Polymerization Kinetics in Propellants of the Hydroxyl-Terminated Polybutadiene–Isophorone Diisocyanate System

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Synopsis

The copolymerization of a hydroxyl-terminated polybutadiene with isophorone diisocyanate in a propellant formulation has been studied. The kinetic rates for four different reaction temperatures have been measured both in gumstock and samples containing ammonium perchlorate. It is shown that the presence of ammonium perchlorate (up to 90% by weight) neither catalyzes nor retards the rate of binder polymerization. It is also shown that the polymerization follows an apparent second-order rate law with an activation energy of 9.8 kcal/mole.

INTRODUCTION

It is usually observed in propellant preparation that end-of-mix viscosities are not constant and that pot life varies. The pot life of a propellant mix is the mixing time available before the viscosity of the mix becomes too high to pour or cast (~40 kilopoises). A typical propellant formulation usually contains binder, oxidizer, metal powder, catalyst, plasticizer, bonding agent, antioxidant, and curing agent. These agents are listed in Table I. The effects of these components on the propellant properties are complicated functions. They can either change the kinetics of the binder polymerization or alter the behavior of another component. Even the impurities in each component can affect the ultimate properties of the propellant. Therefore, it is very important to understand the function of each ingredient. In order to differentiate each individual effect, our approach is first to investigate the binder polymerization and then the effect of each individual ingredient on this process independently. We have studied the kinetics of a polyurethane formation of a hydroxyl-terminated polybutadiene copolymerized with isophorone diisocyanate. The kinetic rates at different temperatures have been obtained and the energy of activation of the polyurethane formation calculated. The effect of solid loading [ammonium perchlorate (AP)] on the polymerization of the binder has been studied by following the kinetics of samples at different solids loading (0%, 10%, 50%, and 75% AP by weight).

The main cause of the difficulty of quantitatively following the chemical reaction is that the binder comprises only a small percentage of the total weight of propellant (usually 10–15%). The high molecular weight of the prepolymer (3000–5000 for the widely used hydroxyl-terminated polybutadi-

1117

TABLE I
Typical Propellant Formulations

Ingredient	Amount	Comment
Binder	10–20 wt-%	this paper focuses on the use of hydroxyl-terminated polybutadiene
Curing agent	0.8 to 1.2 equiv. ratio	isophorone diisocyanate for this study
Oxidizer	60–90 wt-%	generally, ammonium perchlorate of a spectrum of particle sizes and shapes
Metal	6–20 wt-%	generally, aluminum powder to increase impulse and decrease combustion stability; it is not included in this investigation
Burning rate catalyst	0–5 wt-%	generally, metal oxides that control burning rate of final formulation
Plasticizer	0–30% of binder	appears in calculations as part of the binder system; it is used to lower the modulus of the final cured system
Bonding agent	0–5% of binder	appears in calculations as part of the binder system; it can be various organic materials designed to change the dewetting characteristics between binder and oxidizer
Antioxidant	1–3% of binder	appears in calculations as part of the binder system and is used to prevent oxidation of the prepolymer of binder

ene) makes the analysis even more difficult. Viscosity measurement has been used in the propellant industry as an indirect means of measuring the extent of binder polymerization. Complicated factors exist in the interpretation of this type of data, and very doubtful assumptions must be made in order to obtain kinetic parameters from viscosity data. Various other techniques have been employed, but the presence of the other ingredients usually interferes with the measurements and many conflicting results have been reported. During the course of our study, techniques such as dilatometry, infrared spectroscopy, and ^{13}C NMR have been investigated and failed to provide reliable results for our propellant system..Torsional braid measurements have been used by our group and give good results for the earlier phase of the polymerization but do not adequately describe the kinetics beyond the gel point. The method eventually used for the kinetic study is a chemical analysis method similar to that of Stagg.[1] The sample preparation procedure has been changed to adapt the method to the propellant analysis. The details of the procedure are discussed in the next section.

EXPERIMENTAL

The propellant binder contains equimolar amounts of hydroxyl and isocyanate groups from the hydroxyl-terminated polybutadiene and the isophorone diisocyanate, respectively. The solid in the propellant is the oxidizer, AP. The two reactants are completely soluble in each other forming a homogeneous binder system. The AP is not soluble in the binder but its surface is wetted by the binder.

