

# Room-Temperature Kinetics of Castor-Oil-Based Polyurethane/Poly(2-hydroxyethyl methacrylate) Interpenetrating Polymer Networks

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## SYNOPSIS

The kinetics aspects of the formation of castor-oil-based polyurethane/poly(2-hydroxyethyl methacrylate) interpenetrating polymer networks (IPNs) were studied. The effect of parameters such as the polyurethane content, the activator, and acrylic cross-linker on the kinetics of formation of IPN networks was examined at room temperature. The formation of the individual networks, polyurethane, poly(2-hydroxyethyl methacrylate), and their IPNs, was studied by measuring the decrease of absorbance of characteristic absorption peak of each system using IR spectroscopy. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Interpenetrating polymer networks (IPNs) are unique alloys of cross-linked polymers.<sup>1</sup> IPNs synthesized, to date, exhibit varying degrees of phase separation depending principally on the miscibility of the polymers.<sup>2</sup> Several investigators have studied the effect of kinetics of curing reactions on the morphology and properties of IPNs.<sup>3-6</sup> It was found, in general, that the faster the rates of the respective chain extension and cross-linking reactions and the closer they are to simultaneity the more homogeneous are the IPNs.<sup>7</sup> Other investigations revealed that the individual component networks polymerize more rapidly in the IPN than alone, presumably due to a "solvent effect" or "the Trommsdorff effect." The effect of changing reaction variables, such as the NCO/OH ratio, composition, activators, and temperature, was used to study reaction kinetics as well as the phase morphology by different techniques.<sup>8-13</sup> We studied the formation kinetics of the IPNs formed from castor-oil-based polyurethane and poly(2-hydroxyethyl methacrylate) and the individual homopolymers at room temperature.

## EXPERIMENTAL

### Materials

The materials used in the present study were of analytical-grade purity. Benzoyl peroxide was recrystallized from chloroform. 2-Hydroxyethyl methacrylate and ethylene glycol dimethacrylate were freed from the stabilizer prior to use. Toluene-2,4-diisocyanate and dibutyl tin dilaurate from M. Schuchardt, Munich, were used as received. Castor oil from the local market was found to contain a hydroxyl value of 165.3, corresponding to 2.75—OH groups per mol of castor oil according to the literature method.<sup>14</sup>

### Synthesis of IPNs

A standard synthesis of IPNs as reported in the literature<sup>15</sup> proceeds as follows: A known amount of castor oil was mixed with excess toluene-2,4-diisocyanate (TDI) (NCO/OH = 1.6) at room temperature to produce an isocyanate-terminated polyurethane (PU). The PU was mixed with a 2-hydroxyethyl methacrylate (HEMA) monomer. The mixture was stirred vigorously and dibutyl tin dilaurate, benzoyl peroxide, and the cross-linker ethylene glycol dimethacrylate (EGDM) were added. It was stirred for another 10 min. The mixture was then

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poured into a glass mold and cured for 36 h at room temperature. The cross-linking agent for HEMA was EGDM. The molar concentrations of the cross-linking agent were 0.0541 and 0.1082 mol L<sup>-1</sup>. The initiator benzoyl peroxide was selected and the molar initiator concentration was 4.49 × 10<sup>-2</sup> mol L<sup>-1</sup>. As the catalyst for PU formation, dibutyl tin dilaurate was used at concentrations of 2.71 × 10<sup>-3</sup>, 3.62 × 10<sup>-3</sup>, and 4.53 × 10<sup>-3</sup> mol L<sup>-1</sup>.

In the kinetic experiments, the above mixture was placed between two KBr discs and squeezed to form a uniform film. The discs were placed in the chamber of the spectrophotometer.

### The Infrared Spectroscopy

The kinetics study was performed at room temperature using a Perkin-Elmer 983 IR spectrophotometer. Kinetic curves for individual formation of homopolymers and IPN formation were obtained from an individual IR spectrum at regular intervals during the formation of the networks.

