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# STUDIES ON CURING KINETICS OF MULTIFUNCTIONAL ACRYLATES BY INFRA-RED SPECTROSCOPY

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## ABSTRACT

The kinetics of the free radical bulk polymerization of diethyleneglycol diacrylate was studied by infra red (IR) spectroscopy. 4,4'-azobis(4-cyanovaleric acid) was used as a free radical initiator. Measurements were carried out under both isothermal and nonisothermal conditions. Disappearance of C=C peak at 1667-1525 $cm^{-1}$ was monitored and percentage conversion was calculated by various techniques. Structural changes and mechanistic aspects of the pertaining reactions have been elucidated.

## INTRODUCTION

Various conventional methods are currently available to study the kinetics and mechanism of crosslinking. However in case of bulk polymerization complexity occurs either due to the autoacceleration causing the onset of the Trommsdroff's effect at an early stage of polymerization. In fact, the polymerization of acrylates is extremely difficult to analyze by conventional techniques since gelation sets in near zero conversion, probably due to branching and crosslinking caused by chain transfer to polymer[1-4]. Differential scanning calorimetry (DSC) is by far the most widely used experimental technique for measuring the reaction kinetics of thermoset polymers[5-8]. It has the advantages of simplicity and capacity to yield simultaneous information regarding kinetics, energetics and thermal properties. However DSC only measures the overall heat release during the reaction and can not differentiate the changes in chemical reaction during the reaction. Recently IR spectroscopy has been successfully employed to study the kinetics of polymerization[9]. This method is well suited to study the rate of polymerization, reactivity of the monomer and the residual unsaturation, but unlike differential scanning calorimetry, it does not give the heat of reaction during the polymerization. This technique is gaining wide recognition as a new field of intensive research and investigation[10,11]. In course of this study pertaining to the synthesis of the telechelic reactive acrylate oligomers, we had used several methods to study the kinetics and mechanism of the reaction[12]. The present work deals with some preliminary studies on isothermal and nonisothermal bulk polymerization of diethyleneglycol diacrylate (DEGDA) in presence of 4,4'-azobis(4-cyanovaleric acid) (ABCVA) as a free radical initiator.

## MATERIALS AND METHODS

DEGDA was obtained from Polysciences Inc. U.S.A. It was washed with 5.0% solution of sodium carbonate followed by distilled water, and dried over anhydrous magnesium sulfate. ABCVA was recrystallized from absolute ethanol and stored in dark at 4°C. Isothermal and nonisothermal free radical bulk polymerization was investigated by Shimadzu I.R.-470 spectrophotometer. 1.0 % (w/W) of ABCVA was used as an initiator. Special type of heating cell was used to take the IR spectra at different temperatures. This heating cell was placed in IR spectrophotometer and wavenumber was being fixed at 1667-1525 $cm^{-1}$, where the acrylic bond exhibits a sharp and distinct absorption. the detection of IR signal was made by operating the spectrophotometer in the absorbance mode. IR spectrum were recorded after different time periods and at different temperatures.

## RESULTS AND DISCUSSION

Infra-red analysis is based on the fact the each chemical group in a sample absorbs the infra-red radiation of some characteristic frequencies. During the reaction period, peaks of functional groups or characteristic linkages in the specimen will change, which provides a means to measure the reaction kinetics. Peak area was used to calculate the absorbance. Reaction conversion was determined from the change of normalized absorbance[13,14].

$$\alpha = 1 - \frac{A_t}{A_o} \times 100$$

Where $\alpha$ is percent conversion, $A_o$ and $A_t$ are the maximum absorbance and the absorbance after time t.

IR spectra of dietyleneglycol diacrylate is given in Figure 1. Disappearance of the reactive double bonds after heating at 90°C for 30 minutes is also shown in the Figure 1. IR spectra at 1667-1525 $cm^{-1}$ which is a characteristic of c=c stretching vibration peak was monitored at 65°C after different time periods and shown in Figure 2, and at different temperatures in Figure 3.

