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CATALYSIS OF BLOCKED ISOCYANATE- HYDROXYL-TERMINATED POLYBUTADIENE CURE REACTION

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Key Words: Catalysis; Blocked isocyanate; Hydroxyl-terminated polybutadiene; Cure reaction

ABSTRACT

The catalytic activity of three tertiary amines and three organotin compounds in the cure reaction of blocked isocyanate with hydroxyl-terminated polybutadiene was investigated. It was found that the steric factor determines the catalytic activity of the compound. The tin compounds showed higher catalytic activities than the amine compounds. The deblocking catalytic activity of the amine and tin compounds was confirmed by the identification of isocyanate functionality using infrared spectroscopy. The synergistic effect of amine and tin mixed catalysts systems in the deblocking reaction was reported for the first time.

INTRODUCTION

Hydroxyl-terminated polybutadiene (HTPB) is referred to as a workhorse binder used in solid propellants [1] and in rocket motor cases [2]. The polybutadiene chain gives a higher energy value and good mechanical properties. The low viscosity of this prepolymer favors high solid loading (fuel and oxidizer). The

nonpolar hydrocarbon main chain of HTPB provides superior hydrolytic stability. Cured HTPB has tough, rubbery properties, a prime requirement for modern propellants. The very efficient isocyanate-alcohol reaction (urethane formation reaction) is used for curing HTPB. Toluene diisocyanate (TDI) is used as the curing agent. The main problem associated with HTPB is the high reactivity of the primary hydroxyl groups to isocyanate molecules, and hence the system suffers from a short pot-life. This problem may be overcome by the use of a blocked TDI crosslinker instead of TDI as such. At elevated temperatures the blocked isocyanate will dissociate to regenerate the isocyanate functionality in a controlled manner [3]. Then the actual cure reaction will take place between HTPB and the regenerated isocyanate groups. Phenols are the important blocking agents for isocyanates and are widely used in industrial processes [4, 5]. The authors [6-9] have studied the thermal dissociation of a number of phenol-blocked TDI crosslinkers.

The deblocking of blocked isocyanates is catalyzed by bases and organometallic compounds. In the patent literature [4, 10] a wide variety of compounds are disclosed as catalysts, most of which also catalyze the reaction of isocyanate with alcohols [4, 11]. Reports on the catalysis of the deblocking reactions in the presence of hydroxy coreactants are meager [11, 12]. The effect of catalysis on the cure reaction of blocked isocyanate with HTPB has not been reported. The aim of the present report is to determine the catalytic activity of some amine and tin compounds in the blocked isocyanate-HTPB cure reaction.

EXPERIMENTAL

Materials

The preparative method for 2,4-di-*tert*-butylphenol-blocked TDI adduct was described in our previous report [9]. The TDI used was a mixture of isomers containing 80% 2,4-TDI and 20% 2,6-TDI. HTPB (average molecular weight = 2500, hydroxyl value = 43.66 mg KOH/g) and dioctyl adipate (DOA), obtained from Vikram Sarabhai Space Centre, were used without further purification. Diethylcyclohexylamine (DECHA) (Sigma) and tributylamine (Fluka) were distilled before use. Tribenzylamine (Fluka), dibutyltin diacetate (DBTDA) (Merck), dibutyltin dilaurate (DBTDL) (Merck), and stannous-2-ethylhexanoate (Sigma) were used as received. The solvents were purified by reported procedures [13].

Gel Time Studies

One gram (1.8×10^{-3} mol) of the blocked isocyanate and 5 mL DOA were taken in a beaker and placed in an oil bath maintained at 100°C for 30 minutes. After completion of solubilization, the beaker was removed from the oil bath and the solution was mixed with 5 g (2.0×10^{-3} mol) HTPB. The homogeneous mixture of the blocked isocyanate, DOA, and HTPB was placed in an oven maintained at 125°C. The beaker was inverted at regular intervals to observe the flow behavior of the solution. The time at which the solution ceased to flow was taken as the gel time.