Even though the two isocyanate groups of the diisocyanate are not equiva-

lent in reactivity, our assay determines only the total amount of unreacted isocyanate. The difference between the reaction rates of the two isocyanate groups is not included in this study. The material specifications, experimental conditions for the polymerization (cure), and the analytical procedures are described separately.

Materials

The chemicals used in this study were:

Hydroxyl-terminated polybutadiene (R-45M) from Atlantic Richfield Corp.; molecular weight ~3000; hydroxyl value, 0.75 meq/g.

Isophorone diisocyanate or 3-isocyanato-methyl-3,5,5-trimethylcyclohexyl isocyanate from Thorson Chemical Co., Lot 7198006. The formula is
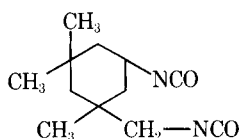
The reagent used was over 99% pure determined by the amine titration method used in this study.

Ammonium perchlorate from Trona Chemical Co., Lot 6090; milled to ~6-μ size; dried in vacuum oven.

N-Dibutylamine from Matheson, Coleman and Bell; reagent grade; dried over molecular sieve.

N,N-Dimethylformamide (DMF) from Matheson, Coleman and Bell; spectroquality; dried over molecular sieve.

Benzene from Matheson, Coleman and Bell; reagent grade; dried over molecular sieve.

Methanol from Matheson, Coleman and Bell; reagent grade.

Propellant Mixing

The propellant mixes were prepared in a Helicone mixer manufactured by Atlantic Research Corp. The binder was briefly mixed before the introduction of AP. Dry nitrogen was continuously purged over the mixture to prevent moisture contamination.

Polymerization

Samples for each kinetic time point were polymerized in individual containers, which were immersed in a constant-temperature bath. Erlenmeyer flasks, 250 ml, with lubricated ground-glass joint stoppers were used for the pregel samples and were weighed precisely to contain 3–5 g binder. The postgel samples were contained in 2-oz polyethylene bottles and were weighed precisely to contain 10–20 g binder.

At each kinetic time point, one or two samples were removed from the bath and quenched into an ice–water mixture. The outside of the container was then washed with acetone and dried by flushing with nitrogen.

Analytical Procedure

Pregel Samples. Immediately after the sample was quenched and the out-side of the container cleaned, a small magnetic stirring bar, 50 ml benzene, and 2 ml of a 1:1 volume ratio benzene and dibutylamine solution were intro-duced into each flask. The stopper was replaced and sealed air tight. The mixture was then stirred to facilitate dissolution of the binder. The solution was kept at room temperature for several hours to assure complete reaction of the unreacted isocyanate with the amine. The amount of excess amine was determined by titration with $1N$ hydrochloric acid. Before titration, 50 ml methanol and several drops of indicator (1% 1:3 bromcresol green and methyl red in methanol) were added. The endpoint was indicated by the change of color from green to yellow ($\sim$ pH 3.5).

As the polymerization approaches the gel point, the binder becomes less soluble in benzene. In these cases, the addition of methanol was deleted and 50 ml DMF was added with the benzene to increase the binder solubility. Blank titrations of both samples and pure isocyanate in various combinations of solvents showed that the solvent mixtures did not affect the results of ti-tration. It was also found that the presence of AP did not interfere with the titration.

Postgel Samples. After quenching and cleaning, as mentioned in the last section, the polyethylene bottle containing the sample was transferred into a dry box and cooled with liquid nitrogen. The polyethylene bottle was slit open and the sample was removed. The sample was then cut into very thin slices. (Liquid nitrogen was required to stop further polymerization and to harden the soft and sticky material for ease of handling.) Moisture contami-nation was avoided by conducting all handling operations in a dry box. The sliced sample was transferred to a 500-ml Erlenmeyer flask containing 100 ml benzene, 100 ml DMF, and 2 ml amine–benzene solution and sealed. The re-maining titration procedure was similar to that used for the pregel samples.

