

Kinetic Study of the Reaction Between Hydroxyl-Terminated Polybutadiene and Isophorone Diisocyanate in Bulk by Quantitative FTIR Spectroscopy

DILEK KINCAL,¹ SAIM ÖZKAR²

¹ Defense Industries Research and Development Institute, TÜBITAK, P.K. 16 Mamak, 06261 Ankara, Turkey

² Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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ABSTRACT: A kinetic study of the reaction between a hydroxyl-terminated polybutadiene (HTPB) and isophorone diisocyanate (IPDI) was carried out in the bulk state by using quantitative Fourier transform infrared (FTIR) spectroscopy. The reaction is shown to obey a second-order rate law, being first order in both the HTPB and IPDI concentrations. The activation parameters obtained from the evaluation of kinetic data are $\Delta H^\ddagger = 41.1 \pm 0.4$ kJ mol⁻¹, $\Delta S^\ddagger = -198 \pm 2$ J K⁻¹ mol⁻¹ and $E_a = 43.8 \pm 0.4$ kJ mol⁻¹, which are quite different from the solution values. However, they are in agreement with the results obtained on propellants by torsional braid measurements. The large negative value of the activation entropy is indicative of an associative mechanism, which is in accord with the second-order rate law for the polyurethane formation.

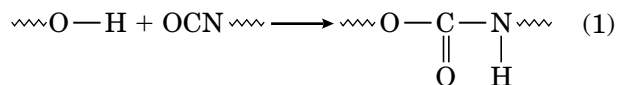
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Key words: HTPB; IPDI; diisocyanate; kinetics; polyurethane; FTIR spectroscopy

INTRODUCTION

Composite propellants based on hydroxyl-terminated polybutadiene (HTPB) have become the workhorse propellants in present day solid rocket motors. Crystalline ammonium perchlorate (AP) and fine aluminum powder are used as oxidizer and metallic fuel, respectively, in the HTPB-based composite rocket propellants. The solid loading, which contributes to the rheological properties and therefore affects the processability and mechanical properties of the propellants, is largely determined by the extent of polyurethane formation. In this respect, the binder used in the propellant plays an important role. The polybutadiene chain, in general, gives higher energy value and better mechanical properties compared to the

other binders, such as poly(vinyl chloride). Furthermore, the low viscosity of HTPB facilitates high solid loading in both fuel and oxidizer of the propellant. At the final stage of a composite propellant preparation, a curing agent, usually a diisocyanate, is added to the heterogeneous mixture containing the prepolymer, fuel, oxidizer, and other ingredients. The prepolymer and diisocyanate react with each other to form the polyurethane network [eq. (1)], which holds the fuel and oxidizer particulates in a composite matrix having mechanical and ballistic properties suitable for rocket applications.



The cure reaction of HTPB with diisocyanate has been found to follow the second-order rate law.¹ The rate and extent of polyurethane formation thoroughly affect the rheological and mechanical proper-

Correspondence to: S. Özkar.

ties of the propellant.² Therefore, knowledge of the kinetics of polyurethane formation is vital for the design and preparation of propellants possessing mechanical, dynamical, and ballistic properties suitable for specific purposes. However, there has been little study of the kinetics of this kind of polyurethane formation. Although most of the applications including the propellant preparation involve polyurethane formation between the HTPB and diisocyanate in bulk, almost all of the kinetic studies have been carried out in solutions.³⁻⁷ Kinetic studies on the reaction between relatively small diols and diisocyanates in various solvents have shown that the solvent has a significant effect on the rate of the polyurethane formation.⁸ The solution data would be pertinent to the processes in the bulk if the solvent used could create a medium similar to the bulk. In an early article, R. Y. Yee and A. Adicoff reported the polymerization kinetics of HTPB and isophorone diisocyanate (IPDI; 3isocyanatomethyl-3,5,5-trimethylcyclohexylisocyanate) in the propellants, followed by torsional braid measurements.⁹ Here, we report a kinetic study on the noncatalyzed polymerization between the HTPB and IPDI in the bulk by using quantitative Fourier transform infrared (FTIR) spectroscopy.

EXPERIMENTAL

Materials

Hydroxyl-terminated polybutadiene (HTPB; R45-M, Atlantic Richfield Chemical Corp., Philadelphia, PA), isophorone diisocyanate (IPDI, Fluka A.G., Leverkusen, Germany), and potassium bromide (Merck, Darmstadt, Germany) were used as obtained without further purification.

