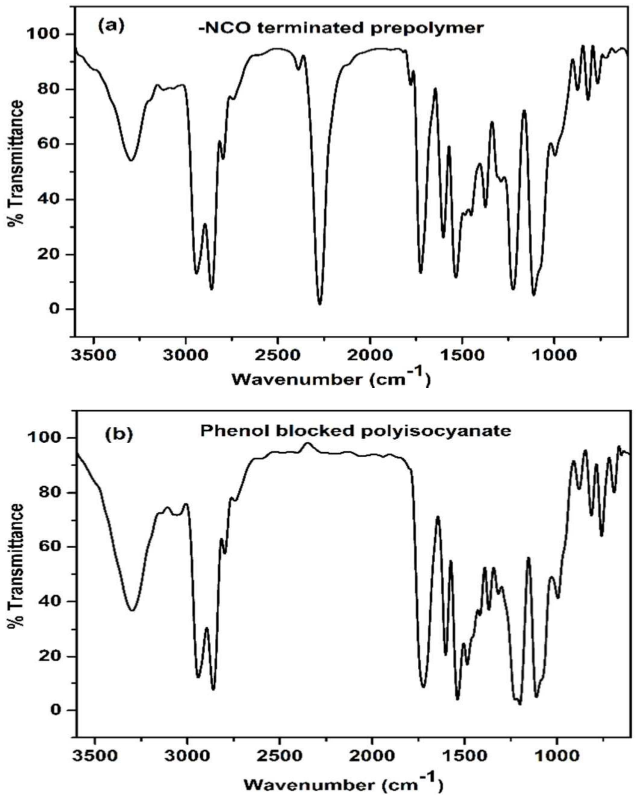

Figure 2. FT-IR spectrum of (a) isocyanate-terminated polyurethane prepolymer and (b) phenol-blocked polyisocyanate.

The FT-IR spectra of all the phenol-blocked polyisocyanates are identical and shown urethane –NH stretching absorption around 3300 cm^{-1}, urethane –NH bending absorption around 1535 cm^{-1}, urethane –C=O stretching absorption at 1730 cm^{-1}, C-O stretching absorption of C-O-C group in polyol around 1100 cm^{-1} and the stretching vibration of the C=O group of the urethane combined with N-H around 1200-1240 cm^{-1}. The absence of absorption at 2270 cm^{-1} indicates that the isocyanate groups were completely blocked with phenol. Typical example spectrum of phenol-blocked polyisocyanate is given in **Figure 2(b)**. Like FT-IR spectra, the ^{1}H-NMR spectra of phenol-blocked polyisocyanates were also identical. All the 1H-NMR spectra recorded in $CDCl_3$ shown urethane proton attached to polyol at 6.82- 6.84 ppm, urethane proton attached to phenolic ring at 6.90-6.94 ppm and aromatic methyl protons at 2.25-2.34 ppm in addition to aromatic protons at 7.10-7.82 ppm. All the ^{1}H-NMR spectra shown a distinct singlet at 7.77-7.82 ppm, which is due to the aromatic ring proton present in between the two urethane groups. This observation is in agreement with D_2O exchange studies reported by Mohanty and Krishnamurti.[45] These characterizations confirm the formation of phenol-blocked polyisocyanates and their structures without any ambiguity.

Blocking kinetics. Hot-stage FT-IR spectrophotometer is the best analytical tool for studying the neat blocking kinetics of –NCO terminated polyurethane prepolymer with phenol, as this tool directly measures the disappearance of isocyanate functional group

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Table 2. Second-order rate constants and activation parameters for amine-catalyzed, neat blocking reactions of polyisocyanate.

Compd. No.	Blocking agents	K_a of Blocking Agent	Second order rate constant k x 10^3 ($eq^{-1}.min^{-1}$)			E_a ($kJ.mol^{-1}$)	$\Delta H^{\#}$ ($kJ.mol^{-1}$)	$\Delta G^{\#}$ ($kJ.mol^{-1}$)	$\Delta S^{\#}$ ($JK^{-1}.mol^{-1}$)
			40 °C	50 °C	60 °C				
2	Phenol	1.05 x 10^{-10}	1.001	1.782	3.019	47.81	45.12	96.34	-158.55
3	o-Cresol	0.49 x 10^{-10}	0.468	0.703	0.904	28.60	25.92	98.84	-225.76
4	p-Cresol	0.52 x 10^{-10}	0.513	0.800	1.035	30.48	27.80	98.49	-218.87
5	o-Methoxyphenol	1.17 x 10^{-10}	0.394	0.525	0.935	37.31	34.64	99.62	-201.21
6	p-Methoxyphenol	0.62 x 10^{-10}	1.033	1.321	1.910	26.56	23.88	97.14	-226.82
7	o-Chlorophenol	20.0 x 10^{-10}	1.645	3.110	4.334	42.08	39.39	94.84	-171.67
8	p-Chlorophenol	4.17 x 10^{-10}	1.424	2.705	3.934	44.12	41.43	95.22	-166.51
9	Methyl 2-hydroxybenzoate	1.34 x 10^{-10}	0.0415	0.115	0.259	79.36	76.67	103.70	-83.69
10	Methyl 4-hydroxybenzoate	30.0 x 10^{-10}	0.484	0.625	0.758	19.45	16.76	99.15	-225.08

of the polyisocyanate during the course of the blocking reaction.[25,27] With the intention of calculating the kinetic and activation parameters for the neat blocking reaction of polyisocyanates, isothermal experiments were carried out at 40 ^{0}C, 50 ^{0}C and 60 ^{0}C. The distinct changes observed in the FT-IR spectrum of each blocking reaction mixture was the steady decease in the intensity of absorption peak at 2270 cm^{-1} range corresponds to –NCO groups, and steady increase at 1730 cm^{-1} range corresponds to urethane carbonyl group with respect to time. We followed the disappearance of isocyanate absorption at 2270 cm^{-1} for the blocking kinetics. Typical FT-IR spectra recorded for different time intervals at three different temperatures for the blocking reaction are given in the **Figure 3**.