The blocked isocyanate was dissolved in 4 mL DOA in the catalyzed experiments. The remaining 1 mL DOA was added in the form of the catalyst solution. In

the experiments involving mixed catalysts systems, the blocked adduct was dissolved in 3 mL DOA. The remaining 2 mL DOA was added as two different catalyst solutions, each in 1 mL portions.

IR Analysis

Identical experiments involving DECHA and DBTDA as the catalyst were carried out without HTPB for 30 minutes. The viscous solutions were diluted with 25 mL chloroform and the IR cell was filled with this solution. The spectra were recorded over the 4000 to 400 cm^{-1} range on a Perkin-Elmer Model 781 spectrophotometer. A blank solution without the blocked isocyanate was taken in the reference cell of the spectrophotometer.

Viscosity

The relative viscosities (η_r) of the gels were measured at a concentration of 0.1 g/dL in toluene at 30°C using an Ubbelohde viscometer.

RESULTS AND DISCUSSION

In the cure reaction between a blocked isocyanate and a polyol, the homogeneity or the solubility of the blocked isocyanate in the hydroxy compound is an important factor. If the blocked isocyanate has poor solubility, it will settle down in the system and a uniform cure will not be possible. In our previous study [6] it was found that an alkyl substituent in the blocking agent improves the solubility of the adduct in hydroxy compounds. For this reason 2,4-di-*tert*-butylphenol was chosen as the blocking agent for TDI. The presence of a bulky tertiary butyl group in the ortho position reduces the dissociation temperature of the adduct to some extent. To get a perfectly homogeneous system, DOA, which is used as a plasticizer in solid propellants [2], was used to solubilize the adduct.

Two types of catalysts were used in this study. The first type consisted of three tertiary amines and the other type consisted of three organotin compounds. The catalytic activity of these compounds in the cure reaction of 2,4-di-*tert*-butylphenol-blocked TDI with HTPB was studied by determining the gel times. The results of uncatalyzed and catalyzed reactions are given in Table 1. The uncatalyzed experiment carried out at 125°C for 315 minutes gave a completely cured gel, but the experiment carried out at room temperature for 24 hours did not show any increase in the viscosity of the reaction mixture and thereby confirmed that dissociation did not occur during solubilization of the adduct at 100°C. In the catalyzed reactions, organotin compounds showed higher catalytic activities than the amine compounds. In both cases the catalytic activity decreased with increasing steric hindrance at the catalytic center. For example, DECHA showed higher catalytic activity than the tributylamine in the amine-catalyzed reactions, while the tribenzylamine was found to be inactive.

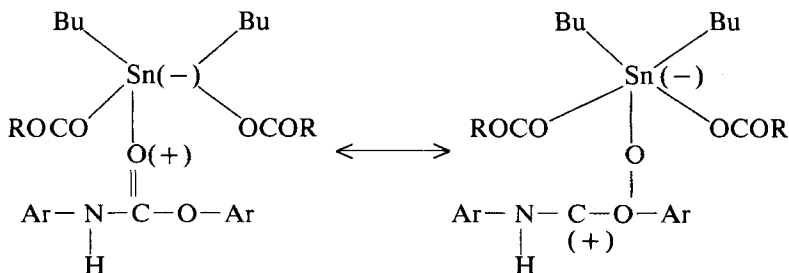
The mechanism (Fig. 1) may involve the abstraction of a proton from the urethane N—H group by the base, leaving a negative charge on the nitrogen atom. Since the bond between the carbonyl carbon and the oxygen of the blocking agent is

TABLE 1. Catalysis of Cure Reaction of 2,4-Di-*tert*-butylphenol-Blocked TDI with HTPB at 125°C

