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POLY(URETHANE-IMIDE)S FROM BLOCKED POLYURETHANE PREPOLYMER AND PYROMELLITIC DIANHYDRIDE: EFFECT OF ALKALI METAL ALKOXIDES AND PHENOXIDES AND SUBSTITUENTS ON THE BLOCKING AGENT IN THE POLYMERIZATION REACTION

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ABSTRACT

Poly(urethane-imide)s were prepared using a series of *N*-methylaniline-blocked polyurethane (PU) prepolymers. The PU prepolymer was prepared using polypropylene glycol of molecular weight 2000 and tolylenediisocyanate, and masked with *N*-methyl aniline, *N*-methyl-*p*-anisidine and *N*-methyl-*p*-nitroaniline. The blocked PU prepolymer was reacted with pyromellitic dianhydride (PMDA) to yield poly(urethane-imide). The effect of alkali metal alkoxides (sodium methoxide and potassium methoxide) and alkali metal phenoxides (sodium phenoxide, potassium phenoxide, potassium *p*-methoxyphenoxide and potassium *p*-nitrophenoxide) as catalysts was studied for the polymerization reaction between blocked prepolymer and PMDA. Phenoxides were found to have effective catalytic activity for the polymerization. Electron withdrawing substituents tend to enhance the catalytic activity of phenoxides while electron donating substituents tend to reduce. The polymerization was faster with *N*-methyl-*p*-anisidine blocked PU prepolymer and slower with *N*-methyl-*p*-nitroaniline blocked PU prepolymer as compared to the polymerization with unsubstituted *N*-methylaniline blocked PU prepolymer. The poly(urethane-imide)s were characterized by FTIR, GPC, TGA, and

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DSC analyses. The thermal stability of the PU was found to increase by the introduction of imide component.

Key Words: Poly(urethane-imide); Polyurethane prepolymer; Thermal stability.

INTRODUCTION

Polyurethanes comprise a class of versatile materials that can be prepared by the reaction of polyol, isocyanate, and chain extenders. Their properties can be tailor-made according to end-uses. A major drawback with polyurethanes is their poor thermal stability. The thermal stability of polyurethanes can be improved by chemical modification of their structure with thermally stable heterocyclic groups. Copolymerization of imides with polyurethanes is one of the methods that can be adopted to improve thermal stability. Polyimides are heterocyclic polymers with remarkable heat resistance and good mechanical and electrical properties [1, 2]. The reaction of an isocyanate terminated polyurethane prepolymer with anhydride can be utilized to introduce imide function into the polyurethane backbone [3]. The advantage of using isocyanate instead of the conventionally used amine is that imidization is achieved in a single-step at a lower temperature [4-7]. However, the high sensitivity of -NCO group towards moisture and its susceptibility to undergo undesirable side reactions makes the use of prepolymers with NCO groups problematic. This problem can be overcome by blocking isocyanate with phenols through the formation of carbamate having a labile bond which can dissociate at an elevated temperature to regenerate isocyanate functionality [8]. Besides phenols, which are environmentally noxious, oximes [9, 10] are widely used for blocking isocyanate prepolymers. Blocked polyisocyanates are preferred for many technical and economic reasons. They are essentially insensitive to moisture with high storage stability and their deblocking temperatures can be brought down by the use of tertiary amine and organo tin catalysts [11].

Jung and Park [4] have disclosed the use of imidazole blocked 2,5-bis[(n-alkyloxy)methyl]-1,4-benzene diisocyanates to prepare rigid rod-like polyimides in which the reaction of imidazole-blocked isocyanate with pyromellitic dianhydride leads to polyimides. Such a type of reaction of imidazole-blocked isocyanate differs from the reaction of polyurethane formation, and this may open a new area of application. Takeichi and coworkers have reported the preparation of crosslinked poly(urethane-imide) by the reaction of PU prepolymer with polyimide precursors [12-14]. A few catalysts have been reported for imidization reaction involving diisocyanate [15, 16].

Recently, our group has studied aromatic secondary amines as blocking agents for isocyanates [17] and has found that in particular, *N*-methylaniline was superior over phenol, a popular blocking agent for isocyanate, in the preparation of poly(urethane-imide) copolymer using blocked-PU prepolymer [18]. The subject of this article is to study the effect of catalysts and substituents on blocking agent in the preparation of copolymers, a task not attempted, as yet.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) (Lancaster) was purified by recrystallization from acetic anhydride, followed by sublimation. 1,3-Dimethyl-3,4,5,6-tetrahydro-2-pyrimidinone (commonly called as dimethylpropylene urea, DMPU) (Aldrich) was distilled under low pressure (146°C/44mm) prior to use. Tolylene diisocyanate (TDI) (mixture of 80% 2,4- and 20% 2,6-isomers) (Aldrich), sodium methoxide and potassium methoxide (Aldrich) were used as received. Phenoxides were prepared and confirmed by the procedure reported by Kornblum and Lurie [19]. Solvents were purified according to standard procedures.

