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Synthesis of Poly(Urethane-Imide): Effect of Solvents with and without Basic Nitrogen Atom and Other Parameters on the Imide Formation Reaction Between Blocked-Isocyanate Prepolymers and Pyromellitic Dianhydride

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N-Methylaniline- and 2-Butanone oxime-blocked isocyanate prepolymers were prepared and their reaction with pyromellitic dianhydride (PMDA) was studied with a view to understand the effect of different parameters like solvents, temperature, blocking agents and deblocking catalysts [diazabicyclo 2.2.2 octane, (DABCO) and dibutyltin dilaurate, (DBTDL)] on the poly(urethane-imide) formation reaction. The reactions were followed by the carbon dioxide evolved during the imidization reaction. The effect of each individual parameter was studied with the reaction time and GPC data. It was found that the reactions proceeded at a faster rate in hexamethyl phosphoric acid triamide (HMPA), a solvent having basic nitrogens, than in mesitylene. Also, in HMPA, it was found that the molecular weights (M_w) of the polymers increased with an increase in temperature up to 125°C and then decreased, whereas in mesitylene, it was found that there was no appreciable change in molecular weight up to 150°C. Of the two blocked isocyanate prepolymers studied, 2-butanone oxime-blocked prepolymer undergoes completion of reaction with anhydride rapidly. Among the two distinct types of deblocking catalysts tried, in the solvent HMPA, the tertiary amine showed no catalytic activity, while the organotin compound showed catalytic activity. In mesitylene, however, the effect of the catalysts on the title reaction was just the opposite. The polydispersity of the polymers was found to be relatively narrow in all cases.

Keywords poly(urethane-imide), blocked-isocyanate prepolymer, hexamethyl phosphoric acid triamide (HMPA)

Introduction

With variations in the use of raw materials and the conditions employed, polyurethanes could be produced in a wide variety of forms. They could be tailor-made for specific applications and attractive for many purposes; however, they suffer from poor thermal stability due to the labile urethane linkages. The thermal stability of polyurethane could be increased by the incorporation of heterocyclic groups like the imide group into the

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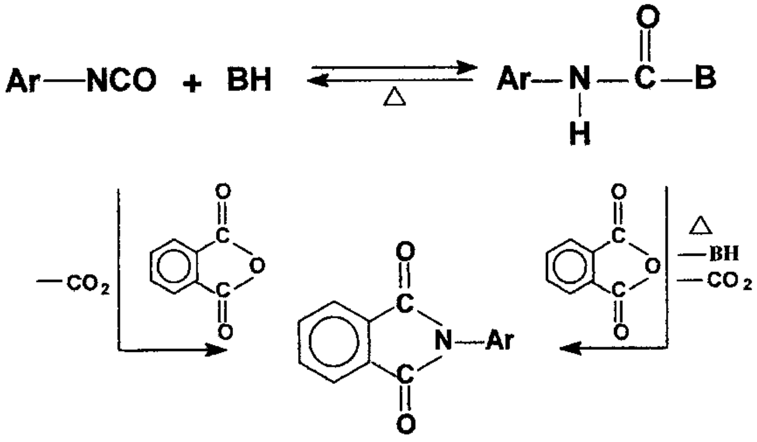
polymer main chain, since heterocyclic polymers are high temperature materials, possessing good mechanical and electrical properties. Recently, it was reported that the introduction of imide moiety into the polyurethane backbone increases the overall thermal stability (10% to 85% wt loss) of polyurethane from 279°C–345°C to 385°C–414°C (1–3). A very recent report (4) describes the synthesis of poly(ester-imide)s from anhydride-terminated polyester prepolymer and diisocyanates and the resultant polymer showed improved thermal stability over blank polyester. A reaction of an isocyanate-terminated polyurethane prepolymer with a dianhydride is the method most often employed to introduce the imide function into the polyurethane backbone (3, 5–7). The use of imide containing diol as chain extenders in the preparation of poly(urethane-imide)s is less often reported (8). Yeganeh et al. (9) have used an isocyanate–anhydride reaction for the preparation of optically active polyimides. Takeichi et al. (10, 11) have reported the preparation of crosslinked poly(urethane-imide) by reacting a PU prepolymer with amine- and hydroxy-terminated poly(amide acid)s. Another report (12) describes the preparation of rigid rod-like polyimides by reaction of an imidazole-blocked diisocyanate with pyromellitic dianhydride. The advantage of using isocyanate instead of the conventionally used amine with dianhydride is that imidization is achieved in a single-step at a relatively lower temperature (12). However, the handling of the isocyanates poses certain problems in terms of toxicity, sensitivity of the –NCO group to moisture, and susceptibility of the isocyanates to undergo side reactions. These could be overcome by blocking the isocyanate groups with suitable blocking agents before reaction with dianhydride: at the relatively elevated temperatures of this reaction, deblocking regenerates the free isocyanate, which on reaction with dianhydride results in polyimide. The overall reaction can be seen as follows:



BH–Blocking Agent

The deblocking reaction is catalyzable and the deblocking temperature can be lowered by the use of tertiary amine bases and organotin compounds as catalysts, or by the use of suitable solvents. A few reviews (13–16) have been published in which number of blocking agents for isocyanates have been described. Phenol, 2-butanone oxime and ε-caprolactam are some of the common blocking agents for isocyanates. Additionally, aromatic secondary amines, particularly N-methyl aniline have been shown to be potential blocking agents for aromatic isocyanates (17).

Blocked polyisocyanates are preferred for many technical and economical reasons. They are essentially insensitive to moisture with high storage stability. Since the isocyanate functional groups are protected, they can be handled more safely and conveniently.

The reactions of isocyanates and blocked isocyanates with anhydrides have received attention recently (1–12) because these reactions produce poly(urethane-imide)s and polyimides in a single step conveniently. But, the basic chemistry aspects involved in these reactions have not been studied in detail. In this report, we describe the blocked isocyanate-anhydride reaction with the aim of understanding the effect of solvents, blocking agents, temperature and deblocking catalysts on the poly(urethane-imide) formation reaction between blocked isocyanate-terminated polyurethane prepolymers and pyromellitic dianhydride (Fig. 1).

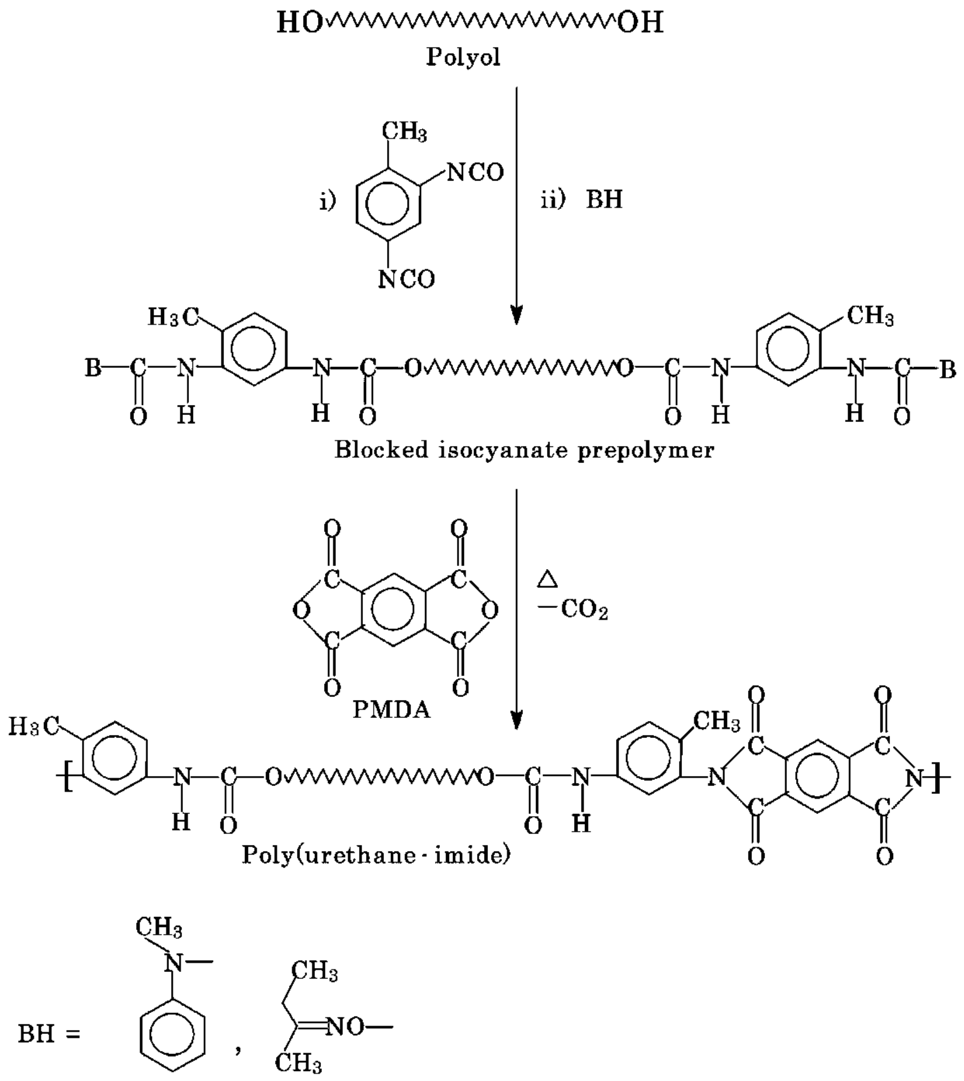


Figure 1. Synthesis of poly(urethane-imide)s using blocked isocyanate prepolymers and pyromellitic dianhydride.

Experimental

Materials

N-Methylaniline (NMA) (Lancaster) and mesitylene (Fluka) were distilled under low pressure before use. Hexamethyl phosphoric acid triamide (HMPA) (Spectrochem) was purified by distillation under reduced pressure and stored in molecular sieve 4A. Pyromellitic dianhydride (PMDA) (Spectrochem) was purified by recrystallization from acetic anhydride, followed by sublimation. Toluene diisocyanate (TDI) (Acros) containing 80% 2,4- and 20% 2,6-isomers, 2-butanone oxime (MEK oxime) (Lancaster), diazabicyclo[2.2.2]octane (DABCO) (Lancaster), dibutyltin dilaurate (DBTDL) (Lancaster) and polypropylene glycol (PPG 2000) (Lancaster) were used as received. Other solvents were purified according to standard procedures.

Preparation of Blocked PU Prepolymers

