

The Use of a Recording Dilatometer to Study the Photopolymerization of Ethylene Glycol Dimethacrylate Using the Isobutyl Ether of Benzoin as Photoinitiator

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Synopsis

A simple recording dilatometer was adapted and used to determine or follow the rates of photopolymerization of ethylene glycol dimethacrylate with the isobutyl ether of benzoin as photoinitiator. The photopolymerization was recorded from 0% to 100% conversion of monomer to polymer, and the results from the dilatometer were compared with other methods (gravimetric, electrical resistance, and differential thermal analysis). The rates of photopolymerization were calculated as a function of initiator concentration, light intensity, and monomer concentration. Gel points could be directly determined along with the degree of conversion of monomer to polymer formation. The recording dilatometer can be used to measure rates of photopolymerization of ultraviolet crosslinking monomers, polymers, or coating systems.

INTRODUCTION

The following or determination of rates of polymerization of crosslinking polymer systems at advanced degrees of conversion can be a difficult experimental problem. Normally, most polymerization rates are determined at initial conditions, but there are many techniques that can be used to study high conversions of monomer to polymer.¹ This paper presents a simple recording dilatometer which was used to measure the rates of photopolymerization of ethylene glycol dimethacrylate (EGDMA) sensitized with various concentrations of isobutyl ether of benzoin (isoBEB) as the photoinitiator. Changes in volume or contraction due to the photopolymerization process of this system are associated with 0% to 100% conversion of monomer to polymer. These changes in volume can be easily monitored and recorded by this technique. Results from this dilatometer study were compared with gravimetric determinations for per cent conversion of monomer to polymer, electrical resistivity techniques, and differential thermal methods.²

EXPERIMENTAL

Materials

The removal of inhibitor from ethylene glycol dimethacrylate (EGDMA) was accomplished through passing the inhibited EGDMA (Sartomer SR-206) over a 2-ft, 1-in.-O.D. column of aluminum oxide, pH = 7.8.

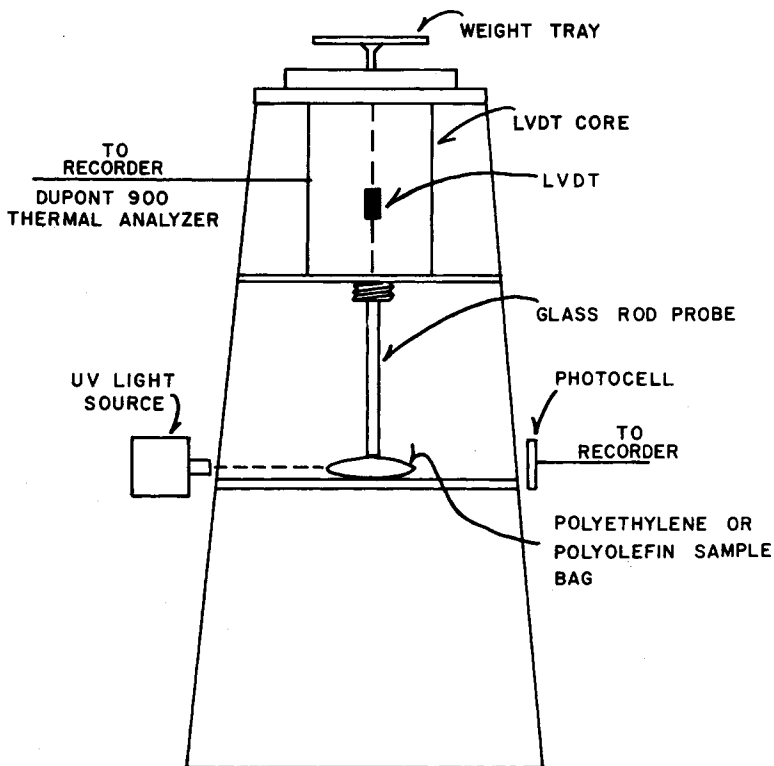
The isobutyl ether of benzoin (isoBEB) was obtained from Stauffer Chemical Company and was used without further purification as the photoinitiator.

Methods

The light source used was a high-pressure 450-watt quartz mercury-vapor lamp (Hanovia) which was placed in a water-cooled quartz immersion well (Ace Glass Company). The entire assembly was housed in a closed box containing a 1-in. circular window which allowed the ultraviolet irradiation to fall onto the reaction cell of the dilatometer or resistivity cavity.

