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A Physico-chemical Study of Elastomeric Polyurethans

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Polyurethan prepolymers prepared by the reaction of polypropylene glycol (PPG) with tolylene diisocyanate (TDI) are cross-linked with trimethylol propane (TMP) to afford elastomeric polyurethans. Although the reaction rate of TDI with PPG increases remarkably with TDI/PPG molar ratio (R), the reaction does not follow a simple second-order mechanism. The curing of the prepolymers with TMP is influenced greatly by R , by the time (t) of prepolymer formation, and also by the amount of TMP.

On the other hand, the effects of other curing agents, temperature and inorganic fillers upon the curing are examined.

I. Introduction

In the field of polyurethan study, attentions have been centered in the processes of elastomer and foam preparation. Polyurethan elastomers are obtained by the reaction of diisocyanates with long chain diols, such as polyester or polyether glycol, followed by the curing reaction in the presence of suitable cross-linking agents (curing agents). The elastomers are employed as hard castings, rubberlike materials and elastic binders of fillers such as ammonium perchlorate in solid rocket propellants.

Although several reports have informed the technique preparing polyurethan elastomers cross-linked with trimethylol propane (TMP)^{1),2)}, much is left uncertain concerning the reaction mechanism involving the curing process. In the present work, pure TMP is chosen as a simple cross-linking agent to elucidate the curing process of the polyurethan prepolymers prepared by the reaction of polypropylene glycol (PPG) with tolylene diisocyanate (TDI).

The rate of prepolymer formation from PPG and TDI increases greatly with TDI/PPG molar ratio (R). In the curing process of the prepolymer with TMP, the time (G) at which gelation occurs is found to depend upon R , upon the time (t) of prepolymer formation, and also upon the amount of TMP.

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In the preparation of an effective solid propellant consisting of elastomeric polyurethane as a binder and fuel, and ammonium perchlorate (NH_4ClO_4) as an oxidant, Warfield³⁾ demonstrated that NH_4ClO_4 in high contents behaved like a strong accelerator on curing. In an attempt to examine the curing of the prepolymers in the presence of NH_4ClO_4 , some experiments resulted in failure to confirm the strong accelerating behavior of NH_4ClO_4 as was reported by Warfield.

2. Experimental

2.1. Materials

PPG (Union Carbide Chemicals Co., Niax Diol PPG-2025) serves as a long chain diol, having an average molecular weight 2030 after the terminal OH group analysis⁴⁾. The water content of PPG is 0.109 wt% by the Karl-Fischer method.

TDI (Mobay Chemical Co., Mondur TD80) used as a diisocyanate is a mixture of 80 wt% 2,4-TDI and 20 wt% 2,6-TDI. After distillation (b. p. $87.0^\circ\text{C}/8\text{ mmHg}$) for submitting to the reaction, the content of NCO group determined corresponds to 99.4 wt% purity of the sample.

The analytical procedure of TDI is similar to that described by Siggia⁵⁾; but di-n-butylamine is substituted for n-butylamine and, as an indicator, bromocresolpurple is used.

TMP is dried *in vacuo* (m. p. $58-59^\circ\text{C}$).

Inorganic fillers, ammonium chloride and ammonium perchlorate, are powdered to about 80 mesh size and dried over phosphorus pentoxide for three days.

2.2. Preparation of Prepolymers

PPG (0.01-0.015 mole) is introduced into 50 ml Erlenmeyer flask and degassed overnight *in vacuo* at room temperature. The amount of TDI required to give the desired R is subsequently weighed into the flask, and the mixture is well stirred magnetically under mercury-sealing.

The sample divided into several portions in each glass tube is kept at $80 \pm 1^\circ\text{C}$ after an additional period of degassing under reduced pressure at room temperature. Thus PPG and TDI are bulk-polymerized to the extent of $R=0.97-2.17$ at t -values within 16 hours in the absence of catalysts.