A 0.08 equivalent (6.96 g) of TDI was placed in a reaction kettle. A 0.04 equivalent (40 g) of polyol (PPG 2000) was added dropwise with stirring; the dropping rate was such that it took 1 h for complete transfer. The reaction time was 4 h; the first period of 2 h was maintained at 50°C and the next 2 h, at 70°C. After 4 h, the temperature was reduced to 40°C and −NCO content was determined by dibutyl amine method (18) which gave a value close to the expected theoretical value (observed value = 4%; theoretical value = 3.6%). Then, the −NCO terminated prepolymer was blocked with a 0.04 equivalent (4.286 g) of NMA at 40°C; the reaction time, as determined by the disappearance of NCO absorption using FTIR analysis, was 105 min. An identical procedure was used for the preparation of 2-butanone oxime-blocked PU prepolymer; the reaction time was 2 h.

Preparation of Poly(urethane-imide) Copolymers

A 5×10^{-3} equivalent each of PMDA and blocked prepolymer, 15 mL of solvent and 5×10^{-4} mol of catalyst in the cases of catalyzed experiments were placed in a reaction kettle fitted with a mechanical stirrer. The other reaction conditions are given in Table 1. The mixture was heated with stirring in an oil bath. The completion of the reaction was ensured by precipitating the evolved CO_2 with the help of nitrogen as carrier gas in a saturated barium hydroxide solution.

The time required for the completion of the formation of precipitate was recorded as the reaction time. The resulting reaction mass was concentrated and subjected to FTIR and GPC analyses.

Measurements

FTIR spectra for the polymers were recorded using a Thermo Mattson Satellite FTIR spectrophotometer in the range of 4000–400 cm^{-1} with a resolution 4.0. A neat technique was used for the cases of prepolymers and blocked prepolymers, whereas, in the cases of polymers, the samples were dissolved in THF and evaporated on a KBr window under IR lamp. M_n, M_w and polydispersity (P_d) were determined by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a 410 differential refractometer (RI detector). DMF containing 0.01% lithium bromide was used as eluent at a flow rate of 1 mL/min. Styragel columns of pore size 10^3, 10^4, 10^5 and 10^6 Å were

Table 1
Effect of different parameters on the polymerisation reaction of blocked isocyanate prepolymers with pyromellitic dianhydride

