Studies on the Kinetics of Free-Radical Bulk Polymerization of Multifunctional Acrylates by Dynamic Differential Scanning Calorimetry

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SYNOPSIS

The course and kinetics of nonisothermal bulk polymerization of multifunctional acrylates were studied by dynamic differential scanning calorimetry (DSC). Measurements were carried out for four straight-chain monomers, diethylene glycol diacrylate (DEGDA), triethylene glycol diacrylate (TEGDA), tetraethylene glycol diacrylate (TTGDA), and poly(ethylene glycol)diacrylate (PEGDA) (mol. wt. 600), to study the effect of the backbone chain length, atmosphere, and type of initiator on the crosslinking kinetics. 4,4'-Azobis(4-cyanovaleric acid) (1.0%, w/w) was used as a free-radical initiator. From the dynamic scanning of polymerization of DEGDA at five heating rates (2–30°C/min), the average heat of polymerization (ΔH_p) was found to be 524.2 J/g. An activation energy of 108.8 kJ/mol and preexponential factor 5.34×10^{12} s^{-1} were obtained from the Arrhenius plot, ln $d\alpha/dt$. The rate of polymerization was found manyfold greater at 20–60% conversion than at the initial stage (2–8% conversion). Polymerization was studied under both nitrogen and air atmosphere. The results corresponded well with the theory of oxygen inhibition. Different types of initiators, e.g., 4,4'-azobis(4-cyanovaleric acid) (ABCVA), 2,2'-azobis-isobutyronitrile (AIBN), and benzoyl peroxide (BPO) were used for polymerization and ABCVA was found to be the most efficient among all. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Multifunctional acrylates and methacrylates are versatile monomers and widely used as speciality coatings and adhesives in microelectronics, engineering, and telecommunication industries.[1,2] Due to their wide range of properties like viscosity (8–10000 cps), modulus (1–200 Mpa), glass transition temperature (−100 to +150°C), optical properties (e.g., refractive index 1.42–1.60), and structural modification feasibility, one can produce a wide range of materials. Because of their low volatility, viscosity, toxicity, and odor, these acrylates can be used as reactive diluents for network property modification. Each diluent has a different level of effectiveness in reducing the viscosity and improving the

application properties. Properties may be tailored for unique and specific applications in the field of optical fiber coating, resistors, and capacitors, printed circuit boards, biomedical and engineering applications, etc.[3]

In spite of having such versatility of the applications, there is not much literature available about the thermodynamic properties of these multifunctional acrylates, especially about their crosslinking behavior and network formation. With multifunctional acrylates, ambiguity exists with respect to the status of unreacted groups. These may be present either in free monomer or as pendent groups. Due to their very fast (< 1 min) and highly exothermic nature of polymerization, most methods of studying the polymerization kinetics (e.g., dilatometry or monitoring of unreacted monomer concentration) are not suitable for studying bulk polymerization and are particularly unsuitable for studying network-forming reactions.[4] By using differential scan-

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ning calorimetry (DSC), inaccuracy is avoided and network formation can be studied at very low conversion. Because only a small sample is required for the experiment, good temperature control can be maintained. This simplifies interpretation of the kinetic data. Thus, DSC has been used in the present study to examine the free-radical bulk polymerization kinetics of four multifunctional acrylates. In our earlier work pertaining to the synthesis and development of telechelic reactive acrylate oligomers, rubber-toughened plastics, etc., we used several nonconventional methods to determine the kinetic parameters for similar reactions.[5-7]

In continuation of our earlier work on speciality acrylates for coatings and adhesives, we undertook systematic studies on multifunctional monomers with special reference to acrylates/methacrylates. The present article deals with the effect of structural changes (in terms of the size of alkyl groups and number of the reactive groups), atmosphere, and different initiators on the kinetics of crosslinking of these multifunctional acrylate monomers. Kinetics

of bulk polymerization of DEGDA was studied in detail. Activation energy (E), preexponential factor (A), rate of polymerization (R_p), and order of the reaction (n) were calculated for diethylene glycol diacrylate (DEGDA) crosslinking.