The recording dilatometer used in these experiments was an adaptation of the du Pont 940 Thermomechanical Analyzer (TMA) in conjunction with the du Pont 900 Thermal Analyzer Recorder (Fig. 1). The weighted glass probe of the TMA apparatus was placed on top of a sealed polyethylene or polyolefin (2 ml) sample bag (irradiated polyolefin shrink tubing can also be used as a reaction cell) containing EGDMA and various concentrations of photoinitiator.

The polyolefin sample tubes were filled and sealed under vacuum or purged with deoxygenated nitrogen. The polyolefin tubing was either heat sealed at one end or folded over and crimped air tight with a metal clamp. This bag could then be filled with sensitized monomer solutions, sparged with



DUPONT 940 THERMOMECHANICAL ANALYZER

Fig. 1. Recording dilatometer.

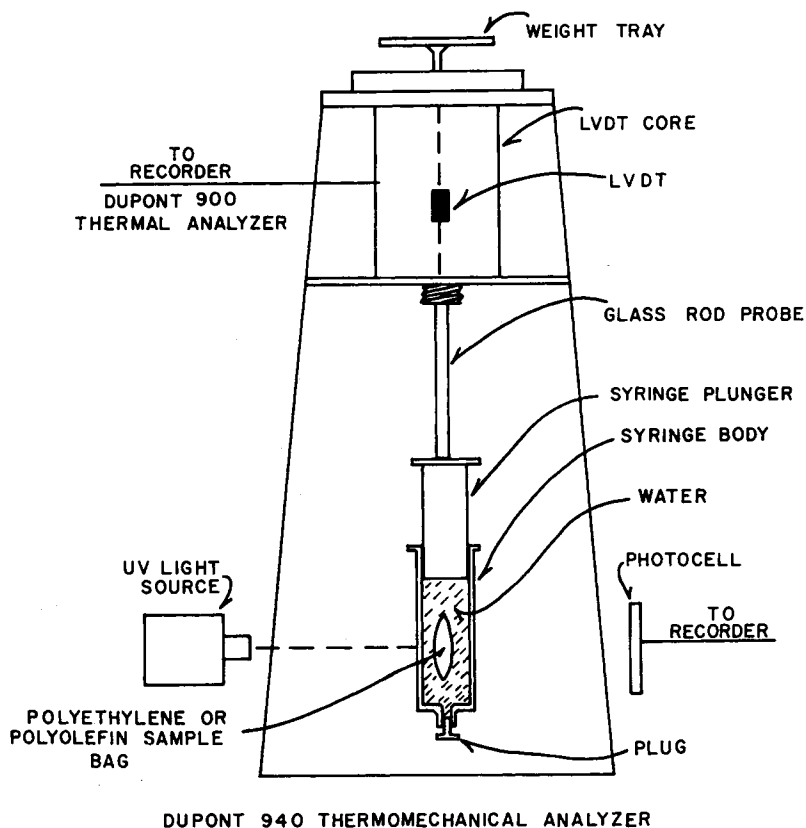


Fig. 2. Recording dilatometer for use in a constant-temperature bath.

nitrogen, and closed off with another metal clamp. The filled sample bag can also be frozen, vacuum pumped (freeze-thaw techniques), and heat sealed. Nitrogen sparge techniques were used in these experiments.

A photocell was placed behind the reaction vessel to measure relative intensity. Changes in ultraviolet light intensity passing through the cell were measured as a function of time. Filters or wire screens were placed between the light source and the sample cell to effect controlled relative changes of light intensity.

Another type of reaction cell (Fig. 2) was obtained by placing the polyethylene sample bag inside a 20-cc glass syringe filled with water. The glass probe of the TMA apparatus was placed on top of the plunger of the 20-cc glass syringe, and change in volume, under irradiation, of the entire system was recorded.

This entire syringe assembly was housed in a constant-temperature bath ($28^{\circ} \pm 0.05^{\circ}\text{C}$). In Figure 3, a moveable glass-tube electrode filled with mercury and a fixed carbon pencil rod, under a constant potential, were used as the sensing devices for measuring relative rate of contraction as a function of change in resistance.³ All samples were irradiated from a distance of 4 in. to the light source.

Electrical resistivity or resistance measurements, throughout the photopo-

lymerization process, were obtained from a Keithley Model 610CR electrometer and continuously recorded by a Honeywell Elektronik 194 recorder. The photolysis reaction cells (Fig. 11) used for these measurements were 1¼-in.-long, ⅜-in.-o.d. clear virgin polyethylene tubes. Two electrodes, ¾- by ⅛-in. strips of aluminum foil, were placed ⅝ in. into the tube and at a distance of ½ in. apart from each other. The tubes were filled with 1 ml sensitized EGDMA and sealed with rubber stoppers. These samples were irradiated at a distance of 1 in. from the light source and received more intensity than the samples of the recording dilatometer.