Blocking agent	Solvent	Temperature (°C)	Catalyst [5×10^{-4} mol]	Reaction time (hrs)	M_n	M_w	p_d
NMA	HMPA	100	—	5.15	19,809	29,016	1.4
NMA	HMPA	115	—	4.15	20,279	29,695	1.4
NMA	HMPA	125	—	3.30	21,232	32,124	1.5
NMA	HMPA	140	—	2.45	22,029	31,351	1.4
NMA	HMPA	150	—	1.45	18,595	26,791	1.4
NMA	HMPA	140	DABCO	2.45	19,951	28,488	1.4
NMA	HMPA	140	DBTDL	1.30	21,784	33,251	1.5
NMA	Mesitylene	115	—	6.45	20,898	29,114	1.4
NMA	Mesitylene	125	—	4.45	19,069	26,442	1.4
NMA	Mesitylene	140	—	3.45	21,930	30,240	1.4
NMA	Mesitylene	150	—	3.00	21,430	30,113	1.4
NMA	Mesitylene	140	DABCO	3.15	—	—	—
NMA	Mesitylene	140	DBTDL	3.45	22,820	32,076	1.4
2-Butanone oxime	HMPA	140	—	1.30	21,164	32,023	1.5
2-Butanone oxime	HMPA	140	DABCO	1.30	22,429	32,965	1.4
2-Butanone oxime	HMPA	140	DBTDL	1.15	23,120	33,684	1.4

used. The molecular weight calibrations were carried out using polystyrene standards having molecular weights (M_w) in the range of 2.9×10^3 to 1.7×10^5.

Results and Discussion

FTIR Analyses

FTIR spectrum (Fig. 2a) of polyurethane prepolymer showed a strong absorption in the 2250–2270 cm^{-1} range due to terminal –NCO groups of prepolymer. Other characteristic absorption bands at 3293 cm^{-1}, 1735 cm^{-1}, and 1533 cm^{-1} are due to urethane N–H stretching, urethane C=O stretching and urethane N–H bending vibrations, respectively. FTIR spectra Fig. 2(b and c) of the blocked polyurethane prepolymers showed no absorption in the 2250–2270 cm^{-1} range, confirming that the –NCO ends of the prepolymers are

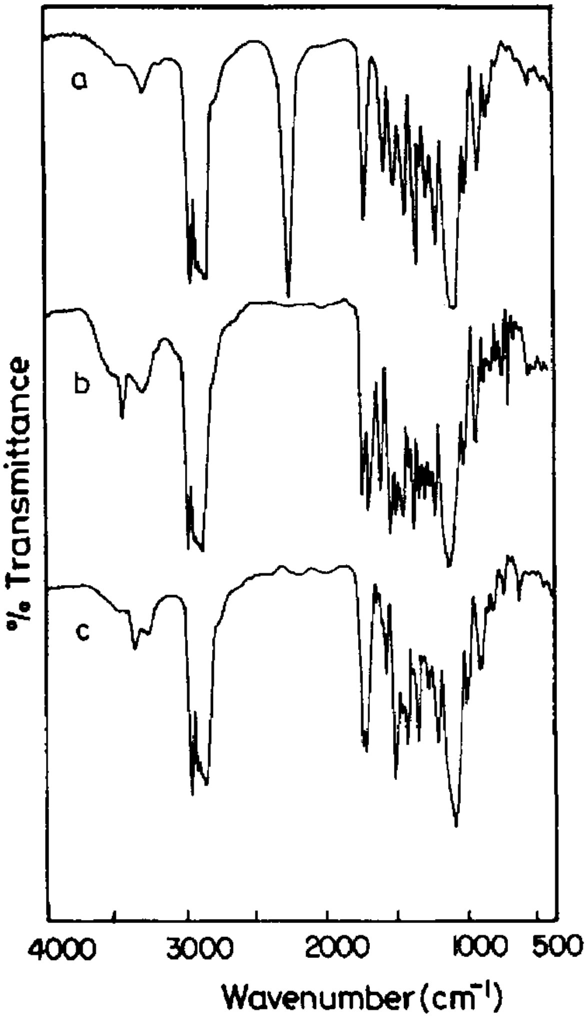


Figure 2. FTIR spectrum of (a) NCO-terminated polyurethane prepolymer, (b) NMA-blocked isocyanate prepolymer and, (c) MEK oxime-blocked isocyanate prepolymer.

completely blocked. IR spectra of polymers are identical, and representative spectra are given in Fig. 3. The polymer showed characteristic imide absorption bands at 1722 cm^{-1} (C=O, out of phase), 1368 cm^{-1} (–C–N–C–) and 747 cm^{-1} (out-of-phase bending of the imide ring) confirming the formation of poly(urethane-imide).