Preparation of Blocked PU Prepolymer [18, 20]

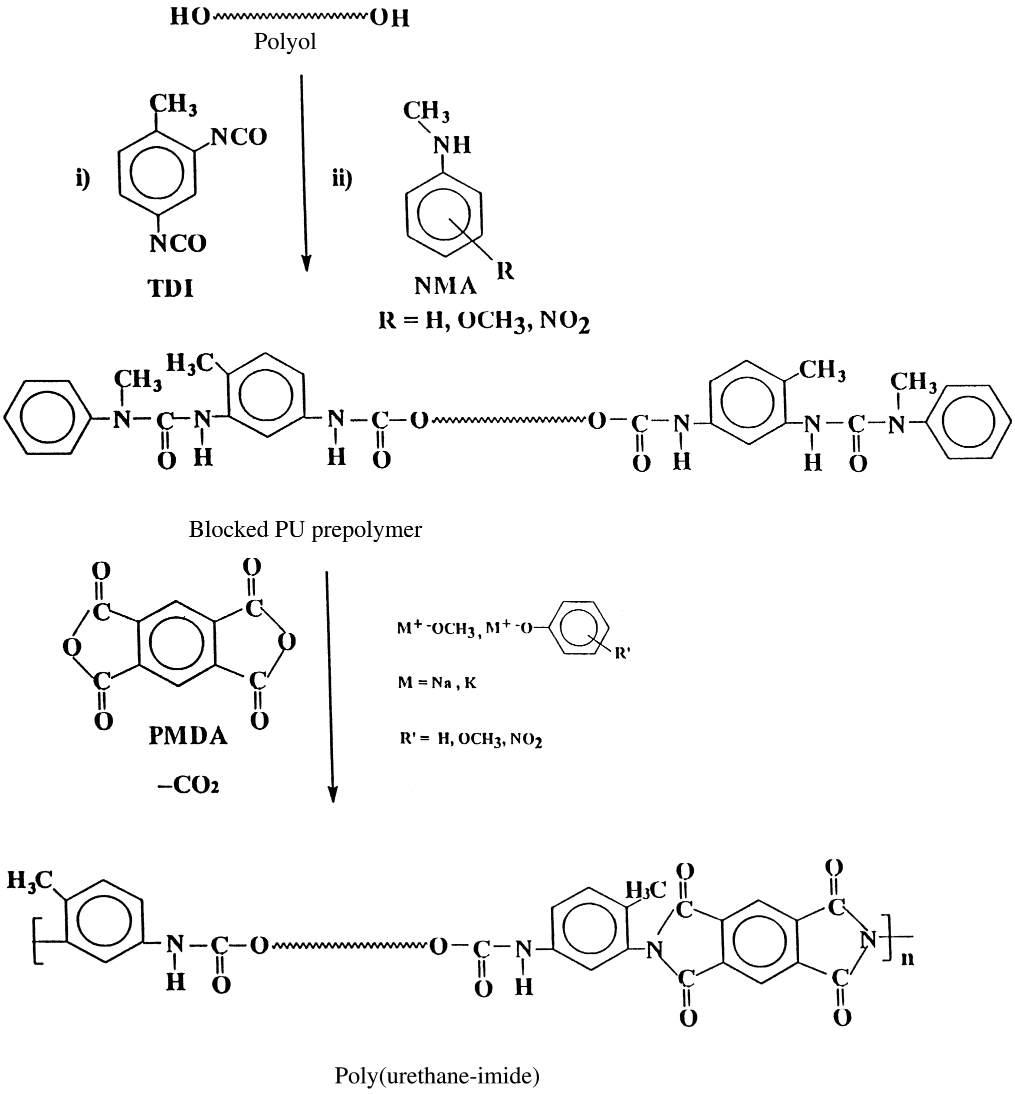
0.18 mol of TDI was placed in a reaction kettle. 0.06 mol of polyol (PPG 2000) was added dropwise with stirring; the dropping rate was such that it took one hour for complete transfer. The reaction time was 4 hours; the first 2 hours was maintained at 50°C and the next 2 hours, at 70°C. After four hours, the temperature was reduced to 40°C and -NCO content was determined by dibutyl amine method [21] and found close to the expected theoretical value (observed value = 6.5%; theoretical value = 6.66%). The -NCO terminated prepolymer was blocked with 0.12 mol of *N*-Methylaniline at 40°C, the reaction time, as determined by the disappearance of NCO absorbance using FTIR analysis, was 2 hours. A similar was used to prepare *N*-methyl-*p*-anisidine and *N*-methyl-*p*-nitroaniline blocked PU prepolymers.