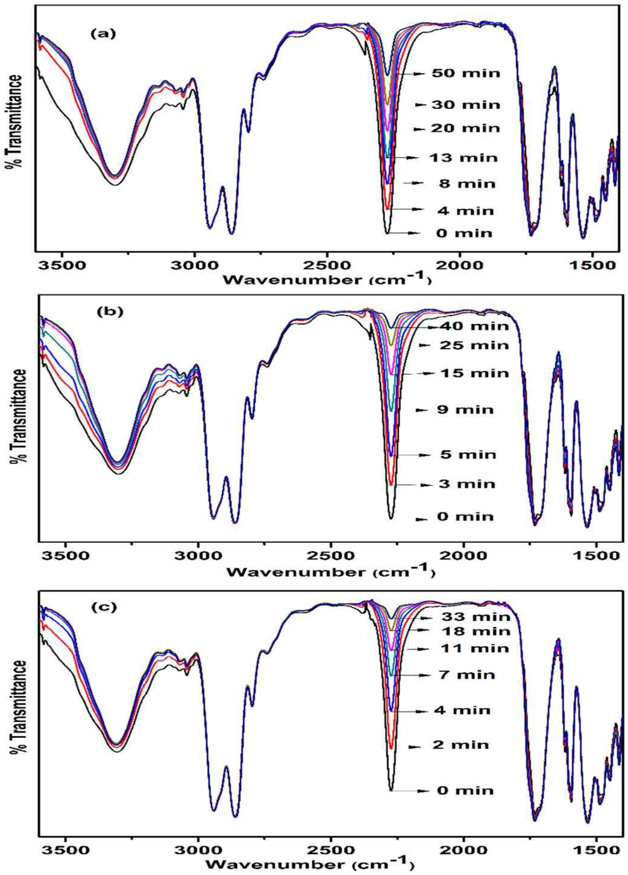

Figure 3. FT-IR spectra recorded for different time intervals at isothermal condition for the blocking reaction of polyisocyanate with phenol: (a) 40 ^{0}C (b) 50 ^{0}C and (c) 60 ^{0}C.

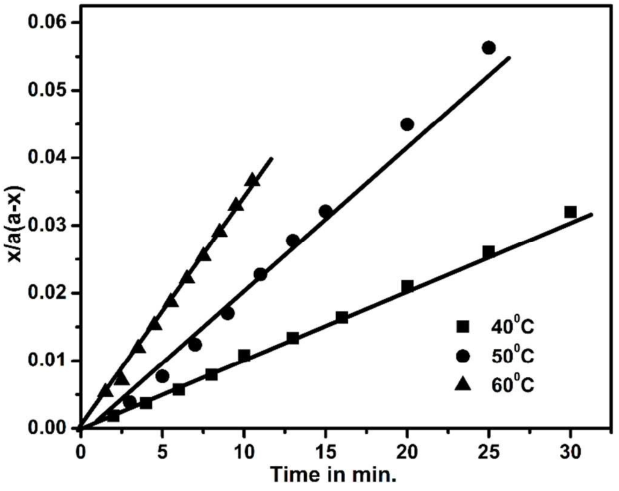

Figure 4. Amine-catalyzed second-order kinetic plots of blocking reaction of polyisocyanate with phenol.

The plots of x / a (a-x) versus time were found to be linear and passes through the origin and confirm that the blocking reaction of polyisocyanates with phenol follows second order kinetics of the type A + B ----> products, in which the two reactants are having the same initial concentration. The isocyanate-alcohol including phenol

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reactions following second order kinetics were well studied.[9] Typical second order rate plots for the tertiary amine catalyzed blocking reaction of polyisocyanate with phenol is given in the **Figure 4** and the second order rate constants for 50% conversion and activation parameters determined are given in the **Table 2**.

In order to know more about mechanistic aspects of blocking reaction, we followed the kinetics of uncatalyzed reaction at 50 ^{0}C. Since the rate of uncatalyzed blocking reaction was too slow, we could follow the kinetics only up to 10% conversion and the rate constants determined are given in the **Table 3**.

Table 3. Second-order rate constants for uncatalyzed, neat blocking reactions of polyisocyanate at 50 °C.

Compd. No.	Blocking agents	K_a of blocking agent [x10^{10}]	Second order rate constant k x10^5 (eq^{-1}.min^{-1})
2	Phenol	1.05	1.007
3	o-Cresol	0.49	0.394
4	p-Cresol	0.52	0.599
5	o-Methoxyphenol	1.17	1.059
6	p-Methoxyphenol	0.62	0.436
7	o-Chlorophenol	20.0	14.008
8.	p-Chlorophenol	4.17	1.827
9	Methyl 2-hydroxybenzoate	1.34	3.011
10	Methyl 4-hydroxybenzoate	30.0	4.153

The rate constant values for the uncatalyzed blocking reaction are found to be increased with increasing the acidity (dissociation constant, K_a) of phenolic compounds. This observation is just opposite of what one would expect. Because, in general, electron releasing substituents in the blocking agent will increase the nucleophilicity of the blocking agent and hence increase the reactivity. Similarly, electron withdrawing substituents will decrease the nucleophilicity of the blocking agent and hence reduce the reactivity with an isocyanate. But, in this complete study, it was found that the electron releasing methyl and methoxy substituents decreases the rate and the electron withdrawing substituents like chloro and ester groups increases the rate of uncatalysed blocking reaction. Moreover, the rate of o-chlorophenol was higher than that of its para isomer; the acidity of ortho isomer is high. These observations ensure that the blocking rate of uncatalyzed phenol-isocyanate reaction depends only on the acidity of blocking agents, i.e., the polarizability of hydroxyl group of phenolic compounds. If the acidity of a particular phenolic compound is high, the more polarized oxygen atom of hydroxyl group will easily attack the partially positive carbon atom of –NCO group, thereby increasing the rate of the blocking reaction.

