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КАТАЛИЗ

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CATALYSIS OF SECONDARY ALCOHOL BLOCKED ISOCYANATE-HYDROXYL TERMINATED POLYBUTADIENE CURE REACTION[1]

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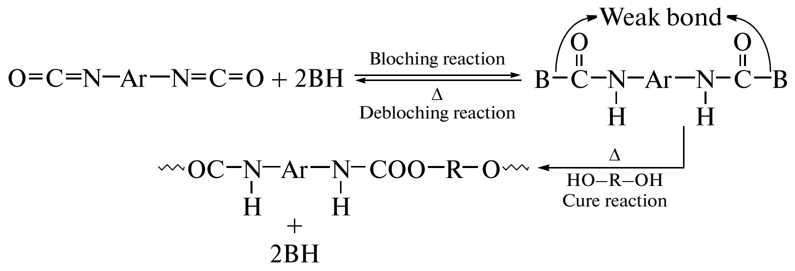
Abstract—1,3-dichloro-2-propanol-blocked isocyanates based on diisocyanates such as 4,4'-methylene bis(phenyl isocyanate), and 1,6-diisocyanato hexane were prepared. Catalysis of cure reaction between blocked diisocyanates and hydroxyl-terminated polybutadiene was investigated. Several tertiary amine and organotin catalysts were used. The catalytic activity of amine and organotin compounds was determined from the cure-time results. It was found that the activity of the catalyst depends upon the steric constrain around the catalytic centre. The organotin compounds showed better catalytic activity than the amine catalysts. The synergistic effect of amine and organotin mixed catalysts on the cure reaction was also investigated.

INTRODUCTION

The polybutadiene chain in HTPB gives a higher energy value and good mechanical properties. HTPB is used to bind the fuel and oxidizer into a solid mass for solid rocket motors. Unsaturation in the HTPB backbone is responsive to oxidative cross-linking, thus, together with nitrous oxide as the oxidizer, it is used to power the rocket motor. The very efficient isocyanate-alcohol reaction is used for curing HTPB.

The main problem associated with HTPB is the high reactivity of the primary hydroxyl groups to isocyanate group, and hence suffers from a short pot-life. This problem may be overcome by the use of a blocked polyisocyanate crosslinker instead of isocyanate as such. The concept of blocked isocyanate can be better understood from the Scheme 1.



where BH is the blocking agent.

Scheme 1. Blocked diisocyanate reaction.

Several compounds which contains active hydrogen atom have been reported as blocking agent for isocyanates [1–15] and investigated the effect of the catalysts on the cure reaction between phenol-blocked isocyanate with HTPB [16].

Recently, we have reported thermal dissociation of 1,3-dichloro-2-propanol-blocked diisocyanates [17] and found that the 1,3-dichloro-2-propanol is potent blocking agent for the isocyanates and hence we intended to study the effect of catalysts on the cure reaction between 1,3-dichloro-2-propanol-blocked isocyanates with HTPB. Several compounds are disclosed as catalysts for the reaction between isocyanates and alcohols [3]. Though, several reports are available on the catalysis of isocyanate-alcohol reaction, the reports on the catalysis of blocked isocyanates-alcohol cure reactions are very meager [16, 18]. The effect of catalyst on the cure reaction of 1,3-dichloro-2-propanol-blocked isocyanate with HTPB has not been reported. Thus we decided to study the catalytic activity of some amine and tin compounds and synergistic effect of amine and tin mixed compounds on 1,3-dichloro-2-propanol-blocked isocyanate-HTPB cure reaction.

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[1] Статья печатается в представленном авторами виде.