RESULTS AND DISCUSSION

Polymerization rates of four different temperature runs of the gumstock (all binder, no AP) studied are shown in Figure 1. The concentration of iso-cyanate is expressed as fraction of IPDI left instead of the "mole/volume" unit. The temperature effect on the polymerization rates is clearly illus-trated by the four different curves. The second order rate plots for the sam-ples of Figure 1 are given in Figure 2. Due to the straight line formed by data points in Figure 2, the reaction apparently followed the second-order rate law. Rate constants (k) at different temperatures were calculated from the slopes in Figure 2. The activation energy was calculated from the slope of the Arrhenius plot of log k against reciprocals of absolute reaction tempera-ture (Fig. 3). It was found to be 9.8 kcal/mole, comparable to the 10.5 kcal/mole value obtained by Adicoff and Dibble[2] on the same binder system using an improved version of the prevously published torsional braid technique.[3,4] It is also close to the 8.1–12.5 kcal/mole values obtained for some simple alco-hol–isocyanate model systems.[5-9] The order of reaction for these model sys-tems, however, was formulated as a third-order reaction but ultimately treat-
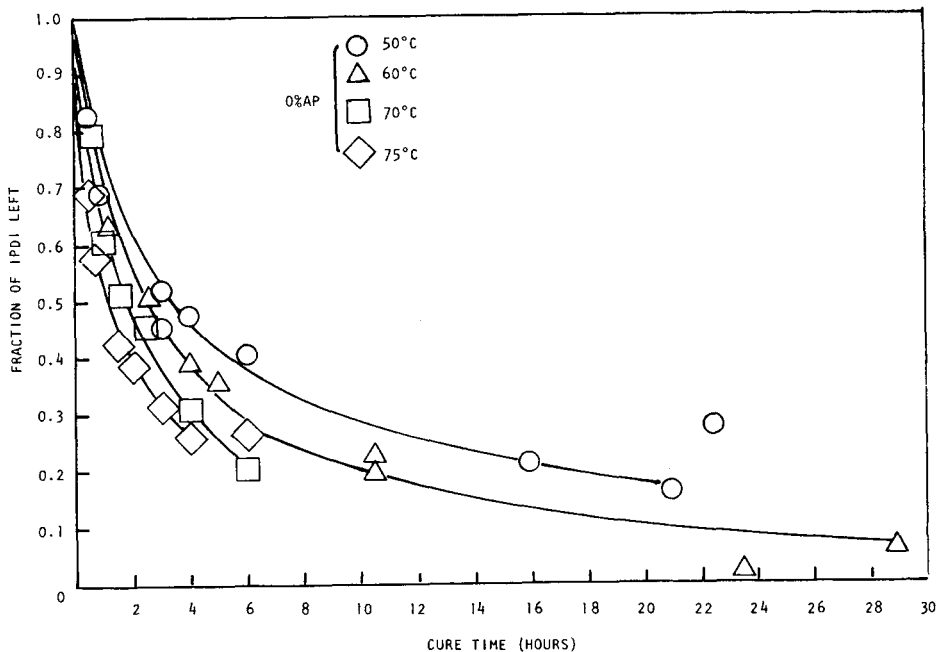
Fig. 1. Rate of isophorone diisocyanate disappearance (gumstock).

ed as a second-order reaction. Complicating effects of reaction products modifying the kinetics in model compounds were not observed in the propellant system.

The effect of solid loading on the rates of polymerization of the binder was studied by following the kinetic rates of samples at different solid loadings (0%, 10%, 50%, and 75% AP by weight). The rates of disappearance of isocya-
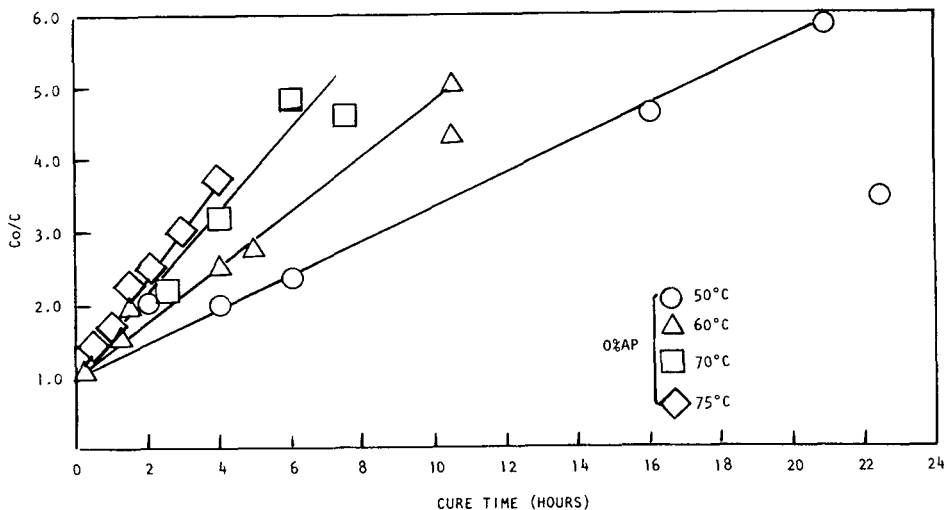

Fig. 2. Second-order isophorone diisocyanate reaction rate plots (gumstock): C_0 = initial concentration of IPDI; C = concentration of IPDI at time t.