Preparation of Poly(Urethane-imide) Copolymer

6×10^{-3} equivalent. of blocked prepolymer, 6×10^{-3} equivalent of PMDA and 20 ml of DMPU [18] were taken in a three-necked flask fitted with a mechanical stirrer and nitrogen inlet and outlet. 3×10^{-4}mol of the catalyst was added. The mixture was heated to 125°C with stirring. The completion of the reaction was ensured by precipitating the evolved carbon dioxide, with the help of nitrogen as carrier gas, in saturated calcium hydroxide solution. The time for the completion of the reaction was recorded. The resulting solution was concentrated, dissolved in toluene, precipitated in petroleum ether (60-80°C) and vacuum dried. The polymer was brownish red in color. Yield: 80-85%.

Measurements

FTIR spectra for the polymers were recorded using Nicolet Avtar 360 FTIR spectrometer in the range of 4000-400 cm^{-1}; the samples were dissolved in THF



Scheme 1.

and evaporated on KBr window under IR lamp. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on Bruker 300.1 MHz and 75.4 MHz specrometer, respectively. Samples were dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) containing tetramethylsilane M_n, M_w, and polydispersity (PD) were determined by gel permeation chromatography (GPC) using Waters liquid chromatograph equipped with a 410 differential refractometer and millennium 20 software. *N,N*-dimethylformamide (DMF) containing 0.01% lithium bromide was used as eluent at a flow rate of 1.0 cm^3/min. Styragel columns of pore size 10^3 A°,10^4,10^5, and 10^6 A° were used. Molecular weight calibrations were carried out using polystyrene standards of molecular weight (M_w) in the range of 2.9×10^3 to 1.7×10^5g/mol.

Thermogravimetric analyses (TGA) were carried out with Du Pont 951 thermogravimetric analyzer. The sample weight was 8-10 mg. Analyses were performed from 30-650°C at a heating rate of 10 deg/min in nitrogen atmosphere with a gas flow rate of 100 cm^3/min. Differential Scanning Calorimetry (DSC) was performed from -100 to 300°C on a Du Pont 910 instrument at a heating rate of 10 deg/min. The amount of sample used was 5-8 mg in a sealed aluminium pan. The experiments were carried out under a dry nitrogen with a purge rate of 50 cm^3/min.

RESULTS AND DISCUSSION

FTIR Analyses and NMR Analyses

IR spectra of polymers are identical and a representative spectrum is given in Figure 1. Strong absorptions appeared at 3200-3400 cm^{-1}, 1530-1560 cm^{-1}, and 1210-1240 cm^{-1} are due to N-H stretching, N-H bending and stretching vibration of C = O group of urea combined with N-H group respectively. In addition to these vibrations of urethane functional group, the polymer also showed characteristic imide absorption bands at 1777 cm^{-1} (C = O, in-phase), 1721 cm^{-1} (C = O,

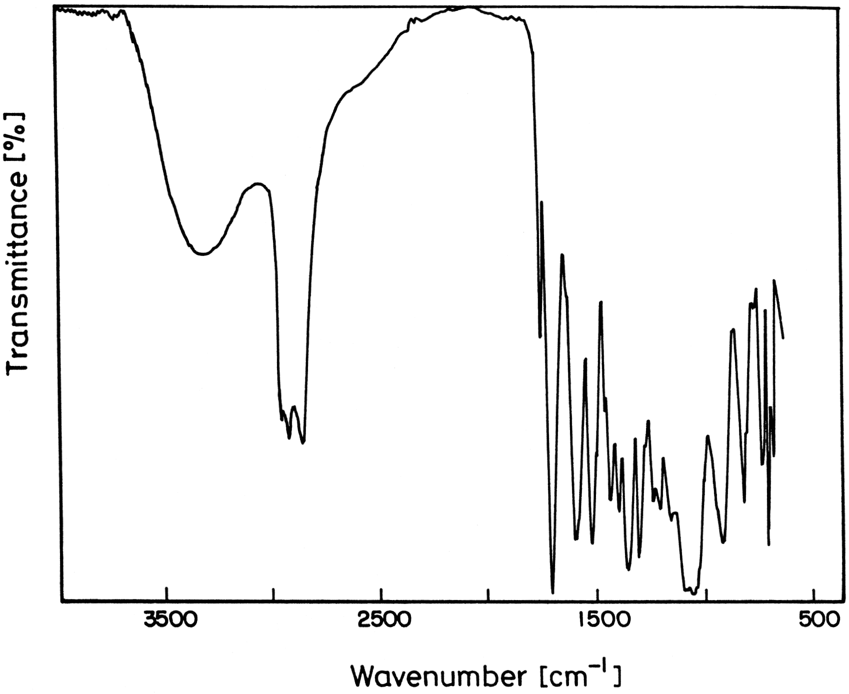


Figure 1. FTIR spectrum of a) N-methylaniline blocked polyurethane prepolymer and b) poly(urethane-imide).