## RESULTS

The use of the Beer-Lambert law allows the determination of the concentration of an absorbing spe-

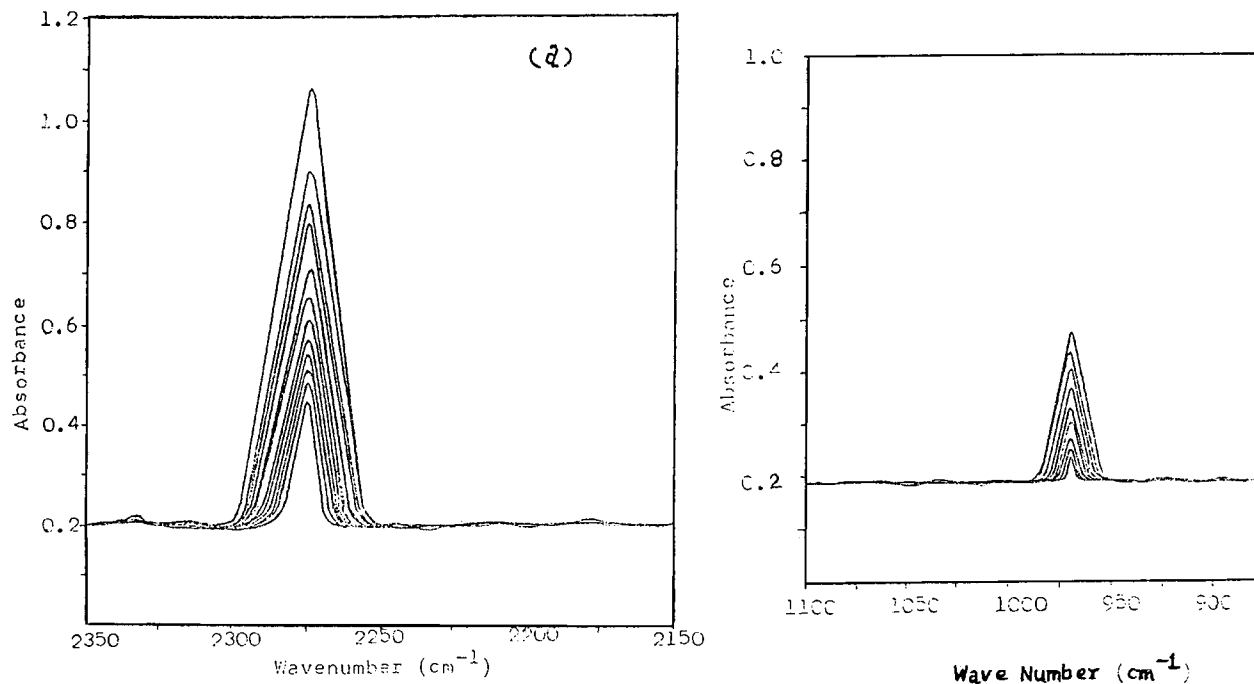
cies through absorbance measurements. It can be expressed as

$$A = \log \frac{I_0}{I} = Ecb$$

where  $A$  is the absorbance;  $E$ , the molar absorptivity compound;  $c$ , the concentration of the absorbing medium; and  $b$ , the thickness of the test sample. The conversion of a monomer to its polymer may be followed by the absorbance measurements if the process involves the variation of a characteristic absorption peak. The applicability of the Beer-Lambert law to the present system is examined hereafter.

### Molar Extinction Coefficients for PU and PHEMA Networks

The isocyanate NCO absorption band at 2275 cm<sup>-1</sup> was chosen for monitoring the reaction between castor oil and TDI for the polyurethane formation and the C=C peak at 970 cm<sup>-1</sup> for the poly(HEMA) (PHEMA) network formation. Neither band is overlapping with its neighbor and both show a gradual decrease as the respective polymerizations proceed (Fig. 1). The Beer-Lambert law is followed up to the concentration of reagents indicated earlier. The variation in the molar extinction coefficients with temperature during the formation



**Figure 1** Decrease of characteristic peak absorbance for (a) the PU system (NCO) and (b) the PHEMA system (C=C) during network formation.