The second-order rate constants for the amine-catalyzed blocking reactions were also found to be in accordance with the acidity of blocking agents except the cases of phenols with ester substituent. Because of phenol is acidic, it can associate easily with tertiary amine base catalyst to form an association complex. Then this complex will again associate with isocyanate group to form a four centred active intermediate complex during the blocking reaction (**Figure 5**). The polarization of the phenolic hydroxyl group by the tertiary amine catalyst is responsible for the multi order (~100 times) increase in the reactivity compared to un-catalyzed reaction.[46] The low reactivity of blocking agents with ester substituents can be explained with this mechanism. Owing to the high acidity of these blocking agents, they can easily associate with basic catalyst. But, the phenolate group become poor nucleophilic due to high electron withdrawing power of ester substituent present in the ring thus the formation of active intermediate complex with –NCO group becomes difficult thereby react with low rate. Though the rate of reaction involving o-chlorophenol was relatively higher than that of with phenol, it was not in proportional to its acidity value compared to unsubstituted phenol. Similarly, the rate of o-methoxyphenol was found to be less eventhough its acidity value is slightly higher than the phenol. In these cases steric factor play a role. Time required for 75% conversion into product given in **Table-1** also support this discussion. The $\Delta G^\#$ of all the blocking reaction of isocyanate reported in this work were found to be almost identical and were in between 95 kJ.mol^{-1} to 103 kJ.mol^{-1}. This clearly indicates that all the reactions follow the same mechanism. This was further verified by both the isokinetic plot and Exner plot; the linearity of $\Delta H^\#$ vs. $\Delta S^\#$ and log k_{obs} (50 ^{0}C) vs. log k_{obs} (60 ^{0}C) respectively confirm that all the reaction follow a common blocking mechanism.[47] The higher negative entropy of activation ($\Delta S^\#$) supports the formation of a rigid complex in the transition state.

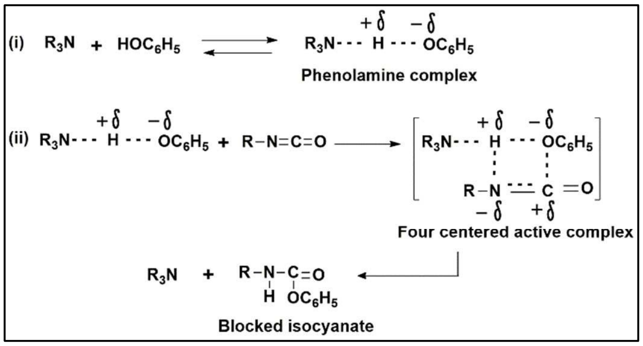

Figure 5. Possible mechanism for tertiary amine-catalyzed blocking reaction of polyisocyanate with phenol.

Deblocking temperatures of phenol-blocked polyisocyanates. As mentioned in the preceding section, hot-stage FT-IR spectrophotometer is the best analytical tool to study the deblocking reaction of blocked isocyanates too as this tool directly measures the regeneration of –NCO functional group and the disappearance of carbonyl group of blocked –NCO group. All the blocked polyisocyanates except the one based on phenol with ortho ester substituent (**9**) were subjected to FT-IR analyses at dynamic condition for the purpose of assessment of deblocking temperatures. The blocked polyisocyanate (**9**) was not included in the deblocking study since its blocking reaction was found to be incomplete for long time and it was cured to hard and insoluble mass after two weeks time, hence it need an exclusively focused

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attention. The spectra recorded from room temperature to 170 ^{0}C for a typical phenol-blocked polyisocyanate are given in **Figure 6** in which some spectra have been removed for the sake of clarity reason and the minimum deblocking temperature determined from these spectra are given in **Table 4**.

Table 4. Deblocking temperatures of phenol-blocked polyisocyanates determined using hot-stage FT-IR spectrophotometer under dynamic condition.

Compd. No.	Blocking agents	Deblocking Temperature (^{0}C)
2	Phenol	130
3	o-Cresol	135
4	p-Cresol	135
5	o-Methoxyphenol	135
6	p-Methoxyphenol	135
7	o-Chlorophenol	85
8	p-Chlorophenol	120
10	Methyl 4-hydroxybenzoate	95