The resulting prepolymers are colorless adhesive syrups that will dissolve in dimethyl formamide in all proportions.

2.3. Curing of Prepolymers

The prepolymers are heated to $100 \pm 1^\circ\text{C}$, and TMP, exactly weighed to

give the desired (TMP)/(NCO in the prepolymer) molar ratio (M), is added. The mixture is agitated vigorously and degassed *in vacuo*. Curing of the mixture proceeds under an isothermal condition to give elastomeric polyurethans.

The observation of fluidity and elasticity is adopted to check the gel time (G)⁶.

2.4. Elastomeric Polyurethans with Inorganic Fillers

The prepolymer ($R=1.61$, $t=5$ hrs.) is mixed with TMP ($M=0.25$) at $100\pm 1^\circ\text{C}$ and mixture (48 parts) is well admixed with inorganic fillers (52 parts) at $100\pm 1^\circ\text{C}$. The samples are cured isothermally at appropriate temperatures.

Gel time of the composites (G^*) is investigated by a similar method described above.

3. Results and Discussions

3.1. Reaction of TDI with PPG

The NCO content in the prepolymer determined by the analytical method stated above relates with the NCO conversion (E) against t so as

$$E (\%) = \frac{(\text{NCO at } t=0) - (\text{NCO at } t)}{(\text{OH at } t=0)} \times 100$$

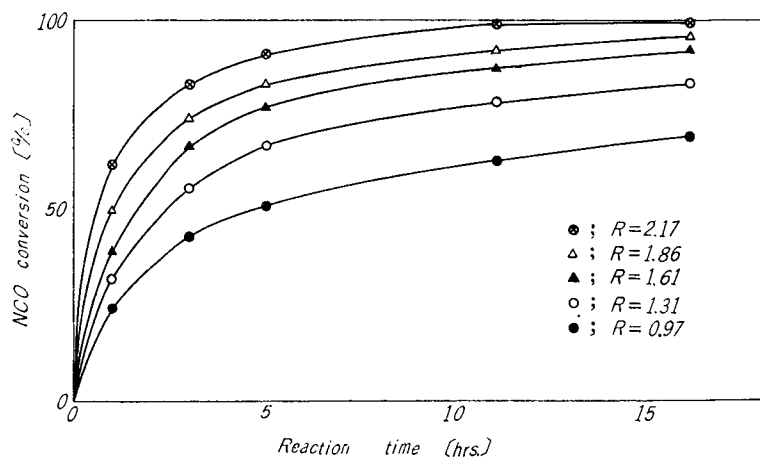


Fig. 1. A plot of NCO conversion against reaction time of TDI with PPG.

A plot of E against t for various R 's shown in Fig. 1 indicates that the reaction rate increases greatly with R in the initial stage of the reaction, and is little influenced by R in the later one.

An investigation of the reaction mechanism is made by calculating the

rate constants summarized in Table 1. Yokoyama⁷⁾ reported that the polyethylene glycol and p-phenylene diisocyanate in toluene was referred to a second-order mechanism. As shown in Fig. 2, however, the proceeding of the reaction between TDI and PPG is observed to deviate from a simple second-order process, and the rate constants are influenced by *t*.

Table 1. Rate constants of the reaction between TDI with PPG calculated after second-order mechanism in unit of g/mole, hr.

<i>R</i> \ <i>t</i>	1	3	5	11	16
0.97	3.38×10^2	2.81×10^2	2.37×10^2	1.77×10^2	1.63×10^2
1.31	3.86	3.24	2.65	1.92	1.75
1.61	4.19	3.62	2.99	2.18	1.96
1.86	5.27	3.92	3.28	2.33	2.11
2.17	6.50	4.50	3.92	3.75	3.75