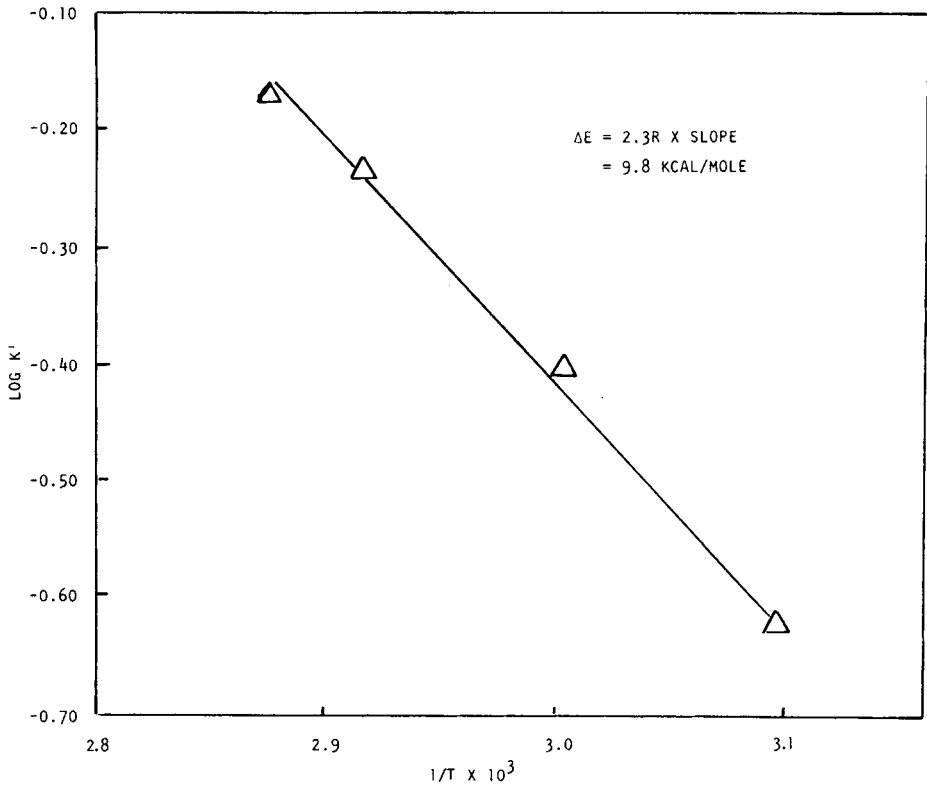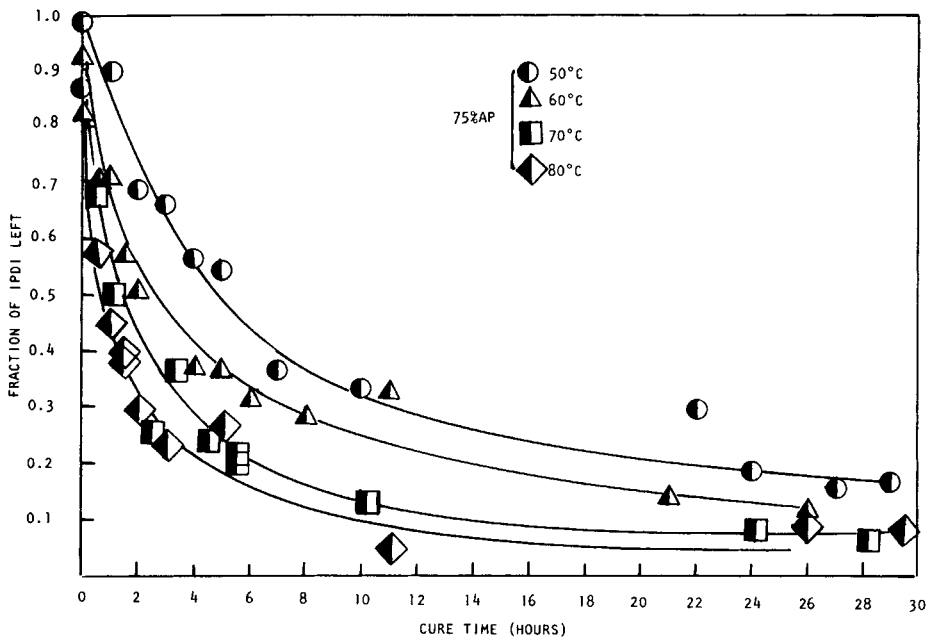$$\Delta E = 2.3R \times SLOPE$$
$$= 9.8 \ KCAL/MOLE$$

