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A Kinetic Study of Crosslinking Vinyl Polymerization by Laser Raman Spectroscopy

Free Radical Polymerization of Diethylene Glycol Bis(allyl carbonate)

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SUMMARY

Kinetic studies of crosslinking vinyl polymerizations are usually only applicable to the initial stages of the reaction, prior to the gel point, due to the subsequent insolubility of the polymer and the great increase in viscosity. We have demonstrated the suitability of laser Raman spectroscopy for quantitative analysis over the entire conversion range in an investigation of the polymerization of diethylene glycol bis (allyl carbonate) in bulk, with benzoyl peroxide initiation, between 70 and 85°C. The rate of consumption of vinyl bonds could be approximated by first-order kinetics up to *ca.* 80% depletion. Lower rates were observed at higher conversions.

INTRODUCTION

The experimental difficulty of following the chemical kinetics of crosslinking vinyl polymerizations beyond the gel point has largely precluded quantitative investigations in this area. For divinyl homopolymerization the gel point occurs at low C=C consumption, but the great increase in viscosity and the insolubility of the polymer effectively prevent most investigations proceeding to higher conversions.

Diethylene glycol bis(allyl carbonate), or 4,6,9,12,14-pentaoxa-1,16-heptadecadiene-5,13-dione, I, is a divinyl monomer widely used to manufacture optical lenses. It is well known in its monomeric or polymeric form as CR-39 resin.

$$CH_2{=}CH{-}CH_2{-}O{-}CO{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CO{-}O{-}CH_2{-}CH{=}CH_2$$

I

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Density (DIAL *et al.* 1955) and refractive index (STARKWEATHER and EIRICH 1955) may be correlated with conversion, but an absolute calibration is necessary. Partly polymerized samples have been hydrolysed and their residual unsaturation determined by iodometric titration (DIAL *et al.* 1955). However, at high degrees of crosslinking, the extent of C=C consumption may be overestimated (STARKWEATHER and EIRICH 1955).

Infrared spectroscopy is unsuitable for high conversion kinetic studies, because C=C bond stretching involves a small change in polarity, and is, therefore, infrared weak. However, the ν(C=C) vibration does involve a large change in polarizability, making it Raman intense.

EXPERIMENTAL

The liquid resin, diethylene glycol bis(allyl carbonate), was supplied by Sola International. ^{13}C NMR spectroscopy indicated high purity, but a subsidiary peak in the carbonyl region suggested small amounts of oligomeric material. This was confirmed by gel permeation chromatography using microstyragel columns. HPLC indicated small amounts of lower molecular weight impurities which may include diethylene glycol, triethylene glycol, tetraethylene glycol, allyl carbonate and diethylene glycol bis(chloroformate) (SOTHMAN 1980). Benzoyl peroxide was purified by recrystallization. Pyrex glass ampoules (5 mm ext. diam.) containing approximately 0.2 ml of reaction mixture were freeze-thaw degassed or flushed with nitrogen and sealed. The ampoules had flat bottoms with curved edges to minimise "cracking" of the system above the gel point.

The polymerization ampoule was mounted in a cylindrical aluminium block containing a cartridge heater and a thermocouple which maintained the temperature within ±1°C via a Eurotherm thermostat. This heated block was mounted in the cell compartment of a Cary 82 Raman spectrometer utilizing a stand which permitted three-dimensional micrometer adjustment of the sample position. The block contained a vertical cylindrical hole for inlet and outlet of the laser beam and a horizontal funnel-shaped hole for outlet of the Raman scattered light. The apparatus is shown in Fig.1. Exciting radiation (514.5 nm) was produced by a Coherent Radiation Model CR-4 argon ion laser with power of 75 mW at the sample.

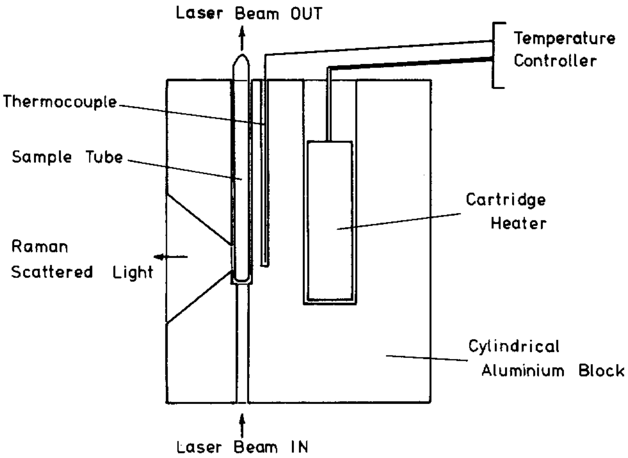

FIGURE 1: Aluminium furnace and polymerization ampoule for studying polymerization kinetics by laser Raman spectroscopy.