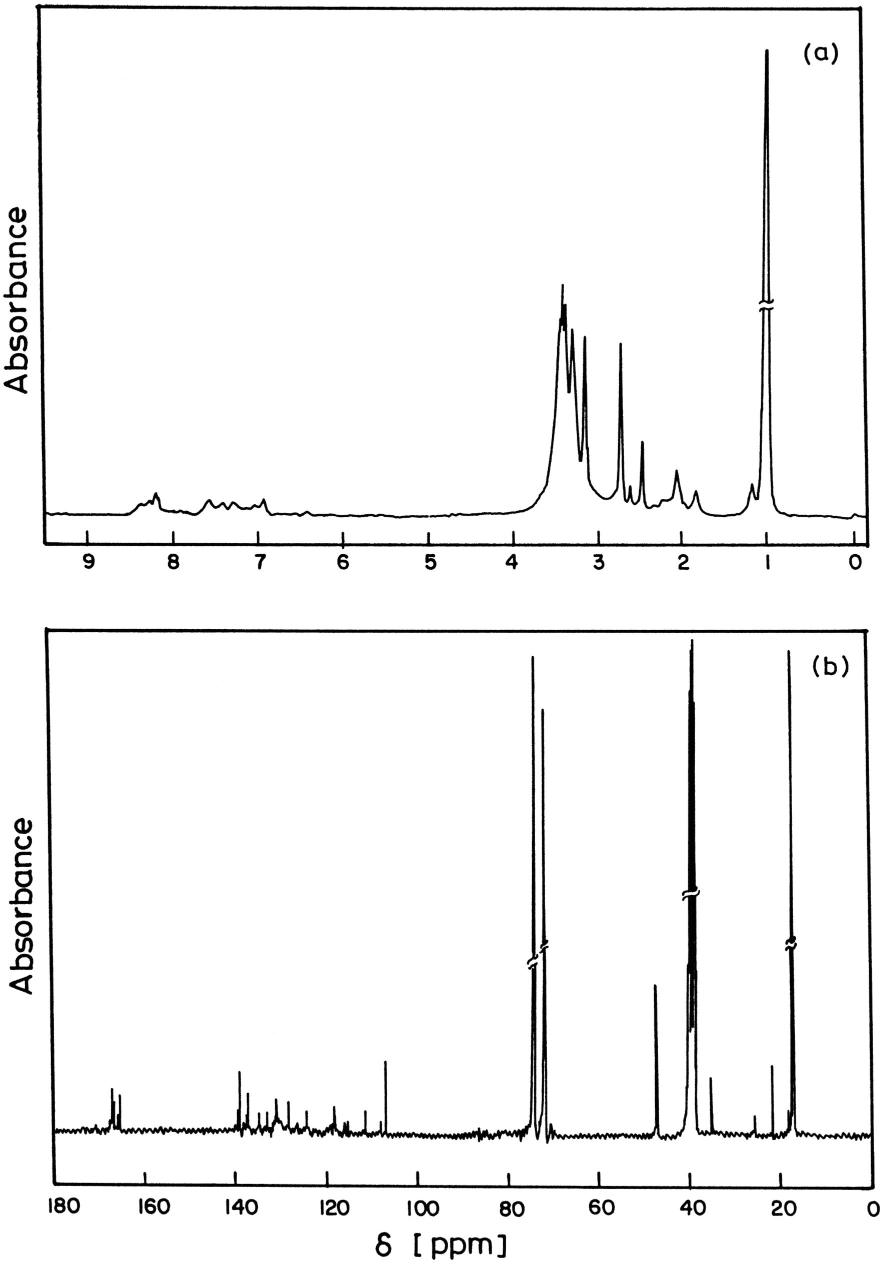


Figure 2. a) ^{1}H NMR and b) ^{13}C NMR spectra of poly(urethane-imide).

out of phase), 1362 cm^{-1} (C - N - C) and 727 cm^{-1} (out of phase bending of imide ring) confirming the formation of poly(urethane-imide).