Thermal detection for the rates of photopolymerization were obtained through the use of a du Pont 900 Differential Thermal Analyzer and recorder (Fig. 13).⁴

RESULTS AND DISCUSSION

The basic principle of these recording dilatometers (Figs. 1 and 2) is that a volume change in the sample cell is sensed by the weighted glass probe of the TMA which produces a signal, through use of a LVDT and detecting coil, that can be continuously recorded as a function of reaction time. In Figure 3, the change in volume of the sample cell causes a change in resistance of the mercury/carbon cell which can also be automatically recorded.

A visual method for dilatometric analysis can be used to study rates of photopolymerization if the reaction rates are slow enough for perception. In Figure 4, the flexible sample bag is placed inside a conventional dilatometer filled with water and the relative rate of contraction can be measured with a cathetometer.

When ultraviolet light falls onto the flexible polyethylene sample bag

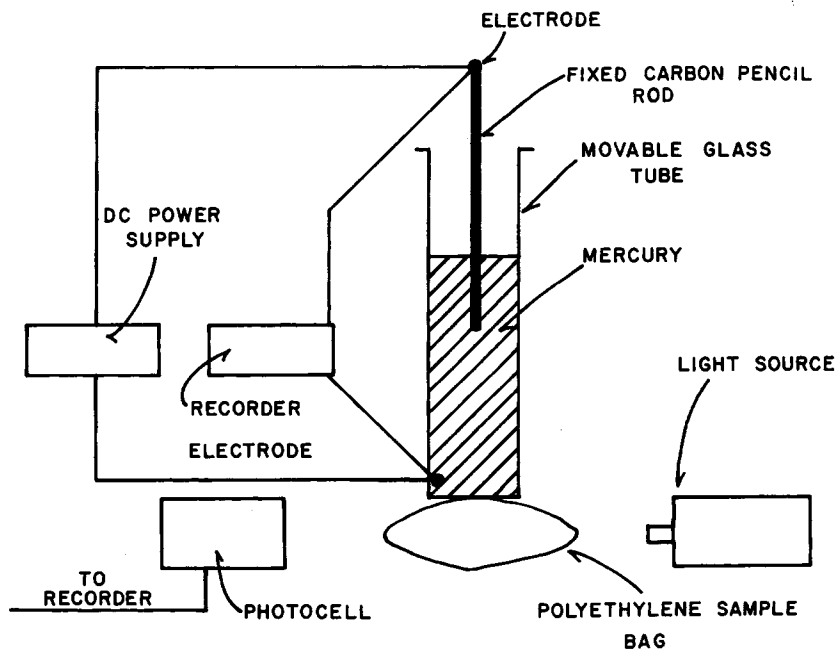


Fig. 3. Recording dilatometer.

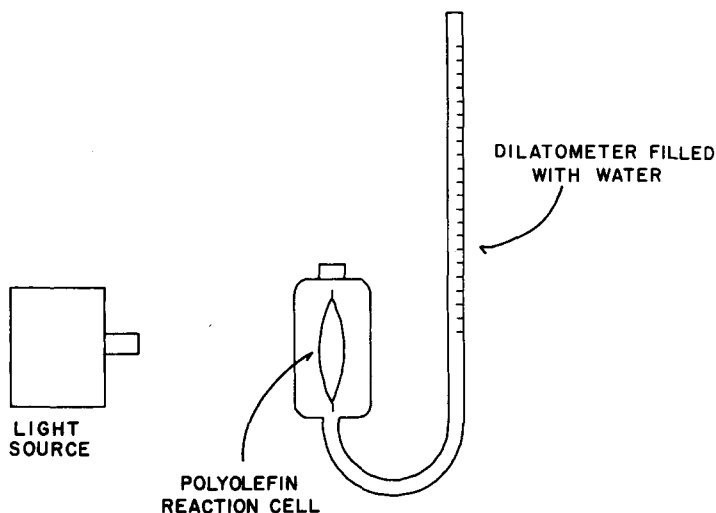


Fig. 4. Dilatometer.