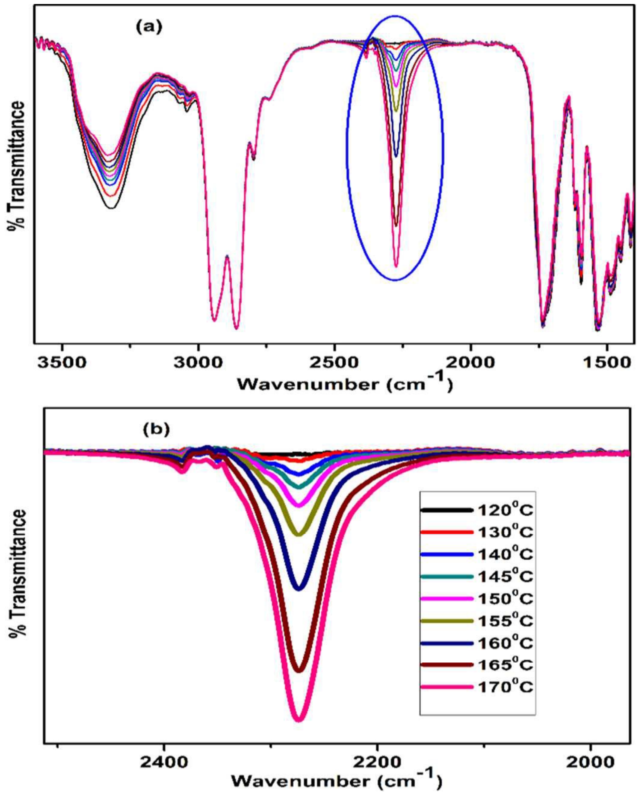
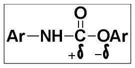


Figure 6. FT-IR spectra of phenol-blocked polyisocyanate recorded at (a) different temperatures. (b) Zoomed range of isocyanate absorption region.

The ease with which a blocked isocyanate will dissociate into the isocyanate and the blocking agent will depend upon the magnitude of charge separation between the carbonyl carbon and the oxygen atom of blocking agent.



$$\mathrm{Ar{-}NH{-}}\overset{\overset{\displaystyle O}{\|}}{\underset{+\delta}{C}}\mathrm{{-}}\underset{-\delta}{O}\mathrm{Ar}$$

Thus, electron-donating substituents in the blocking agent will strengthen the labile bond and electron-withdrawing substituents in the blocking agent will labilize more the bond which results low deblocking temperature. In accordance with this argument, the deblocking temperature obtained are consistent with the electronic effect as well as with the acidity values of blocking agents. If the acidity (dissociation constant) of blocking agent is high, it means that its phenolate anion is loosely bonded with carbonyl carbon. So that the blocking agent with electron-withdrawing substituents like chlorine and ester groups deblock at low temperature whereas the blocking agent with electron-releasing substituents like methyl and methoxy groups deblock at high temperature compared to phenol (**Table 4**). Within the series of phenol with electron-releasing substituents, the effect of acidity on deblocking temperatures is not reflected well, but it is reflected well in kinetic results.

Deblocking kinetics (a comparison with blocking reaction). Based on the minimum deblocking temperature determined, it was decided to do isothermal, amine-catalyzed, deblocking kinetics of substituted phenol-blocked polyisocyanates at 120 °C, 130 °C and 140 °C under neat condition as blocking kinetics were performed. Three changes were observed in the FT-IR spectrum of each blocked polyisocyanate. The first change observed was an increase in the intensity of –NCO absorption at 2270 cm^{-1} with respect to time upto 30% conversion in comparison with quantitatively recorded spectrum of unblocked polyisocyanate and then it becomes constant for some time, after which it was decreased slowly due to the reaction between regenerated isocyanate and –NH group of remaining urethane moiety leading to the formation of allophanate groups. This side reaction was observed by the appearance of a shoulder in the urethane N-H stretching absorption peak at 3300 cm^{-1}. The second change observed was due to the absorption by urethane carbonyl at 1732 cm^{-1} that was decreased due to the cleavage of blocked isocyanate groups. But the change was not as much as in the case of –NCO absorption, because, the other urethane carbonyl derived from polyol and isocyanate also absorbs in the same region. Moreover, the absorption by C=O is not as strong as –NCO group. The third change observed was decrease in the intensity of the absorption by urethane N-H at 3300 cm^{-1} due to the cleavage of blocked isocyanate groups. Here also, the two different urethane N-H groups present in the blocked polyisocyanate absorb in the same region. Hence, the absorption peak of –NCO group at 2270 cm^{-1} was conveniently followed for deblocking kinetics as it absorbs strongly and exclusively in that region. Typical FT-IR spectra recorded for different time intervals at different temperatures for the deblocking kinetic analysis are given in **Figure 7**. The plots of log a/(a – x) vs time were found to be linear and confirm that the amine-catalyzed deblocking of all the phenol-blocked polyisocyanates follow first order kinetics, and typical

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Table 5. First-order rate constants and activation parameters for amine-catalyzed deblocking reactions of blocked polyisocyanates

Compd. No.	Blocking agents	K_a of Blocking Agent	First order rate constant k x 10^3 (min^{-1})			E_a ($kJ.mol^{-1}$)	$\Delta H^\#$ ($kJ.mol^{-1}$)	$\Delta G^\#$ ($kJ.mol^{-1}$)	$\Delta S^\#$ ($JK^{-1}.mol^{-1}$)
			120 °C	130 °C	140 °C				
2	Phenol	1.05×10^{-10}	6.483	9.002	13.612	50.05	46.70	115.51	-170.74
3	o-Cresol	0.49×10^{-10}	1.810	4.130	8.400	103.81	100.46	118.12	-43.83
4	p-Cresol	0.52×10^{-10}	2.900	4.928	8.433	72.15	68.80	117.53	-120.92
5	o-Methoxyphenol	1.17×10^{-10}	2.690	4.730	6.330	57.98	54.63	117.67	-156.41
6	p-Methoxyphenol	0.62×10^{-10}	1.105	1.740	3.230	72.41	69.05	121.02	-128.94
7	o-Chlorophenol	20.0×10^{-10}	13.080	18.400	26.700	48.23	44.88	113.12	-169.32
8	p-Chlorophenol	4.17×10^{-10}	6.631	9.691	13.885	49.40	46.05	115.26	-171.75
10	Methyl 4-hydroxybenzoate	30.0×10^{-10}	12.510	15.270	18.940	28.02	24.67	113.74	-221.02

example plots for three different temperatures are given in Figure 8. The first order rate constants and activation parameters calculated for all the blocked polyisocyanates, except for the blocked polyisocyanate **9** are given in **Table 5.**