^{1}H-NMR and ^{13}C-NMR spectra of the polymers are identical and a representative spectrum is shown in Figure 2. ^{1}H-NMR spectrum of polymers show multiplets at 6.9-7.6 ppm and 8.1-8.4 ppm due to the aromatic protons of TDI and NH protons combined with PMDA moieties, respectively. The methyl protons of propylene oxide and toluene moiety of TDI appears with appropriate intensities at 1ppm and 2.1 ppm, respectively. The methylene protons attached to oxygen and methyne proton appear as multiplets at 3.1-3.5 ppm. In the ^{13}C-NMR spectra the alkyl carbons: primary, tertiary and O-CH_2 appear intensively in accordance with the composition at 18 ppm, 72 ppm and 74 ppm, respectively. The aromatic carbon come to resonance between 107 and 139 ppm. The peaks at 165 ppm and 167 ppm due to urethane carbonyl and imide carbonyl respectively confirm the formation of poly(urethane-imide) copolymer.

Action of Catalysts

The reaction between an isocyanate and an anhydride yields imide and carbon dioxide. This evolved carbon dioxide was monitored to follow the reaction. The carbon dioxide was passed into a saturated solution of calcium oxide to precipitate calcium carbonate. The calcium oxide solution was changed every half an hour. The time at which no precipitation occurs was recorded as the end of polymerization. The time taken for the completion of polymerization using different alkali metal alkoxides and phenoxides as catalysts are given in Table 1. The completion of polymerizations with sodium methoxide and potassium methoxide took the same duration. Similarly, the catalytic activity of potassium and sodium phenoxides was identical. Thus, the change of metal did not affect the efficiency of the catalysts. Polymerization with phenoxides as catalysts showed a lower reaction time as compared to methoxides catalyzed polymerization which had a reaction

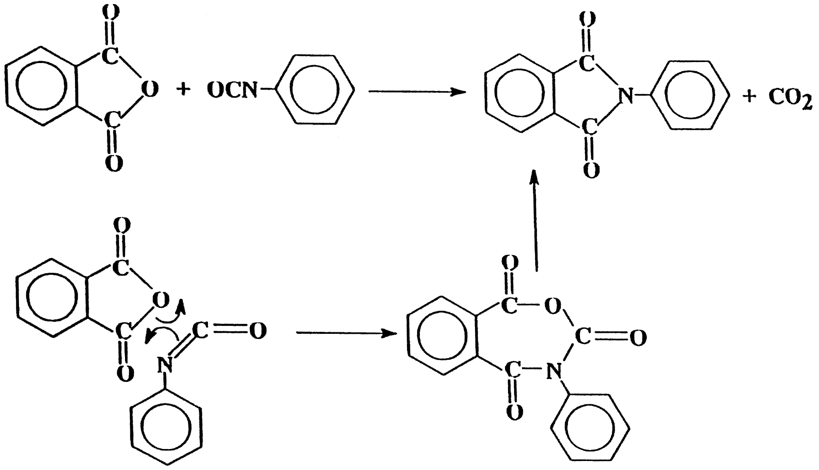
Table 1. Molecular Weights of Poly(Urethane-imides) Obtained from N-Methylaniline-Blocked Toluene Diisocyanate and the Time Taken for the Completion of Polymerization Using Alkali Metal Alkoxides and Phenoxides as Catalysts

Catalyst (3×10^{-4}mol)	Reaction Time (h)	Mn	Mw	Pd
nil	6	43,782	66,213	1.51
$Na^+\ ^-OC_6H_5$	4	48,759	70,504	1.46
$Na^+\ ^-OMe$	6	41,951	61,701	1.47
$K^+\ ^-OC_6H_5$	4	46,877	69,299	1.48
$K^+\ ^-OMe$	6	40,386	59,532	1.47
$K^+\ ^-OC_6H_5p\text{-}NO_2$	3.5	42,218	61,029	1.46
$K^+\ ^-OC_6H_5p\text{-}OMe$	7	42,136	62,697	1.49

Mn - number average molecular weight; Mw - weight average molecular weight; Pd - poly dispersity.

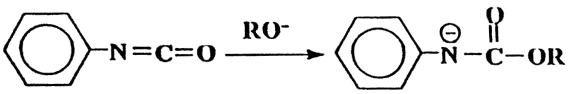
time similar to the uncatalyzed polymerization. Moreover, the molecular weight of the polymers was higher when the polymerization was catalyzed by potassium and sodium phenoxides than the polymer obtained by uncatalyzed polymerization. Polymerization was much faster when the phenoxide contains an electron withdrawing substituent. Phenoxide moiety having an electron donating substituent, on the other hand, retarded the polymerization. Based on these observations, a probable mechanism for the action of metal phenoxides and metal methoxides can be deduced as follows:

According to Hurd *et al.* [22] the imide formation reaction takes place through the formation of a seven-membered ring intermediate which collapses spontaneously to imide.