Fig. 3. Arrhenius plot of second-order rates ($k' = kc_0$).

Fig. 4. Rate of isophorone diisocyanate disappearance (75% AP).

TABLE II
Extent of Polymerization at Gelation

Temperature, °C	Gelation time, hr[a]	Extent of reaction, %
50	22.0	80
60	12.0	81
70	8.5	85
80	4.5	82

[a] Gelation times taken from ref. 2.

nate for the 75% AP sample are given in Figure 4. They are similar to the curves in Figure 1. The composites of all the rates measured for gumstock and different solid-loaded samples are shown in Figure 5. Aside from some scattered data (especially at 50°C), the rates of the solid-loaded samples superimpose on those of their corresponding gumstock samples. Therefore, it is concluded that, contrary to the widely held belief in the propellant industry, the AP has no significant effect on the polymerization rate of the binder with concentrations of AP as high as 75% by weight.

Since a 75% by weight solid loading did not produce any surface effect, a mix containing 90% AP was prepared and its polymerization rate studied. No significant effect was observed.

From the data presented in Figure 5, the extent of reaction at the gel points can be obtained. The gel points and extent of reactions for the four reaction temperatures are presented in Table II. The value of extent of reaction calculated from the functionality equation of Flory is 87%.[10] It is surprising that the agreement between the experimental values and the calculated
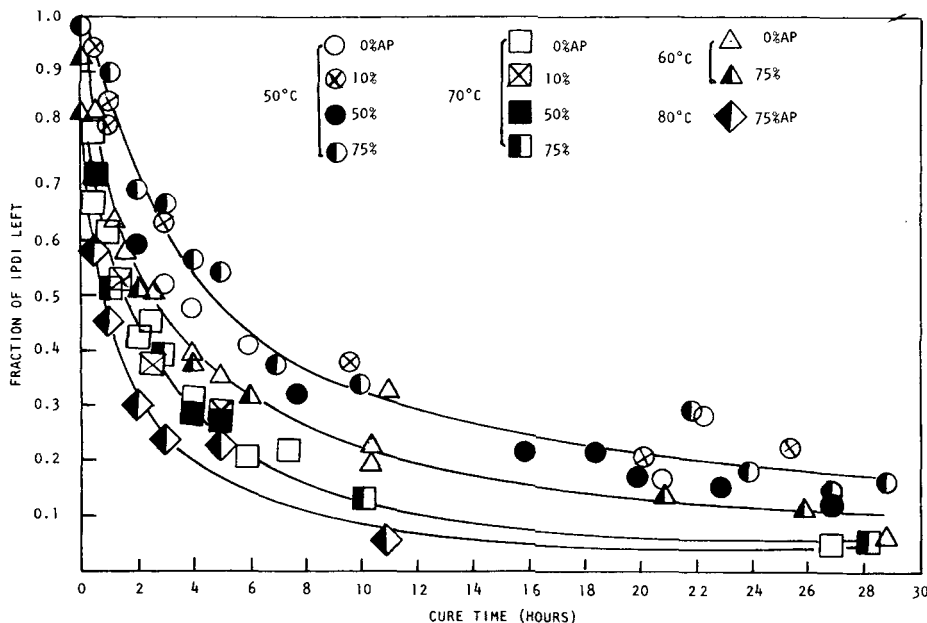

Fig. 5. Rates of isophorone diisocyanate disappearance.

values are in accord, especially in view of the large extent of reaction and the complexity of the system.

SUMMARY AND CONCLUSIONS

The copolymerization of the hydroxyl-terminated polybutadiene with isophorone diisocyanate in the propellant formulation studied follows an apparent second-order rate law with an activation energy of 9.8 kcal/mole. The presence of ammonium perchlorate (up to 90% by weight) neither catalyzes nor retards the rate of binder polymerization.

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