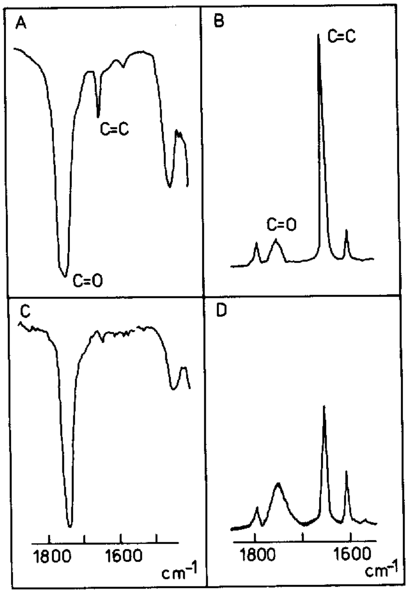

FIGURE 2:

Spectra of CR-39 monomer: A - infrared and B - Raman, and of partly polymerized monomer (*ca.* 80% consumption of C=C bonds): C - infrared and D - Raman.

RESULTS AND DISCUSSION

The infrared and Raman spectra of CR-39 are shown in Fig.2. The unsuitability of the ν(C=C) absorption band in the infrared spectrum for following the polymerization to high conversion is apparent, in contrast to the enhanced ν(C=C) signal observed in the Raman spectrum. The Raman spectra of monomeric and polymeric CR-39 have been reported by JEPPESEN (1956) although with reduced intensity and resolution for the polymer.

Cracking of the polymer gel during polymerization presented a major difficulty since it resulted in considerable scattering of the laser beam and loss of Raman signal intensity. This was minimized by suitable design of the shape and dimensions of the polymerization ampoule. The laser was also operated at low power and the sample moved periodically. This was necessary to minimize micro-void formation in the track of the laser, which was apparently due to enhanced local polymerization.

The strong band at 1643 cm^{-1} in the monomer due to the C=C bond stretching mode and the subsidiary peak at 3017 cm^{-1}, attributed to the stretching vibrations of hydrogen atoms attached to double-bonded carbon atoms decreased in intensity during the polymerization. It was found convenient to use the carbonyl peak at $\approx$1750 cm^{-1} as an internal reference, although it was necessary to correct the area for a subsidiary peak resulting from a fragment of the initiator. This procedure was shown to be satisfactory by using cyclohexane as an external standard. The aluminium block was rotated between the sample and reference positions in these experiments.

The ν(C=C), ν(C=O) and ν(C-H) bands were scanned as frequently as every 30 minutes during isothermal polymerization runs over a time period of about 24 hours. Some broadening of the peaks was observed and therefore peak heights were inappropriate for quantitative measurement. Peak areas were measured by computer integration and manual estimation.

KINETICS

Results for the decrease of the C=C concentration with time during the isothermal polymerization between 70 and 85°C are shown in Fig.3, for an initial benzoyl peroxide concentration of 3 wt%. Good reproducibility was observed up to 95% consumption of C=C; beyond this conversion the inherent sensitivity and the stability of the spectrometer were unsatisfactory.

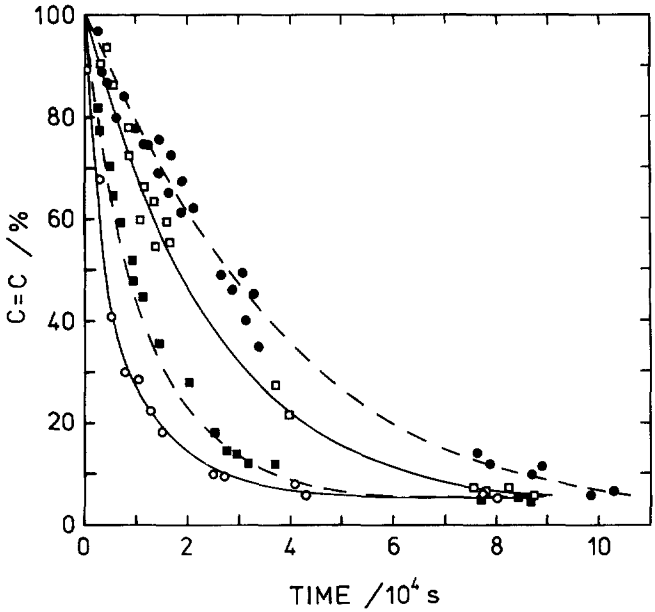

FIGURE 3: Experimental results for consumption of C=C bonds during isothermal polymerization. (●) 70°C, (□) 75°C, (■) 80°C, (○) 85°C.