Catalyst, 1.8×10^{-4} M	Gel time, minutes	η_r
Nil	315	1.486
DECHA	270	1.475
Tributylamine	285	1.480
Tribenzylamine	315	1.475
DBTDA	90	1.480
DBTDL	135	1.480
Stannous-2-ethylhexanoate	270	1.486

labile, the phenoxide group will leave as a phenoxide anion and be protonated by the R_3NH^+ species to form phenol, and the catalyst will be regenerated. The authors have studied the mass fragmentation patterns of a series of substituted phenol-blocked isocyanates and identified the phenolate ion in all cases [10]. Abstraction of a carbamate N—H proton by a base is well reported [14, 15]. Katsamberis and coworker [12] proposed this type of mechanism involving amidine as the catalyst. According to this argument, the greater activity of DECHA can be attributed to its less sterically hindered structure, making the nitrogen more accessible to abstract the proton from the blocked isocyanate. The nitrogen atom is totally inaccessible in the tribenzylamine due to the presence of bulky benzyl groups around it, so it does not act as a catalyst.

DBTDA shows higher catalytic activity than DBTDL in the tin-catalyzed reactions. The mechanism may involve the formation of a complex between the catalyst and the blocked isocyanate by the interaction between tin and oxygen of the carbonyl group:



Owens and coworkers [16] reported 1:2 adducts of SnX_4 with phenyl isocyanate in which the phenyl isocyanate ligands are oxygen bonded to the Sn^{4+} ion. Due to this interaction the labile bond in the blocked isocyanate will be easily cleaved. The lower activity of stannous-2-ethylhexanoate than of DBTDA and DBTDL may be due to the more electronegative character of the Sn^{2+} ion than the Bu_2Sn^{4+} ion.

TABLE 2. Synergistic Effect of Amine and Tin Catalysts for the Catalysis of 2,4-Di-*tert*-butylphenol-Blocked TDI-HTPB Cure Reaction at 125°C

Amine catalyst, 1.8×10^{-4} M	Tin catalyst, 1.8×10^{-4} M	Gel time, minutes	η_r
DECHA	DBTDA	30	1.490
Tributylamine	DBTDA	45	1.475
Tribenzylamine	DBTDA	70	1.480
DECHA	DBTDL	45	1.480
Tributylamine	DBTDL	60	1.490
Tribenzylamine	DBTDL	80	1.490
DECHA	Stannous-2-ethylhexanoate	75	1.475
Tributylamine	Stannous-2-ethylhexanoate	90	1.485
Tribenzylamine	Stannous-2-ethylhexanoate	120	1.485

Robins [17] opined that the more electronegative ions form bonds of considerable covalent character with alcohol and hence lower the nucleophilicity of the hydroxyl group. The catalysis of the isocyanate-alcohol reaction by the amines and metal ions has been reported [18–21].

In both the amine- and tin-catalyzed reactions, the regeneration of the isocyanate functional group is identified by infrared spectroscopy. The spectrum (Fig. 2) obtained before heating the adduct did not show any absorption band in the 2250 to 2270 cm^{-1} range. If any free isocyanate group were present in the adduct, it would strongly absorb in this region. But the spectra obtained after heating the adduct at 125°C in the presence of amine and tin compound showed a strong absorption band in the 2250 to 2270 cm^{-1} range due to the regenerated isocyanate functionality. The spectrum obtained without the catalyst also showed a band in the same region, but the peak intensity is not appreciable.

The relative viscosities (η_r) of the gels obtained by the uncatalyzed and catalyzed reactions were determined by the use of an Ubbelohde viscometer to ensure the constancy of the gelation reaction. It was found that the values of η_r are identical, confirming a uniform cure reaction in all the experiments.