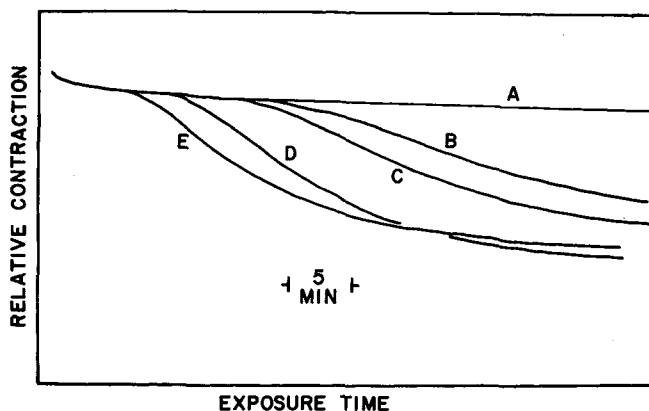


Fig. 5. Photopolymerization of EGDMA (5.31M): (A) no sensitizer; (B) $0.53 \times 10^{-3}M$; (C) $2.8 \times 10^{-3}M$; (D) $4.14 \times 10^{-3}M$; (E) $10.70 \times 10^{-3}M$ isoBEB.

(reaction cell) containing sensitized EGDMA, polymerization is initiated and a contraction of the sample is noticed. The exchange of a double bond and a van der Waals bond for two single bonds for every monomer molecule polymerized can result in 15.7% reduction in volume for the complete polymerization reaction of EGDMA.

Through the use of the TMA apparatus and a flexible polyethylene irradiation or polymerization cell, the rate of contraction due to photopolymerization is very even, and reproducible results can be obtained. Polyethylene is transparent above 2500 \AA and does not interfere appreciably with the $n \rightarrow \pi^*$ transition of the isoBEB photoinitiator. The flexible, UV-transparent polyethylene reaction cell prevents the formation of microcracks during tridimensional polymerization; and since the amount of contraction is directly sensed by the probe of the TMA, the rate of the photopolymerization process can be automatically recorded.

TABLE I

Exposure time, min/ (isoBEB) $\times 10^3$	Conversion predicted by recording dilatometer, %	Actual gravimetric determination of conversion, %
10.75	48.23	48
23	81.9	82
<hr/>		
10.7M		
10.75	29.12	28.9
23	81.9	82
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4.14M		
23	46.41	46
29	65.52	66
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2.8M		
23	29.12	29
29	47.3	47
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0.53M		

Some of the relative contraction curves for the photopolymerization of EGDMA with various initiator concentrations are shown in Figure 5. As the amount of sensitizer was increased (0 to $10.7 \times 10^{-3}M$ isoBEB), the rate of relative contraction versus exposure time also increased to a constant level value, which represents 100% conversion of monomer to polymer. The results of these relative contraction curves were verified with gravimetric analysis determinations on the amount of polymer formed and are shown in Figure 6 and Table I. Rates of photopolymerization (R_p) were calculated from the initial linear region of the % conversion curves. (Per cent conversion = $\Delta V/VK \times 100$, where ΔV = change in volume contraction, V = initial volume, and $K = 0.156$).^{5a}

Rates of polymerization were determined for a range of concentrations of

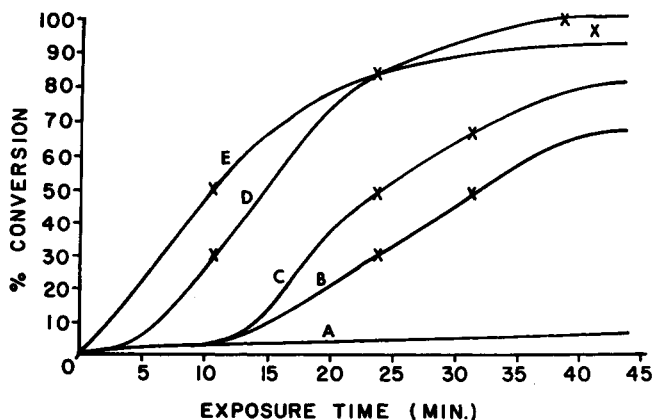


Fig. 6. Actual gravimetric determination (x) polymer formation as compared with apparent predicted polymer formation by the recording dilatometer: (A) no sensitizer; (B) $0.53 \times 10^{-3}M$; (C) $2.8 \times 10^{-3}M$; (D) $4.14 \times 10^{-3}M$; (E) $10.70 \times 10^{-3}M$ isoBEB.