Effect of Solvent and Temperature

The deblocking reaction of blocked isocyanate is sensitive towards a number of factors, of which the solvent is a very important one, especially when using blocked isocyanates for different types of synthetic work. Solvents chosen in the present investigation differ greatly in their polarity and consequently in their capability to interact with N–H group of blocked isocyanate. Mesitylene is a non-basic hydrocarbon solvent having no polar group while HMPA is a polar, aprotic solvent having three tertiary nitrogen atoms which are capable of interacting with the functional group of blocked isocyanate. Farrissey and co-workers (19) have reported that the reaction between an isocyanate and anhydride proceeded well in dipolar aprotic solvent, and that nonpolar solvents required higher temperature. Indeed, HMPA and mesitylene were chosen with a view to understand their effect on deblocking reaction followed by imidization and on urethane linkages in prepolymer chains. The results are given in Table 1. All the reactions that were carried out in HMPA have gone to completion in a shorter time compared to those carried out in mesitylene. This observation is in accordance with the expectation, that the tertiary nitrogen atoms present in the solvent, HMPA, assist the initial stage of the reaction i.e the deblocking reaction. This solvent-assisted deprotonation of deblocking reaction can be explained by the mechanism described in Fig. 4.

In this mechanism, the tertiary nitrogen of the solvent abstracts an N–H proton of the blocked isocyanate group and transfers it to the nitrogen atom of the blocking agent moiety, whereupon both the blocking agent and isocyanate are regenerated. Abstraction of carbamate N–H proton by a base is well reported (20, 21). Katsemberis et al. (22) proposed this type of mechanism involving amidine as the catalyst and this was subsequently confirmed by experimental evidence (23). Tertiary bases like diethylcyclohexyl

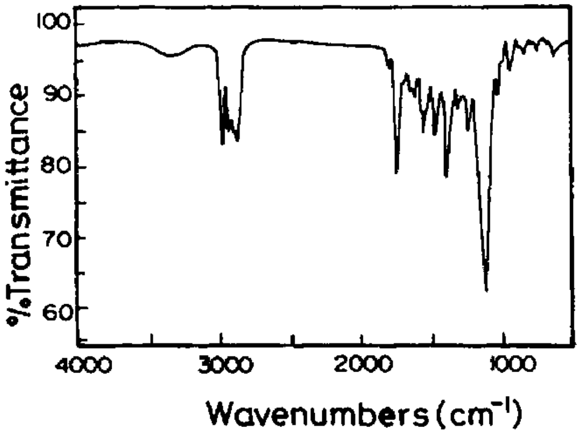


Figure 3. FTIR spectrum of poly(urethane-imide) prepared from NMA-blocked isocyanate prepolymer and pyromellitic dianhydride.

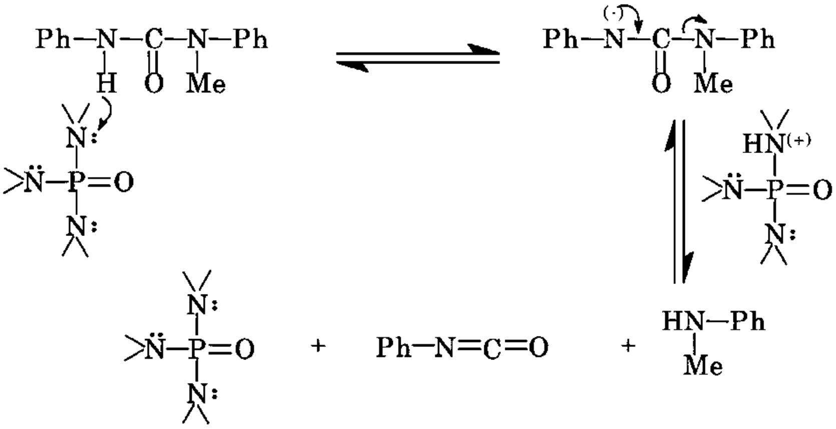


Figure 4. Mechanism of solvent(HMPA)-assisted deblocking of blocked isocyanate.

amine, tributyl amine and N-ethylmorpholine have been reported as catalysts for phenol and N-methylaniline-blocked isocyanates (1, 23). According to this mechanism, active sites influence one another sterically and hence, the apparent catalytic activity of the solvent may be a suppressed value with respect to the total catalytic activity expected.