of networks is around  $0.003 \epsilon_0/\text{degree}$  according to the literature.<sup>16</sup>

### Determination of the Degree of Monomer Conversion

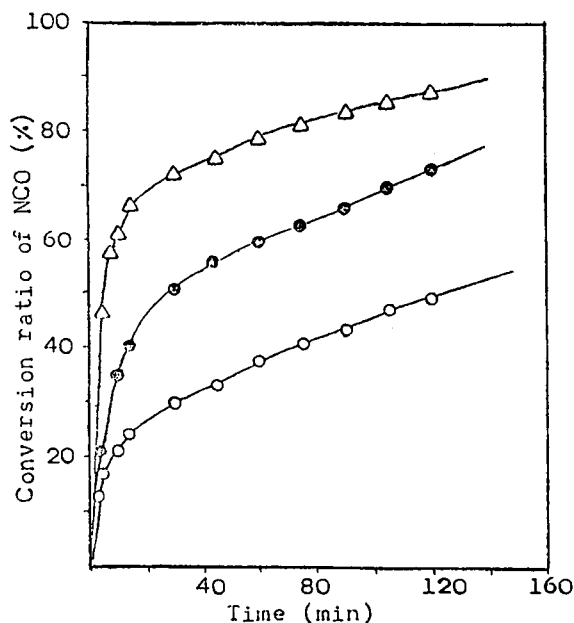
The measure of  $C$ , the concentration of the absorbing species, through the Beer-Lambert law allows the determination of the degree of conversion,  $DC$ :

$$DC = \frac{C_0 - C}{C_0}$$

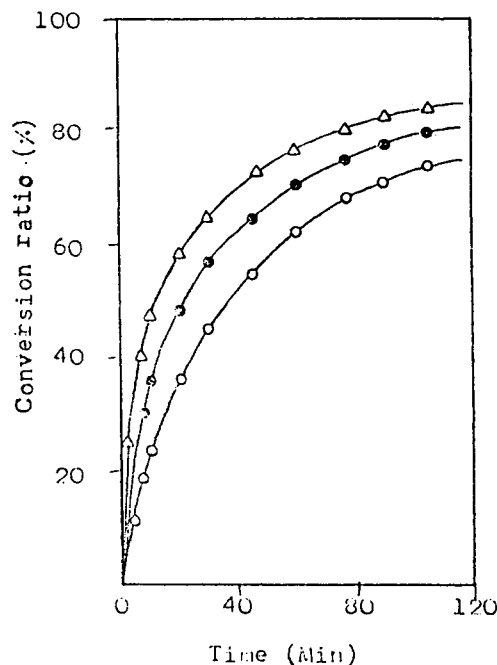
where  $C_0$  is the initial molar concentration, and  $C$ , the molar concentration at time  $t$  for the absorbing species. Figure 2 shows the degree of conversion of the absorbing species, i.e., the disappearance of the isocyanate group, as the function of time  $t$ . The reaction may be followed until complete conversion to PU. Figure 3 shows the degree of conversion vs. time,  $t$ , for the PHEMA network formation.

## DISCUSSION

The validity and the limits of the determination of conversion ratios by absorbance measurements using an IR spectrophotometer has already been established in the literature.<sup>17-21</sup> We applied this method to the individual castor-oil-based PU and PHEMA networks as well as to 60/40 and 40/60 PU/PHEMA IPNs.



**Figure 2** Conversion ratio of NCO as a function of time by IR in ethyl acetate using dibutyl tin dilaurate concentrations: (O)  $2.71 \times 10^{-3} \text{ mol L}^{-1}$ ; (●)  $3.62 \times 10^{-3} \text{ mol L}^{-1}$ ; (Δ)  $4.53 \times 10^{-3} \text{ mol L}^{-1}$ .