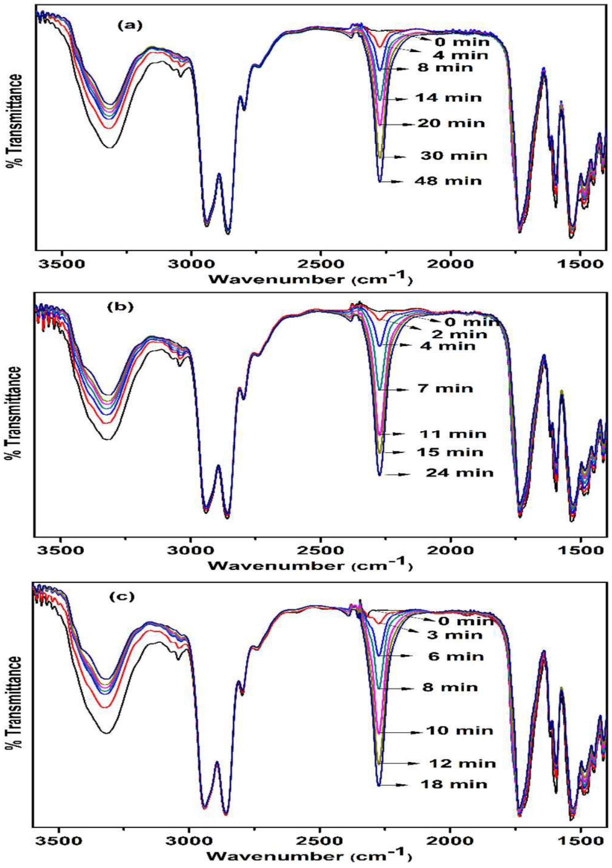

Figure 7. FT-IR spectra recorded for different time intervals at isothermal condition for the deblocking reaction of phenol-blocked polyisocyanate: (a) 120 ^{0}C (b) 130 ^{0}C and (c) 140 ^{0}C.

When compared to deblocking temperature, here, the role of acidity of blocking agent on the deblocking rate is clearly able to seen; deblocking rate decreases with decreasing the acidity of phenol and the reverse is also found true. However, careful analysis of the rate constants (k) and energy of activation (E_a) clearly reveals that unlike blocking reactions, in the deblocking reactions, electronic effect mainly determine the rate of the reaction as discussed for deblocking temperatures. This could be realized when considering the rate of both chloro and ester substituted phenols. That is, when comparing the rate of blocking and deblocking reactions involving blocking agent with chloro and ester substituents, unlike in the case of blocking reaction, here both the substituents increases the rate.

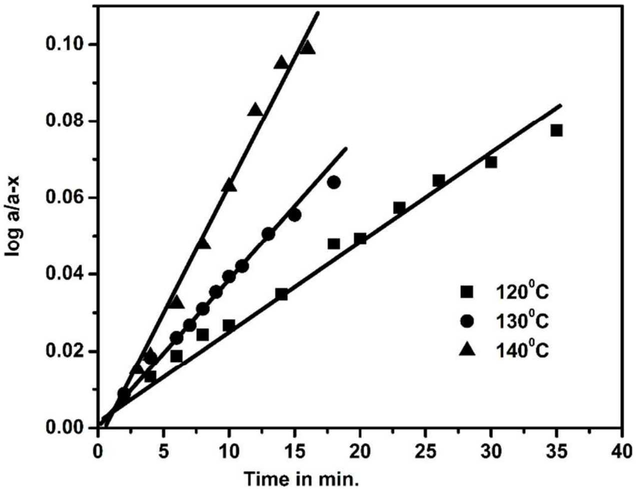

Figure 8. Amine-catalyzed first-order kinetic plots of deblocking reaction of phenol-blocked polyisocyanate.

Also it was found that unlike the case of blocking reactions, here the rate constants (k), energy and enthalpy of activation (E_a and $\Delta H^\#$) are consistent with each other. These results lead to a conclusion that the deblocking in the presence of a basic catalyst proceeds through the deprotonation of urethane N-H by the base

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to form a conjugate base of urethane. The dissociation then proceeds by eliminating phenolate anion from the negatively charged conjugate base of urethane, which then accepts a proton from the protonated base. According to this mechanistic pathway and a comparison with blocking kinetics, a phenol with more acidity and less nucleophilicity will be a better blocking agent and at the same time it will be a better leaving group and which could cleave off easily. The narrow free energy of activation ($\Delta G^{\#}$) obtained confirm that all the deblocking reactions uniformly follow this mechanism.