Conversion versus time and temperature plot as give in Figure 4&5 clearly show that as polymerization proceeds, the viscosity of the reaction medium increases to yield ultimately a solid, highly cross-linked polymer in which the segmental mobility is severely restricted. the encounter probability of the polymer radicals

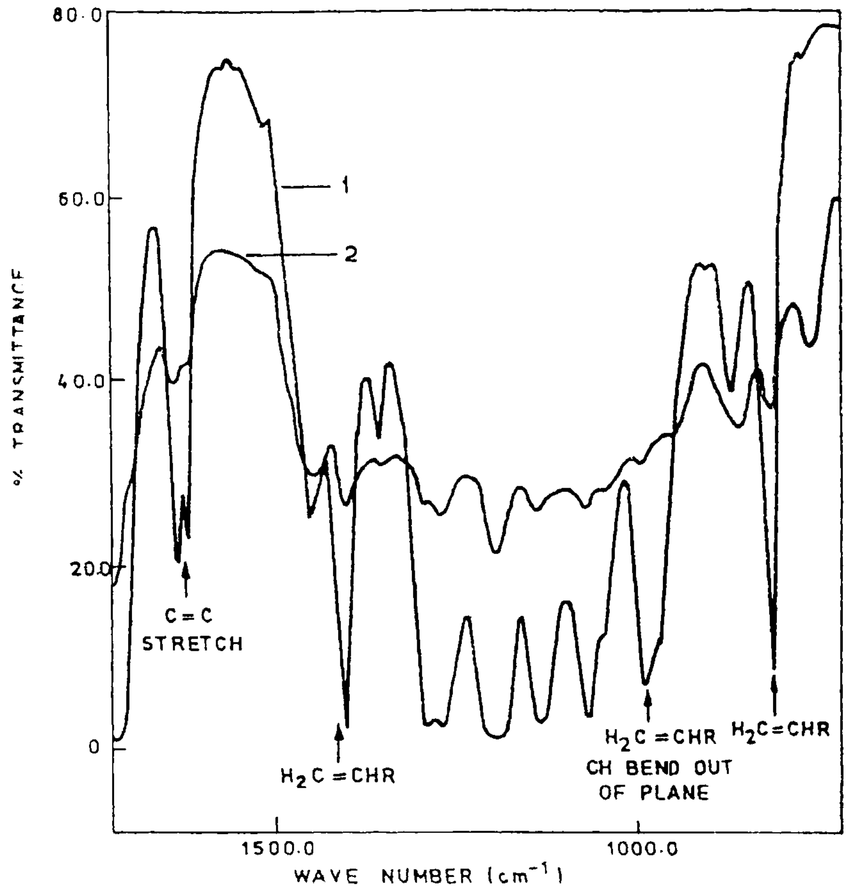

**Figure 1. IR SPECTRA OF DEGDA :1. MONOMER, 2. POLYMER.**

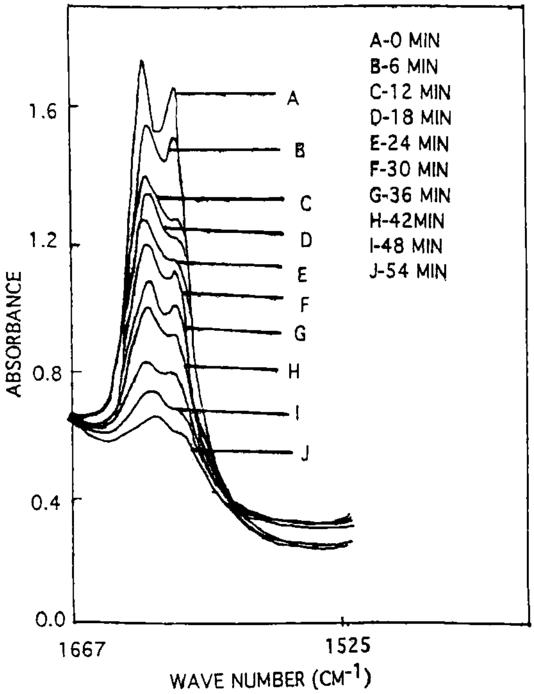

**Figure 2. IR SPECTRA OF DEGDA AT 65°C AFTER DIFFERENT TIME PERIODS. DISAPPEARANCE OF C=C PEAK BETWEEN 1667-1525 CM$^{-1}$.**

with the unreacted double bonds is then sharply reduced, which accounts the rate slowdown observed in the later stages of the experiments. From the slope of the IR kinetic curves it is easy to evaluate the rate of polymerization at any moment of the reaction.