EXPERIMENTAL

Reagent grade (AR) solvents, purchased from the local market, were distilled and dried before use. Di-, tri-, tetra-, and poly(ethylene glycol) (mol. wt. 600), supplied by S. D. Fin. Chem. Ltd., Boisar, India, were used after passing through the silica gel column and drying over magnesium sulfate. p-Toluenesulfonic acid was received from Aldrich Chemical Co., U.S.A., and used as a catalyst for the preparation of multifunctional acrylate monomers. Hydroquinone and benzoyl peroxide were used as purchased from Aldrich Chemical Co.

Multifunctional acrylate monomers of di-, tri-, tetra-, and poly(ethylene glycol) (600) were pre-
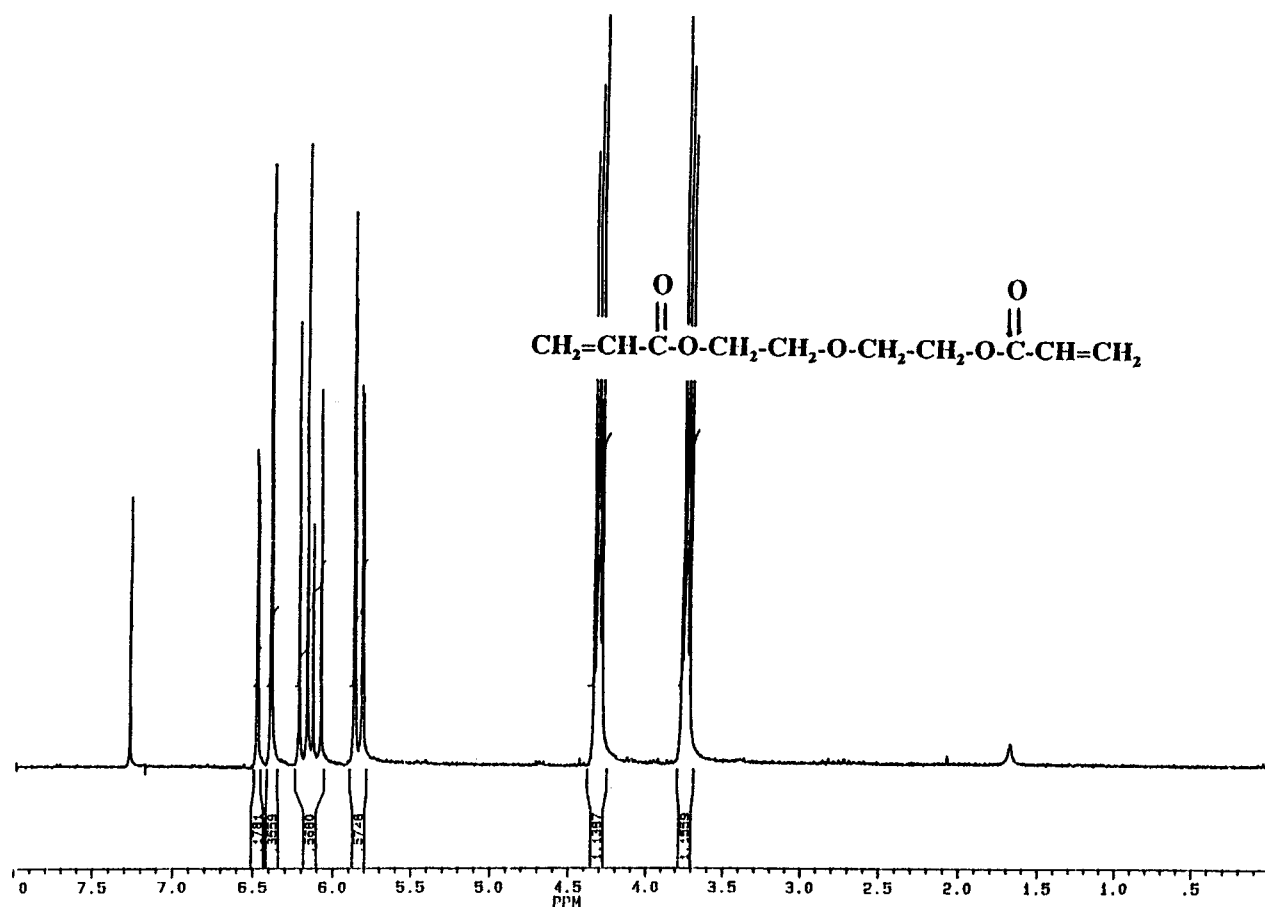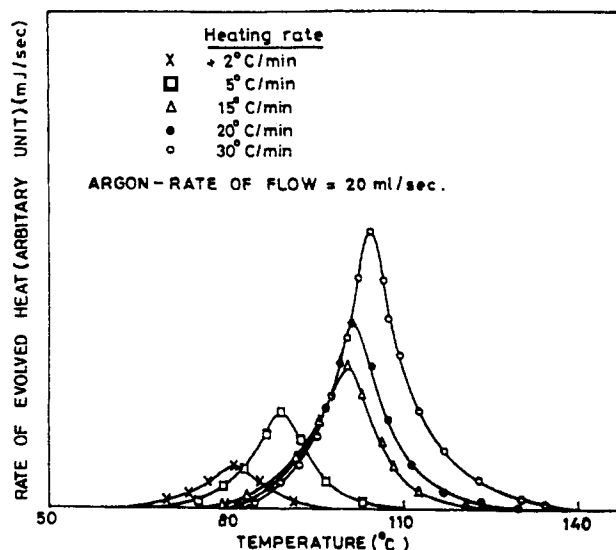