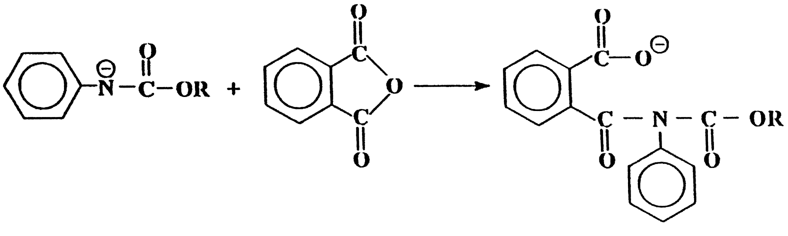
The formation of a seven-membered ring can be explained as follows:

1) The attack of ^{-}OR on isocyanate increasing its nucleophilicity leading to the formation of I.



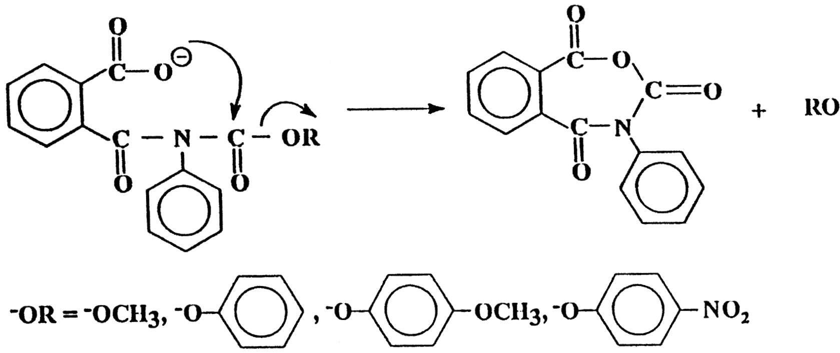
I

2) I reacting with anhydride forming II



II

3) $^{-}$OR leaves II forming the seven-membered ring.



Metal alkoxide and phenoxide can nucleophilize the isocyanate. But methoxide is a poorer leaving group than phenoxide. The leaving ability determines the formation of the seven-membered ring (step 3) hence, phenoxide showed good catalytic activity. The methoxy group at the *para* position reduces the ionization of the metal phenoxide, thereby reducing the nucleophilization of isocyanate. Also, *p*-methoxy phenoxide is a poor leaving group thereby inhibiting the formation of the seven-membered ring. On the other hand, *p*-nitro group increases the ionization of metal phenoxide and hence, nucleophilization. Also, *p*-nitro phenoxide is a good leaving group than alkoxides and methoxy phenoxide, hence the polymerization is faster with potassium *p*-nitrophenoxide.

The above discussion is based on the non interference of the compounds chosen as catalysts in any other reaction like deblocking of the blocked prepolymers. To understand whether the metal alkoxide or phenoxide is involved in the deblocking reaction of blocked isocyanate, polymerization reaction of blocked prepolymer with 1,4-butanediol was studied with and without potassium methoxide or potassium-*p*-nitrophenoxide. On periodically following the arrest of flow [17] of the reaction mixtures, which indicates completion of polymerization, it was found that both with and without the catalyst the reaction time, as given in Table 2, was not altered. Therefore, deblocking was not catalyzed by either metal alkoxides or phenoxides.

Effect of Substituents on N-Methylaniline as a Blocking Agent

To study the effect of substituents on *N*-methylaniline as a blocking agent polymerization was carried out using *N*-methyl-*p*-anisidine and *N*-methyl-*p*-nitroaniline blocked polyurethane prepolymers. The reaction time and molecular weight are given in Table 2. The ease with which the blocking agent cleaves leading to polymerization is determined by the time taken for completion of polymerization ensured by completion of the evolved carbon dioxide.

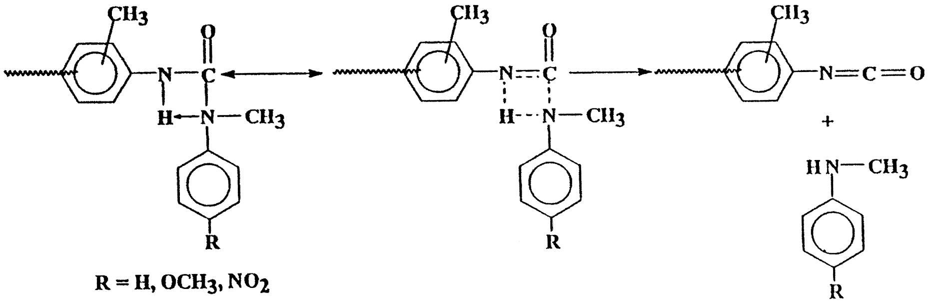
The reactions of isocyanates with active hydrogen compounds involve attack by a nucleophilic center on electrophilic carbon of the isocyanate resulting in the