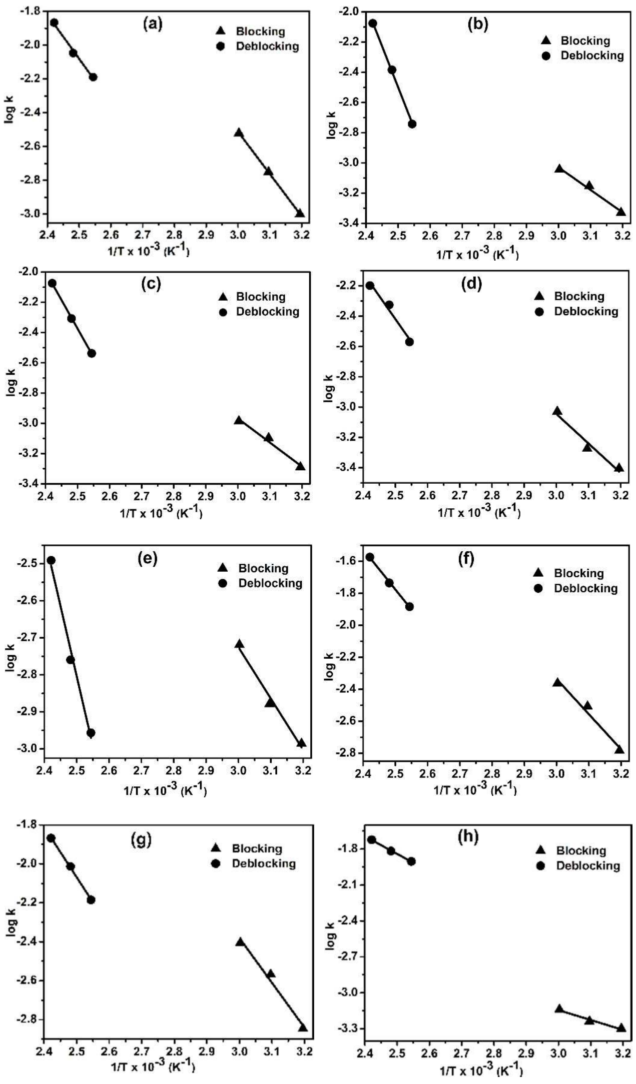

Figure 9. Arrhenius plots of forward and reverse reactions of blocked polyisocyanates. Blocking agent: (a) Phenol, (b) o-cresol, (c) p-cresol, (d) o-methoxyphenol, (e) p-methoxyphenol, (f) o-chlorophenol, (g) p-chlorophenol and (h) methyl 4-hydroxybenzoate.

Analysis of Arrhenius plots of forward and reverse reactions. Arrhenius plots of reversible blocking and deblocking reactions of blocked polyisocyanates are given in **Figure 9 (a)-(h)**. The upper temperature of blocking reaction was extrapolated to determine the maximum temperature upto which forward reaction will takes place. Likewise, the lower temperature of deblocking reaction was extrapolated to determine the temperature below which reverse reaction will never takes place. We believed that extrapolation of such double Arrhenius plot will give new informations about thermally reversible reactions. Typical example of such plot is given in **Figure 10**. Interestingly, all such plots except the one fitted for phenol with ester substituent shown a temperature range (equilibrium temperature range, ETR), within this ETR, both the forward and reverse reactions are found to be coexist and proceed with different rate. The ETR was found relatively narrow (the difference was only 10 ^{0}C) for p-chlorophenol-blocked polyisocyanate and it was found relatively broad (the difference was 47 ^{0}C) for o-methoxyphenol-blocked polyisocyanate. Two important conclusions could be derived from this analysis; (i) forward reaction should be carried out below the lower limit of the ETR and the reverse reaction should be carried out at substantially above the upper limit of the ETR and (ii) the mid-point of the ETR is the most probable equilibrium temperature, in principle, below or above which only forward or reverse reaction respectively will takes place.

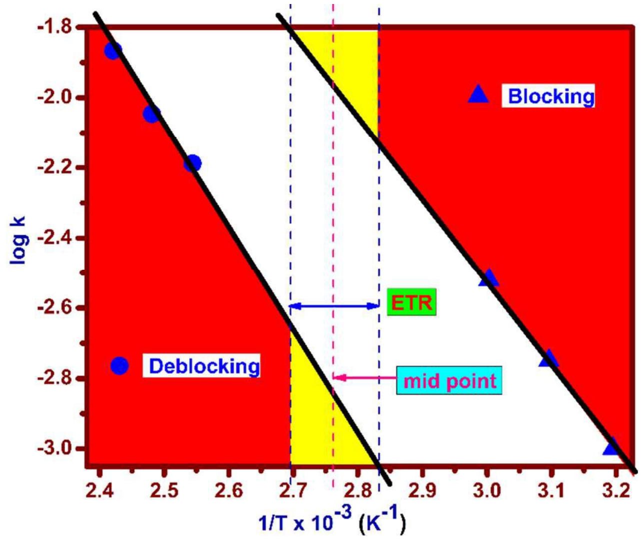

Figure 10. Arrhenius plots of forward and reverse reactions of phenol-blocked polyisocyante showing equilibrium temperature range (ETR) and most probable equilibrium temperature.

To determine the equilibrium rate constant in a typical case, the temperature was shifted 0.5 ^{0}C simultaneously above and below the upper and lower temperature of forward and reverse reaction respectively in the double Arrhenius plot. The log k was identical at one particular shift, from that log k, equilibrium rate constant was calculated and given in **Table 6**. Interestingly, the trend observed in the equilibrium rate constants is similar to that observed in the forward and reverse reactions. It is worth mentioning here that depends upon temperatures at which blocking and deblocking reactions carried out, the apparent ETR may be wide or narrow, but

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Table 6. Thermal equilibrium data of Phenol-blocked polyisocyanates determined using Arrhenius plots for forward and reverse reactions.