Kinetic Measurements

The polymerization reaction between HTPB and isophorone diisocyanate was followed by monitoring the changes in the infrared (IR) absorption band for the NCO stretching vibration. Although the two isocyanate groups in the isophorone diisocyanate are not equivalent in reactivity, our assay determines only the total amount of unreacted isocyanate, as the two isocyanate groups in the isophorone diisocyanate used give only one IR absorption band for the NCO stretching vibration and the peak position remains practically unaltered throughout the reaction. The IR spectra of the bulk samples were recorded on a Nicolet

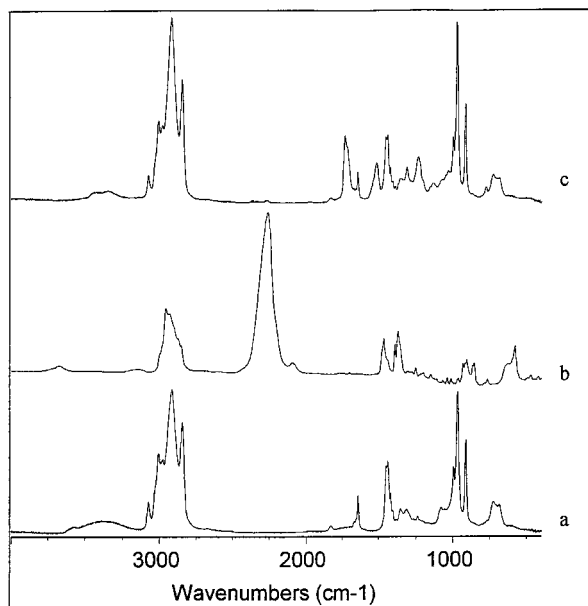


Figure 1 FTIR spectra of (a) HTPB, (b) IPDI, (c) an equimolar HTPB-IPDI mixture after completion of polyurethane formation, taken from the KBr pellet at 65°C.

20SXB FTIR spectrophotometer using the OMNIC program. Samples studied contain equimolar amounts of hydroxyl and isocyanate groups from the HTPB and IPDI, respectively. About 50 mg of anhydrous crystalline potassium bromide was pressed into a self-supporting wafer with a diameter of 13 mm by applying a pressure of 10 tons cm^2 for 60 s. HTPB and IPDI were mixed at room temperature, and a small amount of this mixture was placed between two KBr pellets, which were held together without applying any external force. This sample assembly was heated in a vacuum oven to a preset temperature in the range of 40–65°C for the curing reaction between HTPB and diisocyanate. The reaction was followed by taking the IR spectra of the sample wafer at a proper time interval, depending on the curing temperature. The change in the intensity of the absorption band for NCO stretching at 2255 cm^{-1} for IPDI was monitored and divided by the intensity of the absorption band at 1640 cm^{-1} for the C=C stretching in HTPB, which remains practically unaffected throughout the curing reaction, to ensure that the quantitative results are independent of the thickness of the sample film between two wafers. All the absorption values were then converted to concentrations of NCO by using a calibration curve prepared from the standard samples, which contain known amounts of isophorone diisocyanate in HTPB.