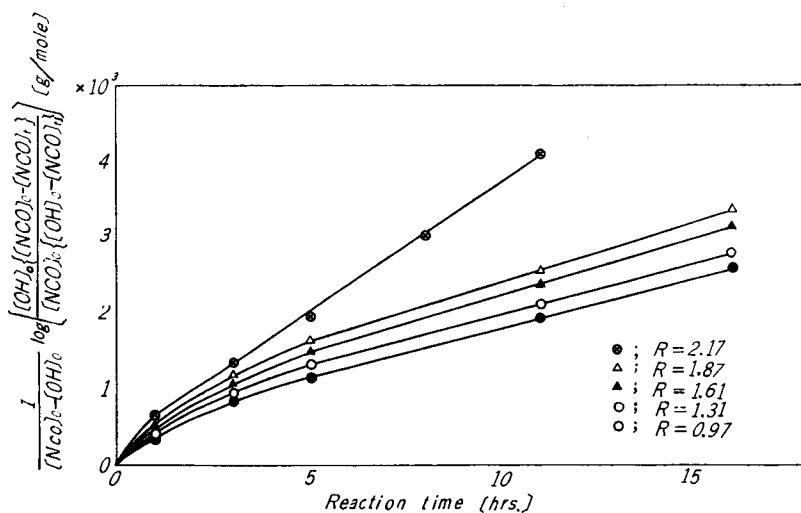


Fig. 2. Proceeding in prepolymer forming reaction of TDI with PPG after second-order mechanism :

$$-\frac{d[\text{NCO}]}{dt} = k[\text{NCO}][\text{OH}]$$

$$kt = \frac{1}{[\text{NCO}]_0 - [\text{OH}]_0} \ln \left[\frac{[\text{OH}]_0 \{ [\text{NCO}]_0 - [\text{NCO}]_t \}}{[\text{NCO}]_0 \{ [\text{OH}]_0 - [\text{NCO}]_t \}} \right]$$

A change in the nature of the reaction through the prepolymer formation is suggested by the fact that the initial rate constants are about three times greater than the ones after 50% conversion. Bailey⁸⁾, Kogon⁹⁾ and Brock¹⁰⁾ stated that the reaction of 2,4-TDI with ethanol or butanol was much complicated

with four parallel and consecutive reaction paths, and that k_1 or $(k_1 + k_2)$ is much greater than k_3 or $(k_3 + k_4)$ as shown in Fig. 3.

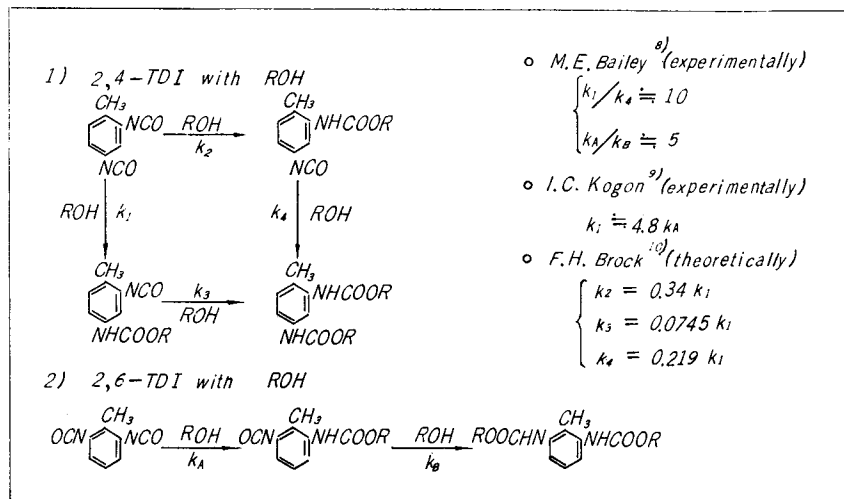


Fig. 3. Reaction process of 2,4-TDI and 2,6-TDI with ROH, and their rate constants.