Figure 1 NMR spectra of DEGDA monomer.

Figure 2 DSC thermograms of DEGDA crosslinking at different heating rates.

pared by a commercially viable process in high yield and purity.[8] Ethylene glycol (di, tri, tetra, and poly) (0.5 mol), a polymerization inhibitor, hydroquinone (1.0%), and an esterification catalyst, p-toluenesulfonic acid (0.5%) were taken in a reaction vessel. An inert solvent such as toluene (200 mL) and a small amount of a chain-terminating agent (0.5%) were then added into the reaction mixture. The contents were refluxed at 110°C with slow stirring. Acrylic acid (1.0 mol) was then added slowly to the reaction mixture over a period of 2 h and the reaction was continued for 2 more h. Water formed as a reaction byproduct was continuously removed azeotropically with toluene through a Dean and Stark trap. The amount of water was collected in a 2 h reaction period, indicating the completion of the reaction. The crude reaction product was purified by washing it with 5.0% sodium carbonate followed by

distilled water. Color of the solution, containing the product, was removed by adding activated charcoal and stirring it at 50°C for 30 min. The charcoal-treated solution was then allowed to stand for 1 h, decanted neatly, and then filtered. Toluene was stripped off under reduced pressure.

4,4'-Azobis(4-cyanovaleric acid) (ABCVA) and 2,2'-azobisisobutyronitrile (AIBN) were received from Aldrich Chemical Co. and recrystallized from absolute ethanol. Benzoyl peroxide (BPO) was used as received. Shimadzu (DT-41) and Stanton Red-craft (STA-625) differential scanning calorimeters (DSC), having 99.9% accuracy, were calibrated with high-purity indium and used for kinetic measurements at different heating rates (2, 5, 10, 15, 20, and 30°C) in different atmospheres (nitrogen and air) and with different initiators (ABCVA, AIBN, and BPO). A concentration of 1.0% (w/w) of each initiator was used to carry out the polymerization. Four samples were tested for each experiment and the average values were obtained and used for the kinetics calculation. To characterize these multifunctional monomers, infrared spectra were obtained by use of a Shimadzu IR spectrophotometer, using the KBr windows. Proton NMR spectra of all multifunctional acrylate monomers in chloroform-d were recorded on a Bruker NMR spectrophotometer.