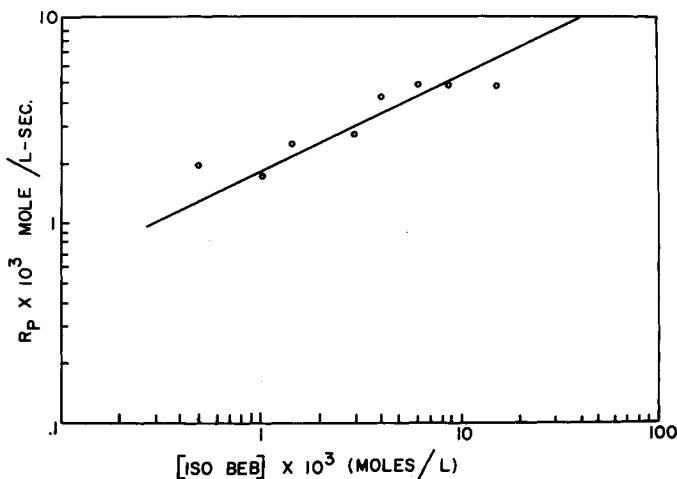


Fig. 7. Rates of photopolymerization of EGDMA (5.13M) sensitized by [isoBEB] = 0.53, 1.0, 1.5, 2.8, 4.14, 6.0, 8.4, $10.7 \times 10^{-3}M$.

isoBEB (0.53, 1.0, 1.5, 2.8, 4.14, 6.0, 8.4, and $10.7 \times 10^{-3}M$), and respective R_p values were 1.9, 1.65, 2.4, 2.65, 4.2, 4.8, 4.8, 5×10^{-3} moles/l.-sec.

The rates of polymerization (R_p) were calculated from curves similar to Figure 6 using the equation

$$R_p \text{ (moles/l-sec)} = \left[\frac{\% \text{ conversion}}{\text{time (sec)} 100} = \text{slope} \right] [\text{EGDMA (moles/l)}]$$

Straight lines drawn through points in Figures 7, 8, 9, and 12 were obtained through least-squares analysis of the data. The slope of Figure 7 was 0.40 ± 0.11 , with a linear point correlation of 0.95.

A log-log plot of rates of photopolymerization against initiator concentration shows approx. half-order dependence on initiator (isoBEB) concentra-

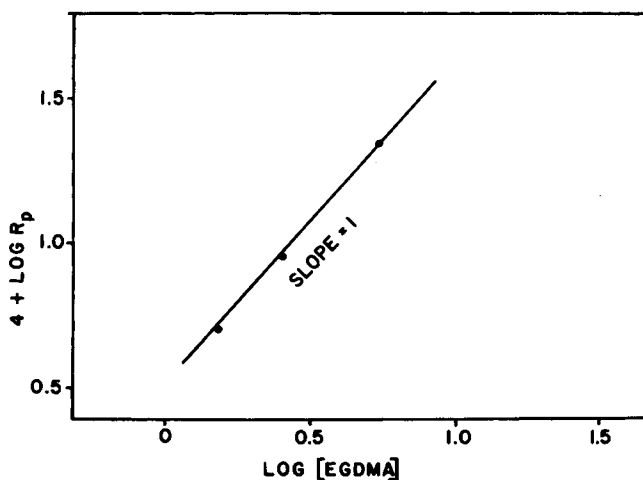


Fig. 8. Influence of the monomer concentration on the rate of photopolymerization: [EGDMA] = 1.51, 2.51, 3.98M in THF; R_p = moles l.-min; [isoBEB] = $4 \times 10^{-3}M$.

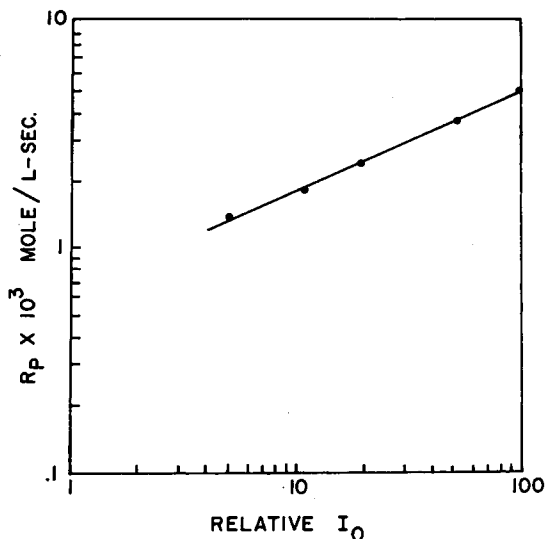


Fig. 9. Influence of the relative light intensity on the rate of photopolymerization of EGDMA (5.31M): [isoBEB] = $8.4 \times 10^{-3}M$.