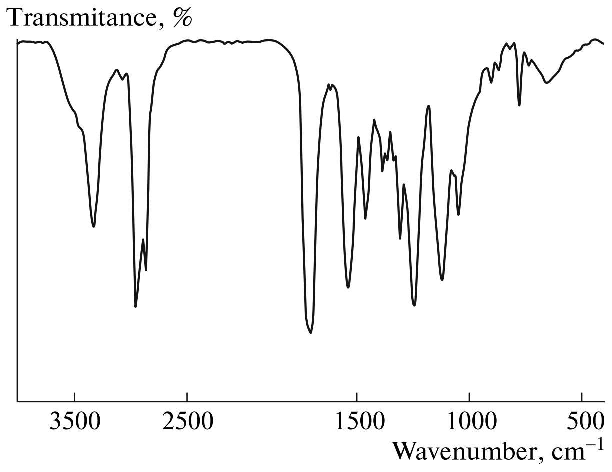


Fig. 1. FTIR spectrum of blocked diisocyanate (BI-1).

EXPERIMENTAL

Materials

The preparative method for 1,3-dichloro-2-propanol-blocked diisocyanates were described in our previous report [17]. Hydroxyl terminated polybutadiene (HTPB) (average molecular weight = 2500) obtained from Sigma Aldrich was used after drying for 2 h at 80°C *in vacuo*. Dibutyltindilaurate (DBTDL) (Aldrich), dibutyltindiacetate (DBTDA) (Aldrich), stannous-2-ethylhexanoate (T"EH) (Aldrich), diethylcyclohexylamine (DECHA) (Sigma), tributylamine (Fluka), and 1,4-diazobicyclo(2,2,2)octane (DABCO) (Sigma) were used as received.

Cure-Time Studies

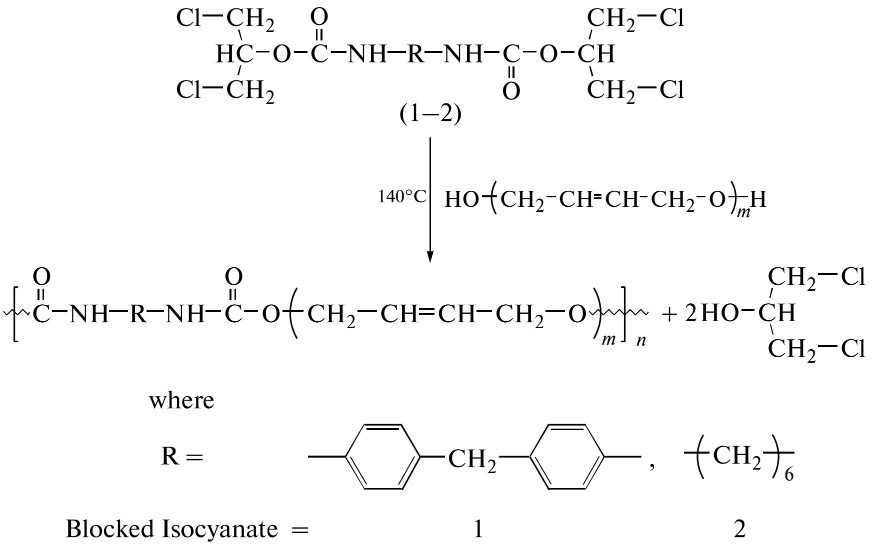
In a typical experiment, 2.5 g (0.002 equiv.) of HTPB was taken in a beaker with 30 mm diameter. To this, 0.002 equiv of 1,3-dichloro-2-propanol-blocked diisocyanate and 2×10^{-4} moles of catalysts were added and mixed thoroughly. Then, the beakers were placed in an air-circulated oven maintained at 150°C. The beakers were inverted at a regular time intervals to observe the flow behavior of the mixture. The time at which the mixture ceased to flow was taken as the cure-time. A duplicate experiment was conducted for each blocked polyisocyanate to ensure the accuracy of the data collected.

Viscosity

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

RESULTS AND DISCUSSION

1,3-dichloro-2-propanol-blocked diisocyanates were prepared according to our reported procedure [17] and the FT-IR spectrum in Fig. 1 shows the absorption bands of –NH and –CO at 3338 cm^{-1} and 1712 cm^{-1}, respectively, confirmed the urethane linkage. The cure reaction of 1,3-dichloro-2-propanol-blocked diisocyanates with HTPB is explained in Scheme 2.