The effect of temperature on the reaction time and molecular weight of the polymer was studied and the results are presented in Table 1. The time required for completion of polymerization decreased in both the solvents, as the temperature was increased. Also, it was found that the molecular weight increases gradually and then decreases with an increase in temperature in HMPA while such a trend was not found in mesitylene. This finding indicates that the polyurethane may undergoes chain scission in HMPA at a high temperature since the urethane groups are thermally labile and are further weakened by the interaction with the basic solvent. This interpretation is supported by the preceding discussion.

Effect of Blocking Agent

Many class of compounds have been suggested as blocking agents for Isocyanates (13–16). They include phenolics, amides (especially ε-caprolactam), oximes (especially methylethyl ketooxime), β-dicarbonyl compounds and heterocyclic compounds containing N–H groups. 2-Butanone oxime (MEK oxime) was chosen in this study for a comparison with NMA; the functional group of the former is =NOH, whereas that of the later is N–H. It is found that the time required for completion of imidization reaction involving MEK oxime-blocked PU prepolymer is less compared to that involving NMA-blocked PU prepolymer. This result reveals that the MEK oxime-blocked prepolymer regenerates isocyanate functionality more readily than the NMA-blocked prepolymer. The autocatalytic effect of NMA-blocked isocyanate has been described recently (1) and such an effect can be expected in the oxime-blocked isocyanate also, since both the blocked isocyanates contain basic nitrogen. While the mechanism of the deblocking of NMA-blocked isocyanate involves four membered-ring transition state (1), MEK oxime could form a five membered-ring transition state, which is more feasible and could involve catalysis more effectively.

Effect of Catalyst

A deblocking reaction can be catalyzed using a variety of compounds (13, 14). Among them, tertiary amines and organotin compounds are highly effective, and hence, have received more attention. In the present investigation, DABCO and DBTDL were used representing amine and tin compound, respectively and the results, both the reaction time and molecular weight data, are given in Table 1. DABCO was found to catalyze the reaction of blocked isocyanate-terminated polyurethane prepolymer with PMDA in mesitylene, whereas it was found to be inactive in HMPA. Conversely, DBTDL was found to be active in HMPA, whereas it was found to be inactive in mesitylene. The deblocking catalytic activity of both DABCO and DBTDL against phenol-blocked isocyanates has been reported (23, 24). The apparent catalytic inactivity of DABCO in HMPA may be due to the presence of a large excess of basic nitrogen atoms in the solvent HMPA, while the catalytic activity of DBTDL in HMPA could be attributed to the formation of an association complex between tin compound and solvent HMPA and the resultant complex catalyzing the reaction. This is in agreement with the report of Garddon and Ranna (25), that dialkyltin dicarboxylate forms 1 : 1 complex with tertiary amines quite readily. The tin-amine synergism in the catalysis of deblocking of blocked isocyanate has also been reported (23). The catalytic inactivity of DBTDL in mesitylene may be due to the coordination of Sn^{4+} ion with carbonyl oxygen of PMDA leading to the non-availability of tin compound for catalysis. The formation of coordination complex between SnX_4 and carbonyl compound has been reported (26). Therefore, it may be concluded, that DBTDL catalyzes only the deblocking reaction and not the imidization reaction. Based on the results generated in this study, it can be concluded that the observed catalytic activity of DABCO is also only with respect to the deblocking reaction since the molecular weight of polymer obtained with DABCO-catalyzed reaction is lower than that obtained with uncatalyzed reaction.

Polydispersity

All the polymers showed relatively low dispersity values and the values are invariably similar. This may be due to controlled regeneration of isocyanate functionality for the polymerization reaction.

Conclusions

NMA- and MEK oxime-blocked polyurethane prepolymers were prepared and reacted with pyromellitic dianhydride to prepare poly(urethane-imide). The reaction between blocked isocyanate and anhydride was studied with respect to the effect of solvents with and without basic nitrogen, blocking agents, temperature, and catalysts. It was found that the reactions proceeded well in solvent having basic nitrogen atoms (HMPA) rather than in mesitylene. Among two distinct type of catalysts that were used, tertiary amine (DABCO) was found to be inactive in HMPA and active in mesitylene whereas in the case of oraganotin compound (DBTDL), this trend was reversed. From the results obtained in this study, it may be concluded, that the catalytic activity (of the two types of catalysts used) is confined to the deblocking reaction alone. It was also found, that the molecular weight of the polymer increased up to 125°C, and then decreased with increase in temperature in HMPA, whereas such a trend was absent in mesitylene.

Finally, the MEK oxime-blocked prepolymer was found to be more reactive towards anhydride.

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