tion (Fig. 7). Figures 8 and 9 are log-log plots of R_p against monomer concentration and relative light intensity. These graphs show respectively first- and half-order monomer and light intensity dependence on R_p under these conditions. The photopolymerization of EGDMA, at low conversion, with isoBEB is represented by the following general equation:

$$R_p = K[\text{EGDMA}][\text{isoBEB}]^{1/2} I_0^{1/2}$$

GEL POINTS

The determination of the point of gelation at any conversion can be directly determined through use of the apparatus described in Figure 10. A small magnetic spin bar was placed inside the flexible polyolefin tubing along with the sensitized monomer solution. This reactive cell was put inside a dilatometer filled with water and placed on a magnetic stirring motor (the entire assembly can be placed in a constant-temperature bath). The magnetic stirring motor caused the small spin bar inside of the polyolefin reaction cell to rotate or oscillate. The point at which the spin bar stopped rotating was taken as the gel point. The % conversion at this gel time could also be directly read from the graduated glass tube of the dilatometer. For EGDMA the gel point occurred at 1% to 2% conversion of monomer to polymer.

This experimental gel point technique was compared with a previous literature method and experimental equipment design (adapted for photopolymerization) for gel point determination.^{5b} Both techniques give gel points at 1% to 2% conversion of monomer to polymer.

Another method of determining relative rates of conversion of monomer to polymer is through the use of electrical resistance measurements.⁶ The rate of change of the logarithm of EGDMA electrical resistivity with respect to

time, under isothermal conditions, is a measure of the rate of photopolymerization.⁷ The type of photolysis reaction cell used in these experiments is shown in Figure 11. The electrodes of the cell were connected to an elec-

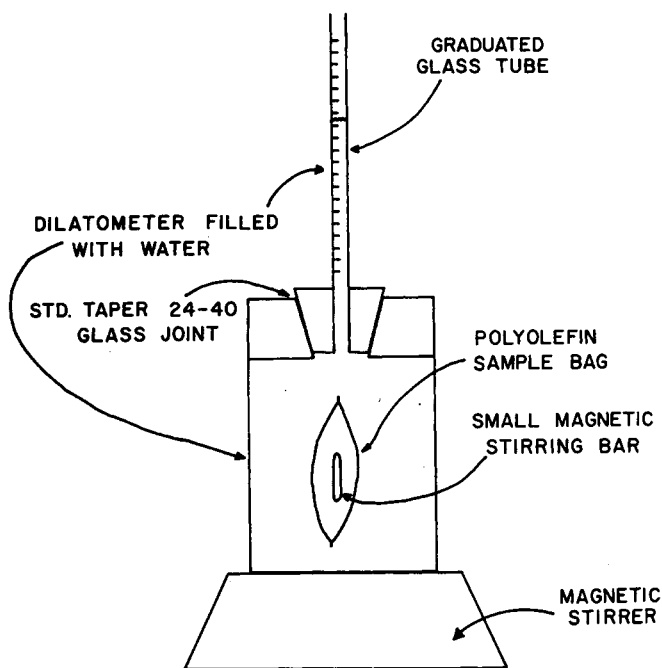


Fig. 10. Gel point apparatus for determining time and % conversion to gelation.

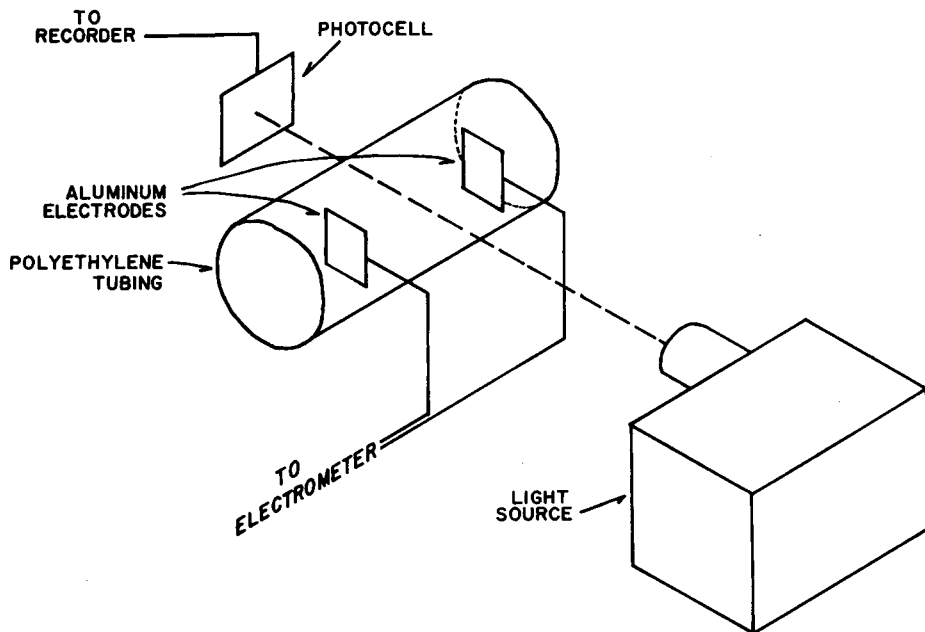


Fig. 11. Electrical resistance cell.