Table 2. Molecular Weights of Poly(Urethane-imides) and the Time Taken for the Completion of Polymerization Using Different Substituted *N*-methylaniline-Blocked Prepolymers and the Influence of the Catalysts on the Deblocking

Blocking Agent	Chain Extender	Catalyst (5 mol%)	Rxn. Time (h)	Mn	Mw	Pd
—	PMDA	—	4.5	29,935	55,631	1.86
N-methylaniline	PMDA	—	6	43,782	66,213	1.51
N-methyl-*p*-anisidine	PMDA	—	5	27,904	47,054	1.67
N-methyl-*p*-nitroaniline	PMDA	—	7.5	34,871	62,844	1.80
N-methylaniline	1,4-butanediol	—	7	—	—	—
N-methylaniline	1,4-butanediol	$K^+ \ ^-OMe$	7	—	—	—
N-methylaniline	1,4-butanediol	$K^+ \ ^-OC_6H_5p\text{-}NO_2$	7	—	—	—

Mn - number average molecular weight; Mw - weight average molecular weight; Pd - poly dispersity.

formation of an adduct containing carbamate or substituted urea functional group depending upon the type of active hydrogen compound used. Blocked isocyanate differs from the carbamate only because of the presence of a labile bond formed between the carbonyl carbon of isocyanate and compounds qualified as blocking agent. The greater the charge difference in the polarized labile bond, the greater the strength of the bond, and if the blocking agent is less nucleophilic, the negative charge density at the blocking agent will be less which makes the bond more labile [17, 24]. If the steric factor is neglected, any electron withdrawing group attached to the blocking agent will make the bond more labile. On the other hand, the electron releasing group on the blocking agent makes the bond less labile. Hence, *N*-methyl-*p*-nitroaniline is expected to cleave easier enabling the polymerization to proceed faster than *N*-methylaniline, whereas *N*-methyl-*p*-anisidine should slower the polymerization. However, the observed trend is contrary to the expectation. This may be due to autocatalysis by *N*-methylaniline moiety which may be explained as that the deblocking occurs through the formation of an intramolecular four-centered complex.



The formation of such a four-centered complex depends on the availability of the unshared pair of electron on the nitrogen atom which is more in *N*-methyl-

p-anisidine and less in *N*-methyl-*p*-nitroaniline than that in *N*-methylaniline, hence, the observed trend.

Formation of such a four-centered transition state in the urethane formation reaction between an isocyanate and alcohol has been reported [24, 25].

Thermal Studies

Thermal properties of the polymers were investigated by thermogravimetry (TGA) and differential scanning calorimetry (DSC). The pattern of TG traces of all the polymers were similar; a representative curve is given in Figure 3. The results of TG analyses showed improved thermal stability of the polymer. The initial decomposition temperatures (Ti) of the polymers are found at around 385°C which is substantially higher than the Ti value (264°C) of a simple polyurethane prepared as reference by chain extending *N*-methylaniline blocked PU prepolymer with 1,4-butanediol. In the case of poly(urethane-imide), the major weight loss