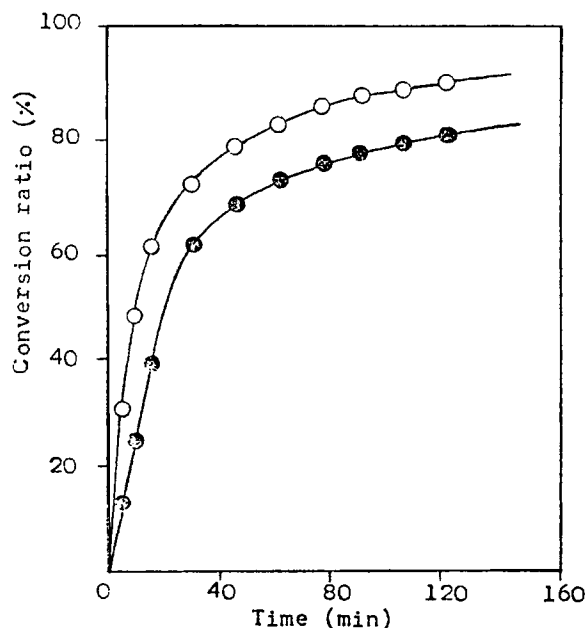
**Figure 3** Conversion ratio of  $C=C$  for molar initiator concentration  $4.49 \times 10^{-2} \text{ mol L}^{-1}$  as a function of time by IR with EDDM cross-linker concentrations: (O) without EGDm; (●) EGDm  $0.0541 \text{ mol L}^{-1}$ ; (Δ) EGDm  $0.01082 \text{ mol L}^{-1}$ .

### Castor-oil-based Polyurethane Network

The HEMA monomer was replaced by the solvent ethyl acetate in order to avoid any accidental polymerization. The parameters affecting the kinetics of the PU network formation from castor oil are the catalyst (dibutyl tin dilaurate), concentration, the concentration of isocyanate in ethyl acetate, and the temperature, although the temperature was kept constant, i.e., at room temperature ( $30^\circ\text{C}$ ). The NCO/OH ratio was fixed to 1.6. Figure 4 shows the influence of the parameters indicated in the individual PU and PHEMA as well as in the 60/40 and 40/60 PU/PHEMA IPN formations.

### PHEMA Networks

Some results of the radical polymerization of acrylic system (HEMA + EDGM) appear in Figure 3. The effect of the cross-linker, EGDm, is to accelerate the reaction; the acceleration is very important in the entanglements as compared to the formation of the linear PHEMA. The presence of dibutyl tin dilaurate has an accelerating effect on the copolymerization of acrylic system in the IPN formation. Similar observations have been reported in the literature.<sup>22</sup>



**Figure 4** Conversion ratio for the PU/PHEMA IPN formation vs. time: (○) 60/40 PU/PHEMA composition; (●) 40/60 PU/PHEMA composition.

#### PU/PHEMA IPNs

The two IPNs containing 60 and 40% PU were prepared and their syntheses were followed up by IR (Fig. 4). Similarly, when benzoyl peroxide is added, castor oil not only reacts with TDI in the formation of the PU network, but also takes part in the free-radical polymerization in the presence of the inherent heat of exothermy of the reaction. These two reactions, polycondensation and radical polymerization, occur simultaneously. The rates increase with the cross-linking during the propagation reaction. An immediate observation is that both curves are identical to those obtained separately for individual PU and PHEMA networks (Figs. 2 and 3).<sup>7</sup> The results and observations of the kinetic studies of PU and PHEMA networks during PU/PHEMA IPN formations indicated that the elastomeric PU acts as a diluent. It allows complete conversion of the acrylic monomer system into PHEMA network and, thereby, interpenetration causes a high mutual dispersion of the phases. As a result, all the domains are small enough to allow monomer diffusion toward a radical, until complete consumption. This may be the Trommsdorff effect that allows complete monomer-to-polymer conversion preventing phase separation, if any.

#### CONCLUSION

The validity of IR spectroscopy for the study of the IPN formations has been established. The results

obtained on the early stages of the reactions of the individual network formation of PU and PHEMA as well as the network formation of PU/PHEMA IPN suggests that the rate of formation of the IPN networks is faster than are the rates of the individual network formations.

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