TABLE II
Relative Normalized Slope Values for Photopolymerization^a of EGDMA

	Slope values			
Recording dilatometer	0.46	0.63	1.0	1.15
Resistance measurements	0.47	0.61	1.0	1.44
Differential thermal method	—	—	1.0	1.92
(isoBEB) $\times 10^3$	0.53M	2.8M	4.14M	10.7M

^a Calculated from Figures 6, 12, and 14.

trometer, and changes in resistance versus exposure time were recorded by the constant-current method (Fig. 12).⁸ At the higher concentrations of photoinitiator (isoBEB), the rate or change in resistance is much greater than those of lower concentration. The difference in exposure time for the rate of reaction of both methods is due to intensity effects of the light source. The recording dilatometer reaction cell was placed at a further distance away from the light source than was the electrical resistivity cell and therefore received less intensity (slower reaction time).

Thermal methods of analysis can also be used to determine the rates of photopolymerization of a given reaction.⁹ The type of photolysis reaction cell used in this experiment is shown in Figure 13.

Relative thermal comparisons were made between sensitized and unsensitized EGDMA samples as followed by the heat of polymerization or the heat given off by the photopolymerization process. The light source fell onto each sample holder with equal intensity, and the thermocouples were connected to a recorder to measure and monitor the heat buildup due to photopolymerization. Results shown in Figure 14 illustrates the effect of increasing photoinitiator concentration on the reaction rate of photopolymerization.

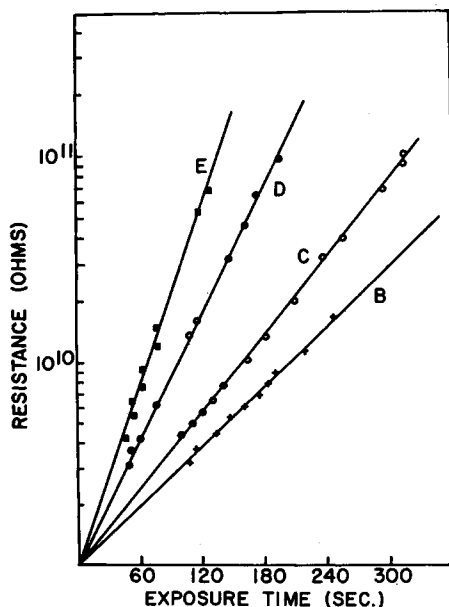


Fig. 12. Photopolymerization of EGDMA (5.31M): (B) $0.53 \times 10^{-3}M$; (C) $2.8 \times 10^{-3}M$; (D) $4.14 \times 10^{-3}M$; (E) $10.70 \times 10^{-3}M$ isoBEB.