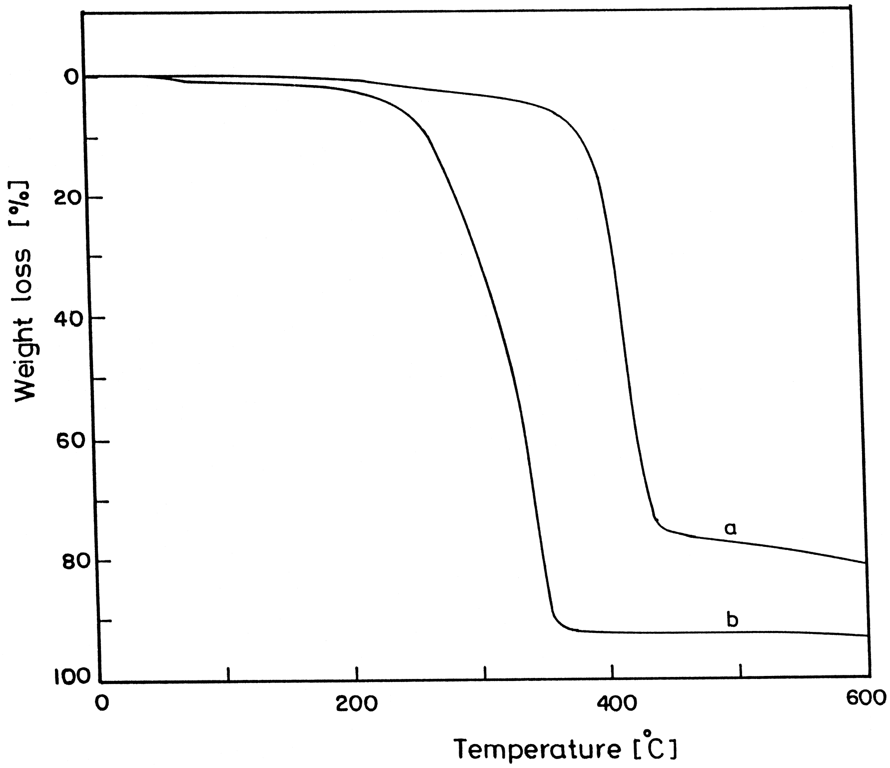


Figure 3. TGA thermogram of a) poly(urethane-imide) and b) polyurethane.

(10-85%) occurred in the range 385-414°C, whereas in the case of simple polyurethane, 10-85% weight loss occurred in the range 279-345°C. Thus, the introduction of imide moieties led to increased thermal stability.

A representative DSC thermogram of the polymer is shown in Figure 4. Polyether polyol based polyurethanes are materials having low glass transition temperature (T_g). The T_g of such materials will be around -60° to -40°C while polyimides show higher T_g (>250). Poly(urethane-imide) is expected to exhibit T_g value in between the above mentioned two distinct temperature range since it is a copolymer. But the observed glass transition temperature (around -40°C) is close to the T_g value of polyether based polyurethanes. This may be due to micro phase separation of ether soft segments and urethane-imide hard segments in the polymer.

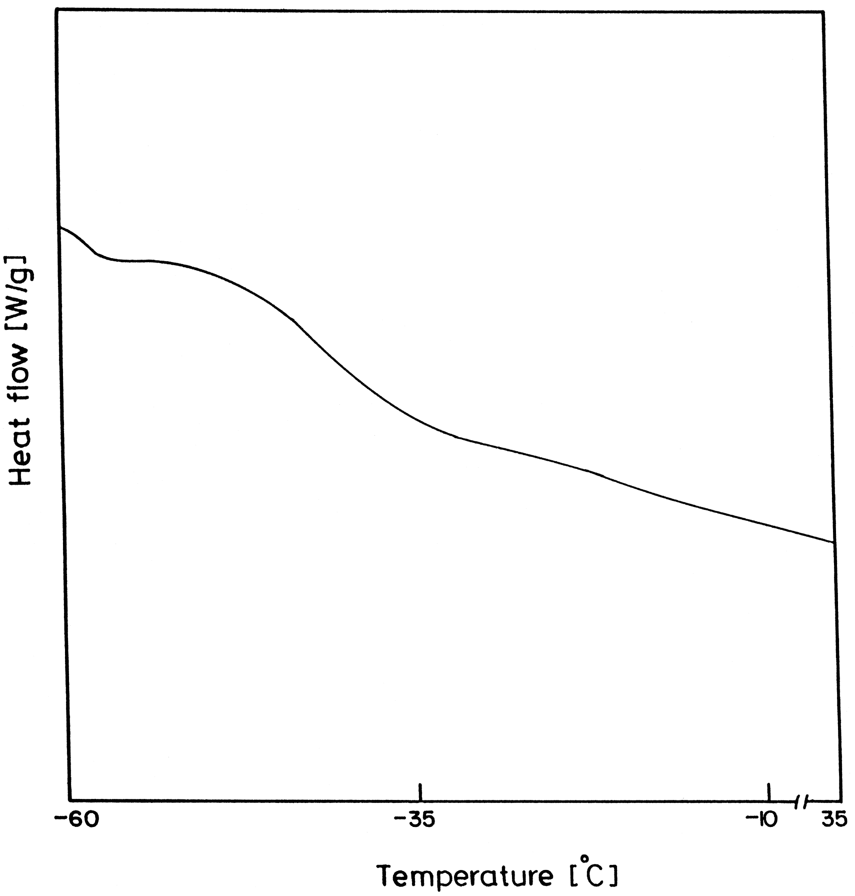


Figure 4. DSC thermogram of poly(urethane-imide).

CONCLUSION

Effects of catalysts and substituents on blocking agent on the preparation of poly(urethane-imide) copolymer using a novel amine blocked prepolymer was studied for the first time. Alkali metal phenoxides were found to catalyze the polymerization of polyurethane prepolymer and pyromellitic dianhydride. Electron withdrawing substituents tend to enhance the catalytic activity of phenoxides while electron donating substituents tend to reduce. Polymerization was faster with *N*-methyl-*p*-anisidine-blocked PU prepolymer and slower with *N*-methyl-*p*-nitroaniline-blocked PU prepolymer as compared to the polymerization with NMA-blocked PU prepolymer. Thermal stability of PU increased by the introduction of imide moieties.

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