Kinetics of the polymerization of diethyleneglycol diacrylate was also monitored at various temperatures. It appeared that as the polymerization of these multifunctional acrylates proceeds, a tight network is formed which sharply

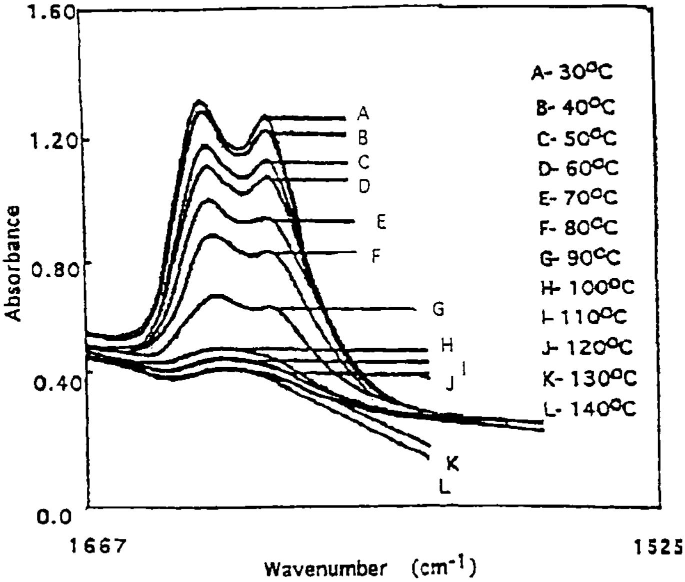

Figure 3. IR SPECTRA OF DEGDA AT DIFFERENT TEMPERATURES. DISAPPEARANCE OF C=C PEAK BETWEEN 1666-1525 CM-1.

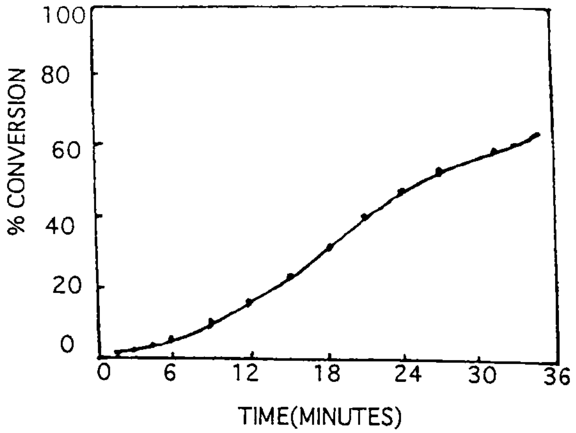

Figure 4. PERCENTAGE CONVERSION VERSUS TIME CURVE AT 65°C FOR C=C PEAK BETWEEN 1667-1525CM$^{-1}$.

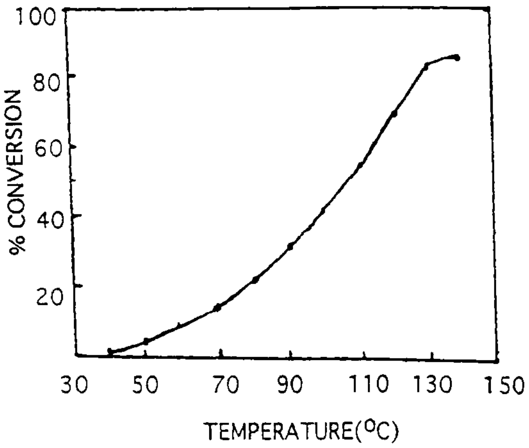

**Figure 5. PERCENTAGE CONVERSION VERSUS TEMPERATURE CURVE FOR C=C PEAK BETWEEN 1667-1525CM$^{-1}$.**

decreases the chain mobility, so that the polymer radicals will finally stop growing and remain trapped in the matrix.

One of unique advantages of the IR techniques is to permit at any given instant, precise evaluation of the amount of unreacted double bonds which remain in the polymer network. It's value is highly dependent on the monomer functionality. The residual unsaturation contents were measured, at 65°C, to be about 15.23% between 1667-1525 cm$^{-1}$ after heating for an extensive period of 2.0 hours and 5.20% between the same wavenumber after heating at high temperature around 140°C.

## CONCLUSION

Infra-red spectroscopy is a versatile technique for quantitative analysis of a continuous polymerization process. It has been applied to investigate the curing kinetics of highly reactive multifunctional acrylates. Percentage conversion versus time and temperature curve and IR spectra allow us to determine the rate of polymerization, nature of the chemical reaction and the amount of residual unsaturation. However, this technique has also some limitations. One of the limitations is, we can not calculate the heat of reaction. One more disadvantage is, in IR characterization, the optical contact between the sample and the cell surface tends to change during the polymerization. Shrinkage resulting from the polymerization further reduces the intensity of IR beam and makes the calculation more difficult specially at high conversion.

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