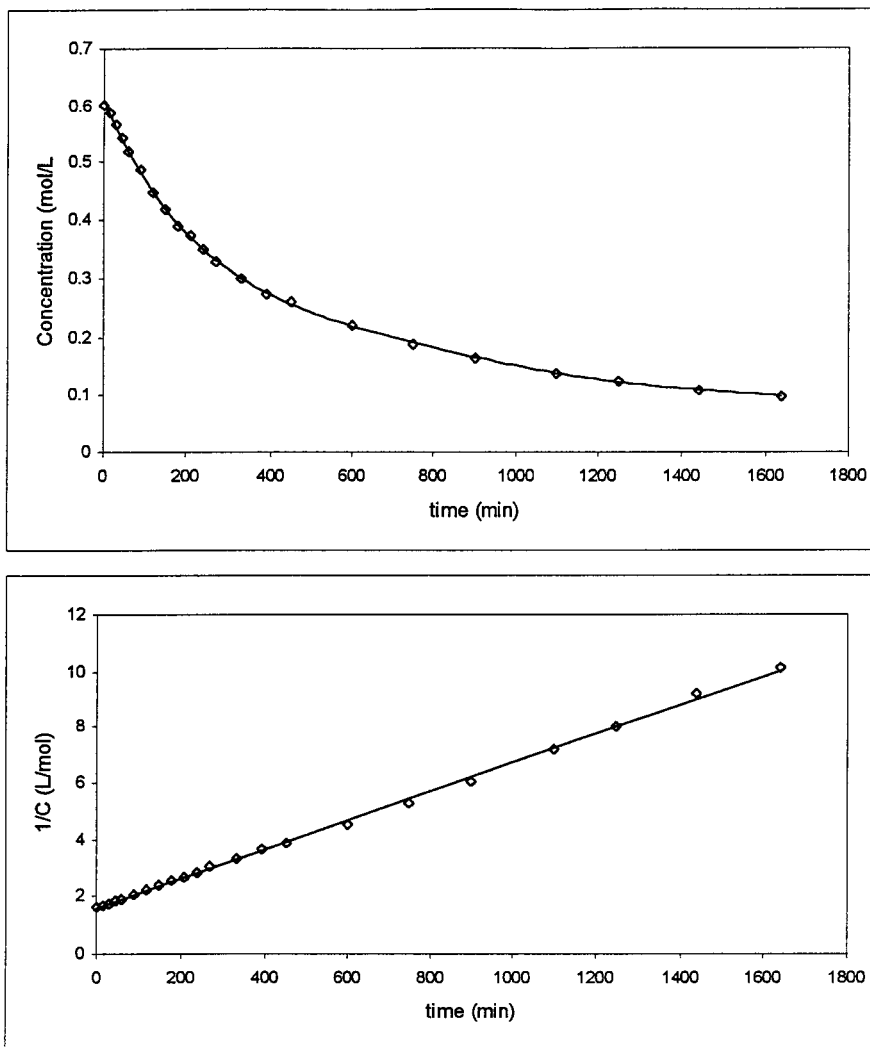


Figure 2 Variation in the concentration (top) and the reciprocal concentration (bottom) of NCO group in an equimolar IPDI-HTPB mixture at 55°C with time.

RESULTS AND DISCUSSION

The IR spectra of HTPB, IPDI, and a 1 : 1 mixture of HTPB and IPDI after completion of polyurethane formation at 65°C are given in Figure 1. A brief inspection of the spectra shows that the absorption band for the NCO stretching of IPDI at around 2255 cm^{-1} [Fig. 1(b)] doesn't interfere with any peak of HTPB; neither does the absorption band for C=C stretching of HTPB at 1640 cm^{-1} [Fig. 1(a)] with any peak of the diisocyanate. During the polyurethane formation between HTPB and IPDI, the NCO stretching band of diisocyanate decreases and ultimately disappears upon completion of the reaction, while the C=C stretching band of HTPB remains practically un-

altered throughout the reaction. A new absorption feature appears at 1725 cm^{-1} upon polyurethane formation [Fig. 1(c)], which is readily assigned to the CO stretching of the polyurethane units (eq. 1). Therefore, the change in the intensity of the NCO stretching band relative to that of the C=C stretching band is used to follow the reaction between HTPB and IPDI. Figure 2(a) demonstrates the time-dependent behavior of concentrations of the two reactants in the course of the thermal polyurethane formation reaction of HTPB and IPDI in bulk at 55°C. This graph exhibits an exponential decay for the starting substances HTPB and IPDI. The reciprocal concentration versus time plot shows a straight line for the polyurethane formation between HTPB and IPDI with equal initial concentrations [Fig. 2(b)].