Scheme 2. Cure Reaction of 1,3-dichloro-2-propanol-blocked diisocyanates (BI-1 and BI-2) with HTPB.

This cure reaction is catalyzed by two types of catalysts. The first type consists of three tertiary amines and the second type consists of three organotin compounds. Cure-time recorded for different amine catalyzed reactions are given in Table 1. Among three amines tried, DABCO showed highest catalytic activ-

Table 1. Tertiary amine catalyzed of cure reaction of 1,3-dichloro-2-propanol-blocked diisocyanates (BI-1 and BI-2) with HTPB at 140°C

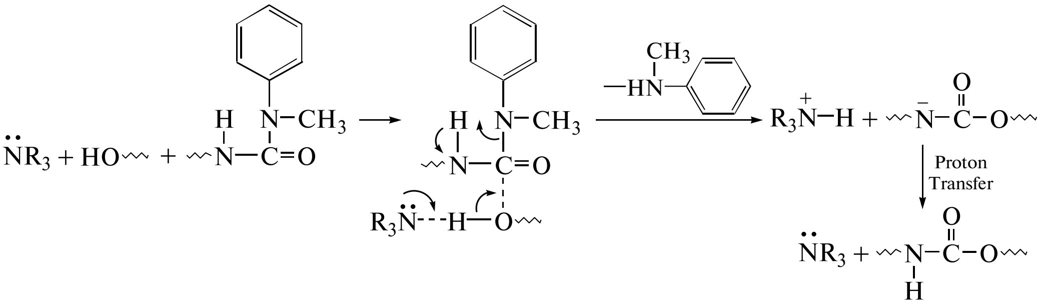
Catalyst [2×10^{-4} M]	Blocked diisocyanate	Cure time, minutes	η_r
Nil	BI-1	300	1.54
Nil	BI-2	530	1.45
DABCO	BI-1	120	1.42
	BI-2	260	1.56
DECHA	BI-1	275	1.44
	BI-2	445	1.47
Tributylamine	BI-1	395	1.44
	BI-2	480	1.54

Table 2. Organotin catalyzeds of cure reaction of 1,3-dichloro-2-propanol-blocked diisocyanates (BI-2 and BI-2) with HTPB at 140°C

Catalyst [2×10^{-4} M]	Blocked diisocyanate	Cure time, minutes	η_r
DBTDL	BI-1	100	1.42
	BI-2	175	1.56
DBTDA	BI-1	165	1.44
	BI-2	255	1.47
Stannous-2-ethylhexanoate	BI-1	220	1.44
	BI-2	350	1.54

ity. Considering a series containing DABCO, DECHA, and tributyl amine the catalytic activity decreases with respect to increase in steric hindrance at the catalytic center. The lowest catalytic activity of DECHA and tributyl amine are due to low basicity of nitrogen atom.

Tertiary amine may abstract a proton from urethane –NH or from –OH of HTPB. Since oxygen is more electronegative than nitrogen, the –OH proton is easily removable compared to –NH proton. Also, there is an association of urethane groups of blocked isocyanate via intramolecular hydrogen bonding of the proton of –NH moiety with the oxygen atom of C=O moiety [17]. Thus, abstraction of a proton from –OH group of HTPB by tertiary amine is more favorable compared to abstraction from –NH group. Subsequently, the alkoxide anion formed will interact with blocked isocyanate group. Accordingly, it is believed that the cure reaction proceeds through addition-elimination mechanism and the proposed mechanism is given in Scheme 3.



Scheme 3. Possible mechanism for amine catalyzed cure reaction of blocked diisocyanate with polyol.

According to this mechanism, the greater activity of DABCO is attributed to its less sterically hindered structures, making nitrogen more accessible to abstract the proton from hydroxyl group. The nitrogen atom is highly inaccessible in the tributylamine and hence showed very little catalytic activity.