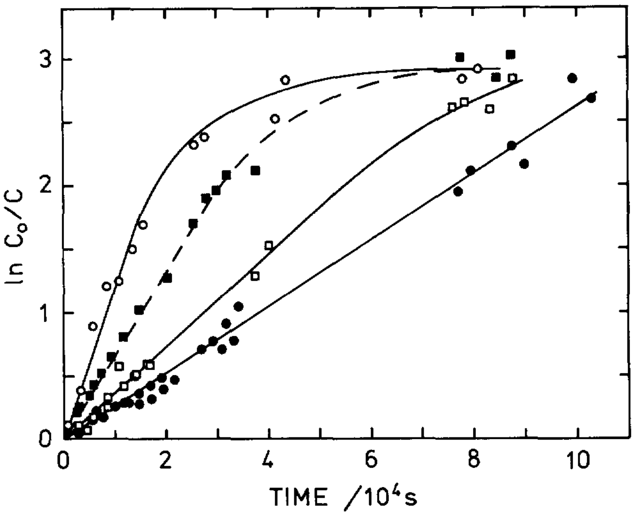

FIGURE 4: First-order kinetic plots for isothermal polymerization. Symbols as in Fig.3.

The possibility of increased temperatures in the polymerization ampoule relative to the temperature-controlled aluminium block, due to the exothermicity of the reaction, was tested by performing the polymerization with a fine thermocouple wire inserted into the CR-39 resin in the ampoule. For the polymerization conditions shown in Fig.3 for 80°C the temperature differential was less than 1°. The small sample volume (0.2 ml) minimized this problem.

The kinetic behaviour of the crosslinking homopolymerization of a divinyl monomer in bulk may be expected to be complicated by the dependence of termination and, later, propagation and transfer, reaction rates on the viscosity of the medium. However, as a first approximation, the first-order plots in Fig.4 for the results of Fig.3 show adequate linear agreement with theory up to about 80% consumption of C=C bonds. Beyond this conversion the rate diminishes.

The first-order rate constants determined from the linear regions of the plots in Fig.4 have been utilized in an Arrhenius plot. A good linear relationship is obtained, giving an activation energy of 104 kJ mol^{-1}. This is in accord with expectations for a vinyl polymerization of a flexible monomer. Similar values have been reported by DIAL *et al.* (1955) and SCHNARR and RUSSELL (1980).

The utilization of CR-39 as an industrial monomer requires very high conversion in the polymerization in order to obtain satisfactory mechanical properties and to stabilize the product. The polymerization cannot be carried out isothermally as this would necessitate high temperatures throughout the reaction which would lead to temperature exotherms, void formation, cracking and discolouration. For these reasons a suitable profile of temperature changes is used. Therefore, in order to make use of our isothermal data for industrial polymerization, it is necessary to investigate whether segments of the isothermal kinetics can be taken sequentially. Fig.5 shows the results of such an experiment: polymerization was performed to approximately 40% C=C consumption at 75°C and then the temperature increased to 85°C and the polymerization continued to 90% conversion. The experimental behaviour in the second phase of the polymerization shows excellent agreement with the prediction from isothermal polymerization from zero conversion at 85°C.

It is an important question whether there is a significant proportion of unreacted C=C bonds after long polymerization times. Our results support those of JEPPESEN (1956) (also using Raman spectroscopy)

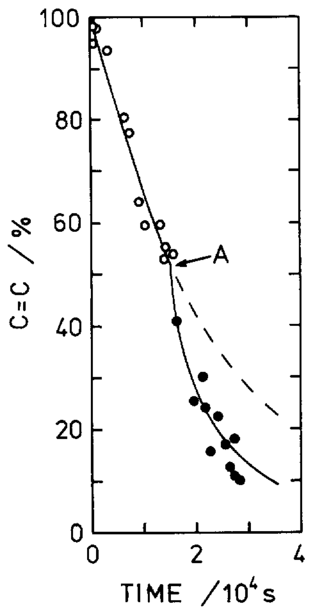

FIGURE 5:

Kinetic test of sequential polymerization at two temperatures.
(○) 75°C, (●) 85°C;
(——) isothermal conversion curves from Fig.3.
(--) continuation of isothermal polymerization at 75°C.
A = time of temp. change.

and of DIAL *et al.* (1955) using hydrolysis and titration of the resultant allyl alcohol, that the conversion of C=C bonds goes virtually to completion. However, this conclusion is in conflict with the results of STARKWEATHER and EIRICH (1955) who deduced from density and refractive index measurements that 30% of the C=C bonds remained unreacted. The explanation of high C=C consumption is uncertain, but may involve intra- and inter-molecular chain transfer and cyclization reactions.

CONCLUSIONS

Laser Raman spectroscopy has been shown to provide a convenient method for quantitative measurements of crosslinking homopolymerization of a divinyl monomer to high conversion. Consumption of C=C bonds reached at least 95%. The effect of polymerization temperature has been ascertained. It has also been shown that isothermal results can be combined to predict the polymerization behaviour when the temperature is increased step-wise during the polymerization.

A detailed kinetic evaluation of the CR-39 homopolymerization will be reported subsequently.

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