Wolf [22] showed that tertiary amines and tin carboxylates are synergistic in the urethane formation reaction. In the present study the mixed catalysts, in equimolar concentrations, showed a synergistic effect, and the results are given in Table 2. It was found that the time taken for gelation with the amine and tin compound mixture is lower than the time taken with any one of the individual compounds (Table 1). Tribenzylamine by itself was inactive; however, when used in combination with tin compounds, it exhibited catalytic activity. Among the nine combinations tried, the DECHA/DBTDA combination showed the highest catalytic activity. Bechara [23] reported the enhanced activity of DBTDL/triethylenediamine mixed catalysts toward the phenyl isocyanate-butanol reaction. More studies are needed to understand the deblocking reaction by these mixed catalysts.

CONCLUSION

1. The cure time of HTPB with 2,4-di-*tert*-butylphenol-blocked TDI was determined for different amine and tin catalysts at 125°C.
2. It was found that the amine and tin compounds are synergistic to each other in blocked isocyanate-HTPB cure reaction.
3. Tribenzylamine was found to be a catalytically active compound when used in combination with tin compounds.
4. The deblocking catalytic activity of amine and tin catalysts was confirmed by the identification of isocyanate functionality using infrared spectroscopy.

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REFERENCES

- [1] R. M. Muthiah, V. N. Krishnamurthy, and B. R. Gupta, *J. Appl. Polym. Sci.*, **44**, 2043 (1992).
- [2] L. S. Gibson, *Rubber World*, p. 34 (November 1990).
- [3] S. Petersen, *Ann. Chem.*, **562**, 205 (1949).
- [4] J. W. Wicks Jr., *Prog. Org. Coat.*, **3**, 73 (1975).
- [5] J. W. Wicks Jr., *Ibid.*, **9**, 3, (1981).
- [6] H. Kothandaraman and A. Sultan Nasar, *Polymer*, **34**, 610 (1993).
- [7] H. Kothandaraman, A. Sultan Nasar, and R. Kamal Lakshmi, *J. Appl. Polym. Sci.*, **53**, 31 (1994).
- [8] H. Kothandaraman and A. Sultan Nasar, *J. Macromol. Sci. – Pure Appl. Chem.*, **A32**, 1009 (1995).
- [9] H. Kothandaraman and A. Sultan Nasar, *Ibid.*, **A32**, 1019 (1995).
- [10] A. Sultan Nasar, Ph.D. Thesis, University of Madras, 1993.
- [11] G. M. Carlson, C. M. Neag, C. Kuo, and T. Provder, *Adv. Urethane Sci. Technol.*, **9**, 47 (1984).
- [12] D. Katsamberis and S. P. Pappas, *J. Appl. Polym. Sci.*, **41**, 2059 (1990).
- [13] A. I. Vogel, *Text Book of Practical Organic Chemistry*, ELBS, London, 1971.
- [14] A. Williams, *J. Chem. Soc., Perkin Trans. 2*, p. 808 (1972).
- [15] A. Williams, *Ibid.*, p. 1244 (1973).
- [16] C. Owens, J. M. Woods, A. K. Filo, L. L. Pytlewski, D. E. Chasan, and N. M. Karayannis, *Inorgan. Chim. Acta*, **37**, 89 (1979).
- [17] J. Robins, *J. Appl. Polym. Sci.*, **9**, 821 (1965).
- [18] S. G. Entelis and O. V. Nesterov, *Russ. Chem. Rev.*, **35**, 917 (1966).
- [19] L. Rand, B. Thir, S. L. Reegen, and K. C. Frisch, *J. Appl. Polym. Sci.*, **9**, 1787 (1965).
- [20] A. Petrus, *Int. Chem. Eng.*, **11**, 314 (1971).

- [21] K. C. Frisch and L. P. Ruma, *J. Macromol. Sci. — Rev. Macromol. Chem.*, C5(1), 103 (1970).
- [22] H. W. Wolf, *Urethane Foam Bulletin*, E. I. du Pont de Nemours & Co., 1960.
- [23] I. S. Bechara, *Am. Chem. Soc. Symp. Ser.*, 172, 393 (1981).

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