Therefore, the prepolymer formation of TDI with PPG may be assumed to consist mainly of two successive reactions, (R-1) and (R-2), with different rate constants. (R-1) is the reaction of PPG and TDI, and (R-2) is the one of PPG and monourethane formed through (R-1). Then it may be concluded that the reaction under $R=2.17$ consists mainly of (R-1), and, in the cases of R less than 1.87, (R-1) is exclusively predominant in the initial stage, and after 50% conversion is reached, (R-2) becomes dominant.

3.2. Curing

3.2.1. Effect of Properties of Prepolymers

Properties of the prepolymers, in particular the chemical behaviors represented by NCO content and molecular weight, can be regulated by R and t . Fig. 4 shows a G against t plot in the curing of the prepolymers under the value of R ranging from 0.97 to 2.17.

It is observed that the property of the prepolymers in relation to the gelation rate depends mainly upon R , and the value of G decreases with increasing R . Furthermore gelation does not occur when R is less than 1.31, even at an increased curing time and elevated temperature. Thus, gelation rates increase with R , as observed in the prepolymer formation. These results show that G is shortened by the increase of NCO content and the decrease of molecular weight of prepolymers.

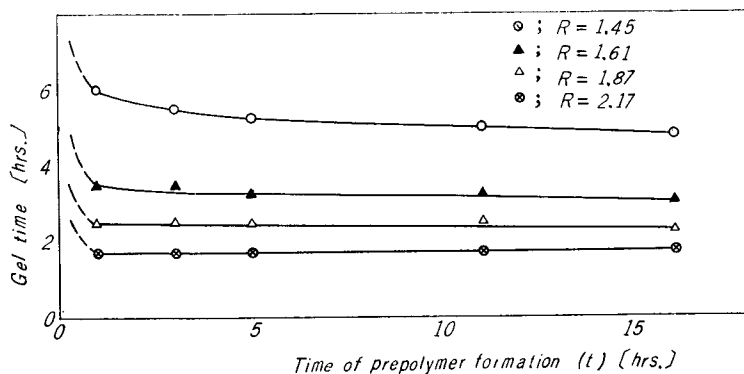


Fig. 4. Effect of properties of prepolymers, regulated by R and t , on gel time. ($M=0.33$)

3.2.2. Effect of the Amount of TMP

(TMP)/(NCO in the prepolymer) molar ratio (M) is chosen in the range of 0.1–0.8. Fig. 5 illustrates the dependence of G on M , showing that the optimum amount of TMP to give the shortest G is obtained in the condition in which $M=0.3$ –0.4, and that gelation does not occur at M -values below 0.1 and also above 0.6.

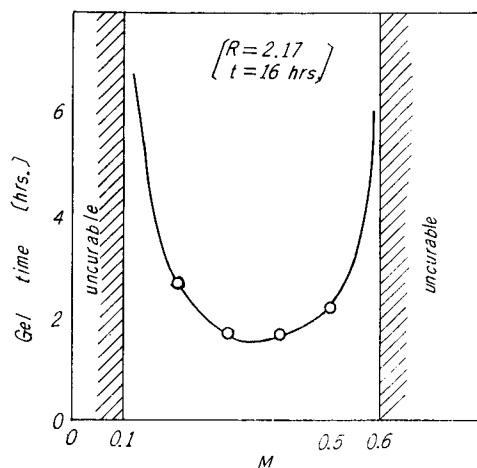


Fig. 5. Effect of (TMP)/(NCO in prepolymer) molar ratio (M) on gel time.

3.2.3. Effect of Several Cross-linking Agents

As shown in Table 2, the gel time of various cross-linking agents is observed and compared with that of TMP. Ease of gelation with curing

agents decreases in the following order : triethanolamine, diethanolamine, monoethanolamine, TMP, 1,2,6-hexanetriol and glycerol. Various aminoalcohols accelerate considerably the curing of prepolymers since the presence of the amino group catalyzes the NCO condensation, and in this case the behavior is more complicated in comparison with simple hydroxy cross-linking agents.