Compd.No.	Blocking agents	Equilibrium temperature range for forward and reverse reaction (^{0}C)	Most probable equilibrium temperature for forward and reverse reaction (^{0}C)	Equilibrium rate constant k x 10^3
2	Phenol	80 – 98	90	4.898
3	o-Cresol	102 – 142	121	1.072
4	p-Cresol	89 – 122	105	1.549
5	o-Methoxyphenol	75 – 122	98	1.622
6	p-Methoxyphenol	85 – 119*	101	-
7	o-Chlorophenol	64 – 102	82	8.709
8	p-Chlorophenol	80 – 90	85	5.623
10	Methyl 4-hydroxybenzoate	-	-	

*Coexistence of forward and reverse reaction not found in this case.

the most probable equilibrium temperature will not be changed. There was a surprising observation from this analysis that the p-methoxyphenol-polyisocyanate system found not passes through the equilibrium state, however it was a thermally reversible system (**Figure 11**). Finally it should be mentioned that the extrapolation of Arrhenius plots of ester substituted phenol-polyisocyanate system was found out of the temperature range studied. As already mentioned, this need a separate investigation.

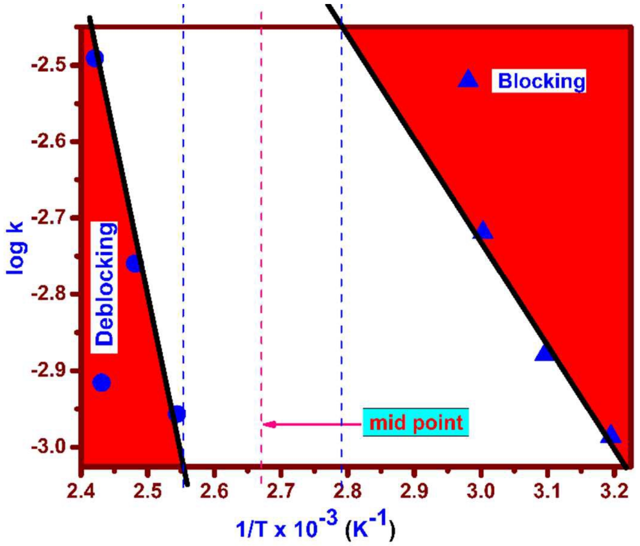

Figure 11. Arrhenius plots of forward and reverse reactions of p-methoxyphenol-blocked polyisocyante not showing equilibrium.

CONCLUSIONS

In this article, we report (i) synthesis of a series of blocked polyisocyanates using phenol with methyl, methoxy, chloro and ester substituents at 2- and 4-position as blocking agents. (ii) Both forward and reverse reactions of these blocked polyisocyanates were studied in detail without using solvent. (iii) The rate of uncatalysed forward reactions were found to be in proportional to the acidity of the blocking agent. (iv) Identical trend was observed in the time required for 75% conversion into products and rate of catalyzed forward reaction. (v) The rate of amine-catalyzed forward and reverse reactions were found to be in proportional to the acidity of the blocking agent except the phenol with electron withdrawing ester substituents at 4-position. (vi) Chlorophenols found to block the isocyanate quickly and at the same time they cleaved off easily compared to all other phenols studied. (vii) Phenol with ester substituent was found to block the isocyanate group slowly and deblock quickly. (viii) There was an expected trend between rate and activation parameters only in deblocking reactions and no correlation found between activation parameters of forward and reverse reactions. (ix) The most probable equilibrium temperatures were assessed using double Arrhenius plots for the first time and these values and the trend present in these values were found in agreement with deblocking temperatures and the kinetic and activation parameters of reverse reactions. (x) The trend observed in the equilibrium rate constants is similar to that observed in forward and reverse reactions. (xi) The p-methoxyphenol-polyisocyanate system found not passes through the equilibrium state, however it was a thermally reversible system.

Acknowledgement

One of the authors (S.K) thank University Grants Commission, India for the award of Teacher Fellowship under Faculty Development Programme of UGC-XII Plan to carry out this work. The authors also thank CSIR for providing FT-IR with hot-stage accessories under a scheme No. 02(0100)/12/EMR-II. Dt.31.10.2012.

Notes and references

1 Z. Ranjbar, Sh. Montazeri, M. Mohammad Raei Nayini and A. Jannesari, Prog. Org. Coat., 2010, 69, 426-431.
2 T. A. Potter, J. W. Rosthanser and H. G. Schmeler, Proceedings of the 11th International Conference on Organic Coatings Science and Technology, Athens, Greece, July 1985.
3 H. L. Schreuder-Gibson, Rubber World, 1990, 34.
4 Z. W. Wicks Jr, Prog. Org. Coat., 1975, 3, 73-99.
5 Z. W. Wicks Jr, Prog. Org. Coat., 1981, 9, 3-28.