Cure-time recorded 1,3-dichloro-2-propanol-blocked diisocyanates with HTPB catalyzed by different organotin compounds are also given in Table 2. It is found that the catalytic activity decreases in the following order: DBTDL > DBTDA > stannous-2-ethylhexanoate.

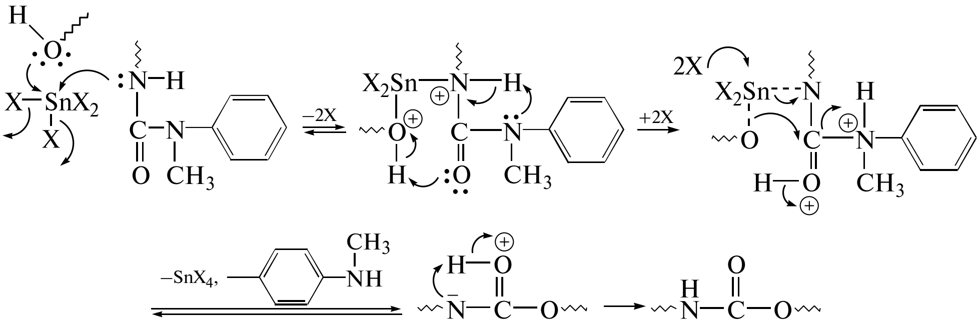
The mechanism may involve the formation of a ternary complex through interaction between Sn, oxygen of alcohol and nitrogen of urethane–NH group. Formation of such a ternary complex in urethane formation reaction has already been described by few researchers [19, 20]. In the present study, this type of interaction leads to regeneration of catalyst and blocking agent. The cure-time results obtained are consistent with the mechanism given in Scheme 4.

Table 3. Synergistic effect of amine and tin catalysts on the cure reaction of blocked diisocyanate (BI-2) with HTPB at 140°C

Amine catalyst [2×10^{-4} M]	Tin catalyst [2×10^{-4} M]	Cure time, minutes	η_r
DABCO	DBTDL	35	1.49
DECHA	DBTDL	50	1.48
Tributylamine	DBTDL	70	1.47
DABCO	DBTDA	40	1.48
DECHA	DBTDA	65	1.48
Tributylamine	DBTDA	80	1.48
DABCO	Stannous-2-ethylhexanoate	70	1.48
DECHA	Stannous-2-ethylhexanoate	95	1.49
Tributylamine	Stannous-2-ethylhexanoate	135	1.49

Table 4. Synergistic effect of amine and tin catalysts on the cure reaction blocked diisocyanate (BI-1) with HTPB at 140°C

Amine catalyst [2×10^{-4} M]	Tin catalyst [2×10^{-4} M]	Cure time, minutes	η_r
DABCO	DBTDL	25	1.45
DECHA	DBTDL	45	1.40
Tributylamine	DBTDL	60	1.45
DABCO	DBTDA	30	1.40
DECHA	DBTDA	45	1.45
Tributylamine	DBTDA	60	1.46
DABCO	Stannous-2-ethylhexanoate	60	1.40
DECHA	Stannous-2-ethylhexanoate	85	1.45
Tributylamine	Stannous-2-ethylhexanoate	120	1.40



Scheme 4. Possible mechanism for organo-tin catalyzed cure reaction of blocked diisocyanate with polyol.

During the course of the reaction, the acetate anion in DBTDA and laureate anion in DBTDL are replaced by the oxygen of HTPB and nitrogen of blocked isocyanate moiety. Since laureate anion is better leaving group than the acetate anion due to structural reasons, the laureate anion is easily replaceable and hence showed higher catalytic activity than DBTDA. The lower activity of stannous-2-ethylhexanoate than of DBTDA and DBTDL may be due to more electronegative character of the Sn^{2+} ion than the Sn^{4+} ion.