DIFFERENTIAL THERMAL ANALYSIS

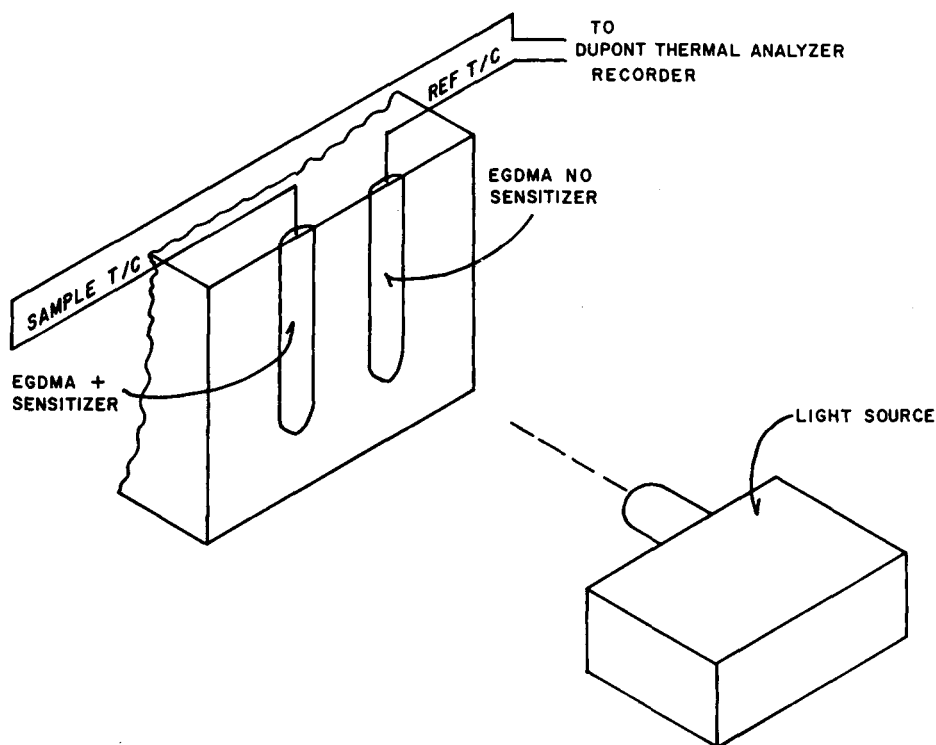


Fig. 13. Differential thermal analysis cell for the photopolymerization of EGDMA.

Normalized relative slopes for the change in resistance and rate of thermal heat evolution for photopolymerization with exposure time as compared with the normalized relative initial slopes for % conversion (after correction for intensity) versus exposure times are given in Table II. These normalized slope values give a comparative measure of the relative rate of photopolymerization as determined by the three different methods.

The relative normalized initial linear slopes (9.1; 7.9; 5.0; 3.6×10^{-4} conversion/sec) in Figure 6 were compared with the relative normalized slopes of Figure 12 (6.0; 4.16; 2.55; 1.95×10^{-3} change in \ln resistance/sec \propto conversion/sec) and Figure 14 (4.3; 2.24×10^{-3} change in temperature/sec \propto conversion/sec).

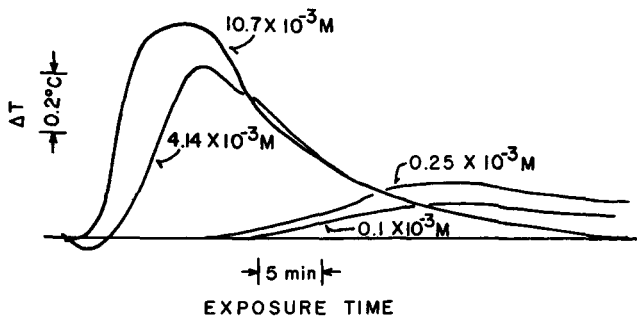


Fig. 14. Thermal curves for the photopolymerization of EGDMA (5.31M): [isoBEB] = 0.10, 0.25, 4.14, 10.7×10^{-3} M.

The values for the slopes in Figure 12 assume that the initial relative changes in resistance (\ln ohms/sec) is directly proportional to per cent polymer formation at low conversion. A value range of $\ln 1 \times 10^{10}$ to $\ln 2 \times 10^{10}$ ohms represents a linear 0% to 12% conversion as determined by gravimetric analysis.

The values for the slopes in Figure 14 assume that the initial relative changes in temperature (Δt /sec) are also directly proportional to per cent polymer formation at low conversions. A value of 0.1°C temperature change represented 10% conversion as determined by gravimetric analysis.

There is relative agreement between sets of normalized slope values for the recording dilatometer and resistance measurements at photosensitizer levels of 0.53 to $4.14 \times 10^{-3}M$ (isoBEB). At higher concentrations of photosensitizer, agreement between the two methods is less, and this is probably due to an intensity or self-quenching effect of the isoBEB with itself.

The lack of agreement associated with the differential thermal method as compared with the recording dilatometer and resistance measurements is probably due to uneven heat of reaction and non ideal isothermal conditions of the reaction cell. Determination of rates of polymerization by thermal methods is better achieved through use of a differential scanning calorimeter (DSC).⁹

The rates of photopolymerization for these reactions were determined at low % conversion (1% to 6%) in which a volume contraction is related to additivity of densities for monomer and polymer mixtures.¹⁰ In order to determine the actual % conversion beyond 50%, depending on the system being studied, one would have to determine the densities of monomer and polymer mixtures at these high conversions or use the mathematical equation of Rubens and Skochdopole¹⁰ for dilatometric measurements.

The recording dilatometer described in this paper is a very simple method for measuring gel points and % conversion, as a function of contraction, for crosslinking ultraviolet sensitive monomers, polymers, and coatings systems.

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