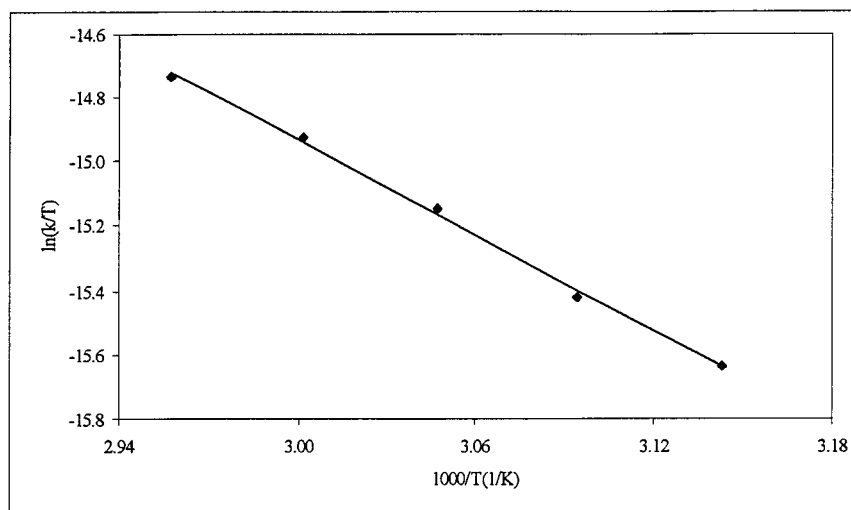


Figure 3 Eyring-Plot of the second order rate constant for the polyurethane formation between HTPB and IPDI in an equimolar mixture.

This indicates that the polyurethane formation between HTPB and IPDI obeys second-order kinetics with a correlation constant greater than 0.99. The rate law for this second order reaction is given in eq. (2); as follows:

$$\text{rate} = k[\text{OH}][\text{NCO}] \quad (2)$$

where [OH] and [NCO] stand for the concentrations of the hydroxyl groups in HTPB and isocyanate groups in IPDI, respectively, and k is the rate constant. Since the initial concentrations of hydroxyl and isocyanate groups are taken to be equal in this study ($[\text{OH}]_0 = [\text{NCO}]_0 = C_0$), the rate equation can be integrated to retrieve the concentration–time relationship.

$$\frac{1}{C} = kt + \frac{1}{C_0} \quad (3)$$

The slope of the straight line obtained by plotting the reciprocal concentration versus time gives the rate constant for the second-order reaction. The polyurethane formation between HTPB and IPDI was conducted at five different temperatures to determine the activation parameters of the reaction. The Eyring plot for the thermal curing reaction between HTPB and IPDI are illustrated in Figure 3, which gives a straight line. The activation enthalpy and entropies can be obtained from the evaluation of the Eyring plot in Figure 3. The activation enthalpy is found to be $\Delta H^\ddagger = 41.1 \pm 0.4 \text{ kJ mol}^{-1}$. This is comparable to the

values given in the literature for the polyurethane formation between alcohols and isocyanates.¹⁰ However, since the activation energy is given in the literature for the polyurethane formation between HTPB and IPDI, a similar evaluation of the kinetic data in an Arrhenius plot was carried out to obtain the value of activation energy, $E_a = 43.8 \pm 0.4 \text{ kJ mol}^{-1}$, for a better comparison. This result is close to the value of 43.9 kJ mol^{-1} obtained for the same system by torsional braid measurements,¹¹ but slightly different from the value of 40.8 kJ mol^{-1} reported by Yee and Adicoff.⁵ However, this result is, not unexpectedly, quite different from the activation energy obtained for the similar systems in solution; for example, $E_a = 49 \text{ kJ mol}^{-1}$ in toluene.³ This observation indicates that one has to be cautious in adopting solution values for the reaction kinetics in the bulk.

From the evaluation of the kinetic data in an Eyring plot (Fig. 3), the activation entropy can be found to be $\Delta S^\ddagger = -198 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$. The activation enthalpy and entropy values can be used to understand the mechanism.¹² The large negative value obtained for the activation entropy is indicative of an associative mechanism in the transition states.¹³ This is in agreement with the second-order rate law obtained for the polyurethane formation between HTPB and IPDI. Support for this assignment of an associated mechanism in the transition states for the polyurethane formation between HTPB and IPDI comes from comparison of the activation enthalpies with the bond energies of the O—H and C=N bonds,

which are broken in the reaction. The activation enthalpy is much smaller than the bond energy.¹⁴

CONCLUSIONS

The kinetics of the polymerisation reaction between HTPB and a diisocyanate in the bulk state was readily followed by using quantitative FTIR spectroscopy. The activation parameters obtained from the bulk state kinetic data are quite different from the solution values. However, they are in agreement with the results obtained in propellants by torsional braid measurements. Thus, the use of quantitative FTIR spectroscopy provides a simple and fast tool for the collection of reliable kinetic data for the polyurethane formation in the bulk state, which can be used in manufacturing the composite rocket propellants. Our investigation on the kinetics of the polyurethane formation between the HTPB and diisocyanate of various types is continuing. Special emphasis will be given on the effect of NCO to OH and triol to diol ratios on the kinetics of polyurethane formation.

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