Researchers showed that tertiary amines and tin carboxylates are synergistic in the urethane formation reaction [12, 21, 22]. In this present study the mixed catalysts, in equimolar concentration, showed a synergistic effect, and the results are given in Table 3 and Table 4. It was found that the time taken for cure process employed with amine and tin mixed compounds are lower than the time taken with any one of the individual compounds (Table 1 and Table 2). Tributylamine is found to be not much inefficient; however, when used in combination with tin compounds, it exhibited significant catalytic activity. Among several combinations tried, the DABCO/DBTDL combination showed the highest catalytic activity. In this case fully cured product was obtained 20 and 35 minutes for blocked diisocynate 1 and blocked diisocyanate 2, respectively. This low cure time is very attractive in industrial point of view. More studies are needed to understand the mechanism of cure reaction catalyzed by these mixed catalysts.

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

CONCLUSIONS

Catalysis of 1,3-dichloro-2-propanol-blocked polyisocyanate-HTPB cure reaction was studied. The cure-times were determined at 140°C and were reported. Compare to amine the organotin catalysts found to be better caltaysts. Blocked diisocyanate based on MDI shows good curing than the blocked diisocynate based on HDI. DABCO/DBTDL mixed catalyst system was very efficient for the cure reaction due to synergistic effect.

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REFERENCES

1. R. M. Muthiah, V. N. Krishnamurthy, and B. R. Gupta, J. Appl. Polym. Sci. **44**, 2043 (1992).
2. H. L. Schreuder-Gibson, Rubber World (November, p-34 1990).
3. D. A. Wicks and Z. W. Wicks, Jr. Prog. Org. Coat. **36**, 148 (1999).
4. D. A. Wicks and Z. W. Wicks, Jr. Prog. Org. Coat. **41**, 1 (2001).
5. Z. W. Wicks, Jr. Prog. Org. Coat. **3**, 73 (1975).
6. Z. W. Wicks, Jr. Prog. Org. Coat. **9**, 3 (1981).
7. T. J. Loontjens, Polym. Sci. Part. A: Polym. Chem. **41**, 3198 (2003).
8. K. S. Ho and L. W. J. Chen, J. Polym. Sci. Part. A: Polym. Chem. **35**, 1703 (1997).
9. A. Muehlebach, J. Polym. Sci. Part. A: Polym. Chem. **32**, 753 (1994).
10. H. Kothandaraman and R. Thangavel, J. Polym. Sci. Part. A: Polym. Chem. **31**, 2653 (1993).
11. P. Michaud and Y. Camberlin, J. Polym. Sci. Part. A: Polym. Chem. **25**, 1717 (1987).
12. H. Kothandaraman and A. Sultan Nasar, Polymer **34,** 610 (1993).
13. H. Kothandaraman, A. Sultan Nasar, and R. Kamal Lakshmi, J. Appl. Polym. Sci. **53**, 31 (1994).
14. H. Kothandaraman and A. Sultan Nasar, J. Macromol. Sci. Pure. Appl. Chem. **A32, 5,** 1009 (1995).
15. H. Kothandaraman and A. Sultan Nasar, J. Macromol. Sci. Pure. Appl. Chem. **A32, 5,** 1017 (1995).
16. H. Kothandaraman, A. Sultan Nasar, and K. R. Suresh, J. Macromol. Sci. Pure. Appl. Chem. **A33, 6,** 833 (1996).
17. Gvoindarajan Sankar and A. Sultan Nasar, J. Polym. Sci: Part. A: Polym. Chem. **45**, 1557 (2007).
18. D. Katsamberis and S. P. Pappas, J. Appl. Polym. Sci. **41**, 2059 (1990).
19. K. Wongkamolsesh and J. E. Kresta, ACS Symposium Series **270**, 111 (1985).
20. Shan-Guo Luo, Hui-Min Tan, Jian-Guo Zhang, Yi-Jie Wu, Feng-Kui Pei, and Xiang-Hong Meng, J. Appl. Polym. Sci. **48**, 1217 (1997).
21. H. W. Wolf, Urethane Foam Bulletin, E. I. du Pont de Nemours & Co., 1960.
22. I. S. Bechara, Am. Chem. Soc. Symp. Ser. **172**, 393 (1981).