Table 2. Curing of polyurethan prepolymer ($R=1.61$, $t=16$ hrs.) with several cross-linking agents.

curing agent	m. p. (°C)	b. p. 760 mm (°C)	M	G (hrs.)	visual observations
triethanolamine ($\text{CH}_2\text{CH}_2\text{OH}$) ₃ N	21.2	360	0.32	1	white, opaque, hard
diethanolamine ($\text{CH}_2\text{CH}_2\text{OH}$) ₂ NH	28.0	268.8	0.39	2	white, opaque, adhesive
monoethanolamine ($\text{CH}_2\text{CH}_2\text{OH}$)NH ₂	10.3	170.8	0.32	3	white, opaque, hard
trimethylolpropane (CH_2OH) ₃ CCH ₂ CH ₃	58.8 -59.0	—	0.33	3	colorless (yellow), transparent, hard
1, 2, 6-hexanetriol CH ₂ OHCHOH(CH ₂) ₃ CH ₂ OH	—	176.0 (4 mm)	0.33	5	light grey, transparent, hard
glycerol (CH_2OH) ₂ CHOH	17.8	290.0 (decpn.)	0.32	8	light grey, transparent, hard

3.2.4. Effect of Curing Temperature

The effect of curing temperature upon G is illustrated by Fig. 6 (a). Gel time decreases greatly by increasing temperature of curing.

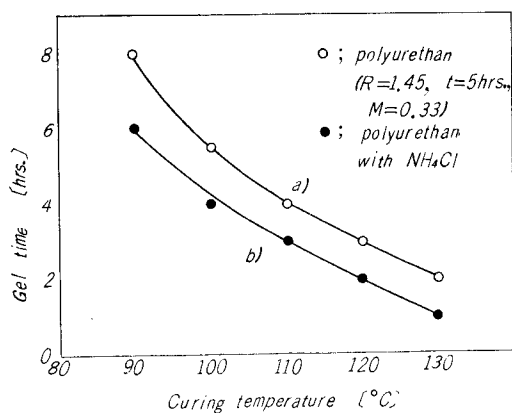


Fig. 6. Effect of curing temperature on gel time.

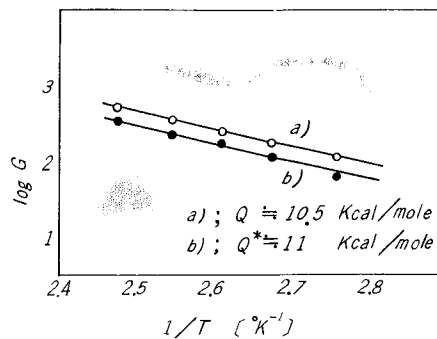


Fig. 7. A plot of $\log G$ and $\log G^*$ against $1/T$.

Since G is reciprocal to the rate of curing reaction, the Arrhenius equation can be derived as follows;

$$\ln G = Q/RT - \text{const.} \quad (1)$$

Thus, $\ln G$ is plotted against $1/T$, and a linear relation is obtained as shown in Fig. 7 (a). From the slope of this plot, the apparent activation energy (Q) for curing of such a polyurethan prepolymer is calculated to be approximately 10.5 Kcal/mole¹¹.

3.2.5. Effect of Inorganic Fillers in High Concentrations

Elastomeric polyurethan containing an inorganic filler such as ammonium chloride (NH_4Cl) or ammonium perchlorate (NH_4ClO_4) appears to have a shorter gel time (G^*) than that of the sample cured without filler. Both of these inorganic fillers indicate the same behavior for gelation and the apparent activation energies lie in the range of the same order. When the filler content reaches 52 wt%, the activation energy is evaluated to be about 10–13 Kcal/mole according to the equation (1).

For example, Fig. 6 (b) shows the change of G^* with varied temperature of curing. It indicates that G^* is shorter than G . The apparent activation energy (Q^*) for curing of the mixture of elastomeric polyurethan and NH_4Cl (52 wt% of total weight of the mixture) is calculated to be ca. 11 Kcal/mole by the equation (1).