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6 D. A. Wicks and Z. W. Wicks Jr, Prog. Org. Coat., 1999, 36, 148-172.
7 D. A. Wicks and Z. W. Wicks Jr, Prog. Org. Coat., 2001, 41, 1-83.
8 D. A. Wicks and Z. W. Wicks Jr, Prog. Org. Coat., 2001, 43, 131-140.
9 E. Delebecq, J. Pascault, B. Boutevin, and F. Ganachaud, Chem. Rev., 2013, 113, 80-118.
10 S. Guo, J. He, W. Luo and F. Liu, Materials, 2016, 9, 110.
11 M. S. Fedoseev, O. A. Noskova and L. F. Derzhavinskaya, Polym. Sci., Ser. D, 2016, 9, 199-204.
12 C. Lou and M. Di, J. Adhesion Sci. Technol., 2013, 27, 2340-2351.
13 A. Sultan Nasar, V. Shrinivas, T. Shanmugam and A. Raghavan, J. Polym. Sci. Part A: Polym. Chem., 2004, 42, 4047-4050.
14 T. Shen, M. Lu and L. Liang, Macromol. Res., 2012, 20, 827-834.
15 P. E. Engonga, V. Marchetti, P. Gerardin, P. Tekely and B. Loubinoux, J. Fluorine Chem., 2000, 101, 19-25.
16 I. Muramatsu, Y. Tanimoto, M. Kase and N. Okoshi, Prog. Org. Coat., 1993, 22, 279-286.
17 A. Sultan Nasar, S. N. Jaisankar, S.Subramani and G. Radhakrishnan, J. Macromol. Sci., Pure Appl. Chem., 1997, A34, 1237-1247.
18 A. Li, G. Fan, H. Chen and Q. Zhao, Res. Chem. Intermed., 2012, DOI 10.1007/s11164-012-0863-8.
19 A. Wenning and F. Schmitt, Ger. Offen., DE 19 627 951, 1998.
20 T. Shen, D. Zhou, L. Liang, J. Zheng, Y. Lan, and M. Lu, J. Appl. Polym. Sci., 2011, 122, 748-757.
21 L. Yin, Y. Liu, Z. Ke and J. Yin, Eur. Polym. J., 2009, 45, 191-198.
22 M. Bertoldo, C. Cappelli, S. Catanorchi, V. Liuzzo and S. Bronco, Macromolecules, 2005, 38, 1385-1394.
23 L. van Ravenstein, W. Ming, R. D. van de Grampel, R. van der Linde, G. de With, T. Loontjens, P. C. Thune and J. W. Niemantsverdriet, Macromolecules, 2004, 37, 408-413.
24 J. H. Macmillan, E .R. Bertozzi and B. E. Streeter, US Patent, 4 430 489, 1984.
25 G. Sankar and A. Sultan Nasar, J. Polym. Sci. Part A: Polym. Chem., 2007, 45, 1557-1570.
26 A. S. Nasar, S. Subramani and G. Radhakrishnan, J. Polym. Sci. Part A: Polym. Chem., 1999, 37, 1815-1821.
27 G. Sankar and A. Sultan Nasar, J. Appl. Polym. Sci., 2008, 109, 1168-1176.
28 A. M. Issam and G. Shankar, Polym. Sci. Ser. B, 2011, 53, 52-56.
29 I. Ahmad, J. H Zaidi, R. Hussain and A. Munir, Polym. Int., 2007, 56, 1521-1529.
30 H. Yeganeh and M. A. Shamekhi, Polym. Int., 2005, 54, 754-763.
31 Y. Zhang, F. Cao, H. Tan and F. Gu, Pigment & Resin Technology, 2014, 43/4, 194-200.
32 Z. Zhou, H. Lv, X. Wang, F. Ren, and W. Xu, J. Appl. Polym. Sci., 2013, 597-599.
33 Y. Zuo, J. Gu, Y. Zhang, H. Tan, P. Li and M. Di, J. Adhesion Sci. Technol., 2012, 26, 1685-1698.
34 Y. Zhang, F. Gu, X. Fiang, L. Zhu and H. Tan, Pigment & Resin Technology, 2011, 40, 379-385.
35 A. Muehlebach, J. Polym. Sci. Part A: Polym. Chem., 1994, 32, 753–765.
36 S. Petrak, V. Shadurka and W. H. Binder, Prog. Org. Coat., 2009, 66, 296-305.
37 S. Subramani, Y. J. Park, Y. S. Lee and J. H. Kim, Prog. Org. Coat., 2003, 48, 71-79.
38 J. M. Lee, S. Subramani, Y. S. Lee and J. H. Kim, Macromol. Res., 2005, 13, 427-434.
39 E. Querat, L. Tighzert and J-P. Pascault, Die Angewandte Makromoleculare Chemie, 1994, 219, 185-203.
40 X. Tassel, D. Barbry and L. Tighzert, Eur. Polym. J., 2000, 36, 1745-1751.
41 S. Maier, T. Loontjens, B. Scholtens and R. Mulhaupt, Angew. Chem. Int. Ed., 2003, 42, 5094-5097.
42 S. Maier, T. Loontjens, B. Scholtens and R. Mulhaupt, Macromolecules, 2003, 36, 4727-4734.
43 T. Loontjens, J. Polym. Sci. Part A: Polym. Chem., 2003, 41, 3198–3205.
44 M. Szycher, Szycher's Hand book of Polyurethanes, Second edition, CRC Press, Taylor and Francis group, New York, 2013, pp. 88-133.
45 S. Mohanty and N. Krishnamurty, Eur. Polym. J., 1998, 34, 77-83.
46 J. E. Kresta, A. Garcia, K. C. Frisch and G. Linden, ACS Symp. Ser., 1981, 172, 403-417.
47 J. E. House, Principles of Chemical Kinetics, 2nd edn., Academic press, USA, 2007, pp. 190-191.

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GRAPHICAL ABSTRACT

Synthesis and studies on forward and reverse reactions of phenol-blocked polyisocyanates: An insight into blocked isocyanates

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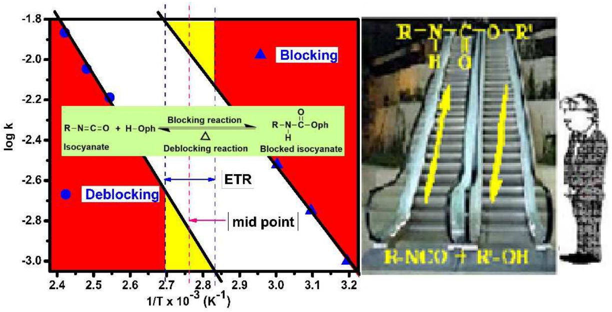

Industrially important blocked polyisocyanates were studied in detail using a hot-stage FT-IR spectrophotometer adapting neat condition with an aim to resolve complex questions on the relationship between the forward and reverse reaction parameters.

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