So long as Q^* is almost equal to Q , the rates of these two gelation reactions also must be almost the same, provided that no difference is expected between their frequency factors. Nevertheless, G^* is shorter than G .

In order to investigate the effect of admixture of the filler on G^* , G^* is plotted against volume % (V) of NH_4Cl in the mixture of the prepolymer ($R=2.17$, $t=16$ hrs., $M=0.33$) and NH_4Cl as shown in Fig. 8.

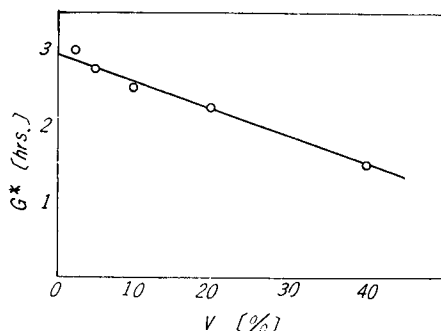


Fig. 8. A plot of gel time (G^*) of the mixture of polyurethan and NH_4Cl against volume % (V) of NH_4Cl .

It is found that G^* decreases with the increase of V in such a way as

$$G^* \text{ (hrs.)} = -0.033V + 3 \quad (2)$$

G^* at $V=0$ in the experimental equation (2) is 3 hrs., which is identical with G (gel time of elastomeric polyurethan without the filler).

Therefore, it is concluded that the influence of higher amounts of inor-

ganic fillers on the gelation of elastomeric polyurethan might be only of a physical or mechanical character. It seems probable that the "true" gel time could not depend upon the presence of the filler such as NH_4Cl or NH_4ClO_4 . Thus, the "true" point of gelation of polyurethan elastomer with inorganic fillers is difficult to determine precisely, and is influenced by mechanical interaction, such as adhesion and the like, between the polyurethan and the surface of the particles of the fillers. Hence, in an investigation of the effect of inorganic fillers, measurement of the activation energy would be requisite.

In contrast, some typical Friedel-Crafts catalysts, such as anhydrous ferric chloride and aluminum chloride, cause a drastic and exothermic acceleration in this curing reaction.

4. Conclusion

1. In the reaction of polypropylene glycol (PPG) with tolylene diisocyanate (TDI), the rate increases with TDI/PPG molar ratio (R), and a kinetic consideration indicates that the reaction is not a simple second-order mechanism, but consists mainly of two consecutive reactions having different rate constants.

2. The property of the prepolymers obtained depends greatly upon R , and the gel time (G) decreases with the increase of R . Gelation does not occur below $R=1.31$ even at increased curing time.

3. The optimum amount of trimethylol propane (TMP) to give the shortest G is observed to be obtained by $M=0.3-0.4$, where M is (TMP)/(NCO in the prepolymer) molar ratio, and gelation does not occur at $M>0.1$ and $M>0.6$.

4. Ease of gelation in the presence of several cross-linking agents decreases in the following order: triethanolamine, diethanolamine, monoethanolamine, TMP, 1,2,6-hexanetriol and glycerol (anhydrous).

5. Gelation is much accelerated by increasing curing temperature. The apparent activation energy for the curing reaction of polyurethan prepolymer with TMP is calculated to be approximately 10-12 Kcal/mole.

6. The presence of inorganic fillers such as ammonium chloride (NH_4Cl) or ammonium perchlorate (NH_4ClO_4) in large amounts shortens the gel time. The apparent activation energy for the curing of the mixture is about 11-13 Kcal/mole.

7. The gel time (G^*) of polyurethan elastomer containing fillers decreases with the increase of volume % (V) of NH_4Cl in the mixture in such a way as

$$G^* \text{ (hrs.)} = -0.033V + 3$$

“True” gel time of polyurethane lastomers seems to be unaffected by the presence of inorganic filler, such as NH_4Cl or NH_4ClO_4 .

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