RESULTS AND DISCUSSION

The reaction of acrylic acid with an alcohol in the presence of p-toluenesulfonic acid as a catalyst and an inhibitor hydroquinone at reflux temperature yields an ester:
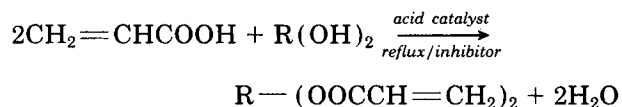
$$2CH_2 = CHCOOH + R(OH)_2 \xrightarrow[reflux/inhibitor]{acid\ catalyst}$$

$$R - (OOCCH = CH_2)_2 + 2H_2O$$

Table I Curing Characteristics of DEGDA with 1.0% (w/w) ABCVA, Obtained from DSC at Different Heating Rates

Heating Rate (°C/min)	ΔH_p (J/g)	T_i (°C)	T_p (°C)	T_f (°C)	t (min)	t_{gel} (min)	$R_p' \times 10^4$ (s^{-1})	$R_p'' \times 10^3$ (s^{-1})
2	121.2	63.4	82.9	95.9	16.25	7.33	2.71	2.05
5	588.0	66.6	88.7	104.2	7.52	3.66	4.75	6.50
15	641.5	76.6	99.9	121.1	2.96	1.50	10.80	19.50
20	639.0	76.6	101.9	125.9	2.46	1.16	19.00	39.00
30	632.9	83.3	103.1	133.7	1.68	0.83	25.33	78.00

ΔH_p = heat of polymerization; t = total time taken for completion of reaction; t_{gel} = gel time; R_p' = rate of polymerization (2–8%); R_p'' = rate of polymerization (20–60% conversion); T_i = initiation temperature; T_p = peak temperature; T_f = finishing temperature.
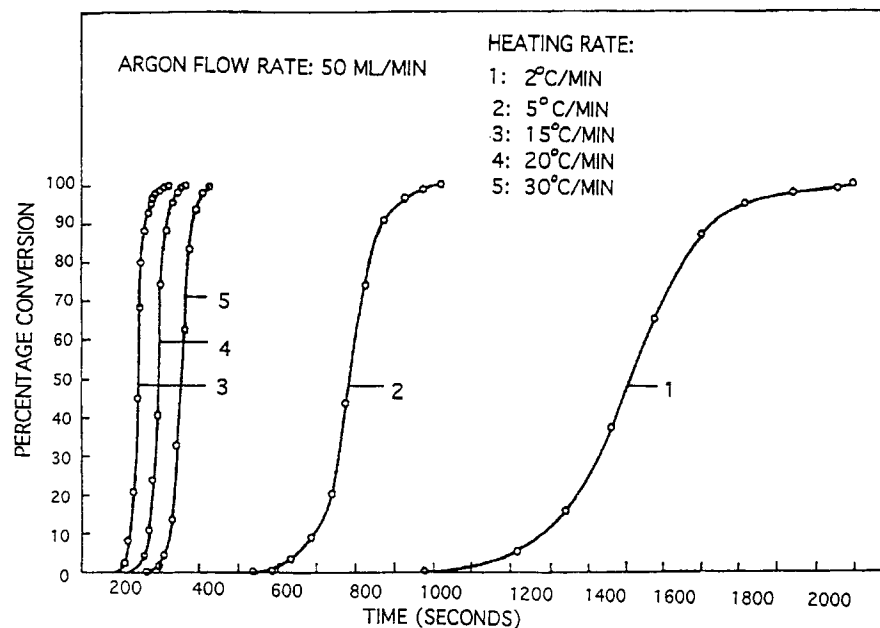
Figure 3 Percentage conversion vs. time plot of DEGDA crosslinking.

$R = C_4H_8O \; C_6H_{12}O_2 \; C_8H_{16}O_3$ and $C_{32}H_{64}O_8$ for di-, tri-, tetra-, and poly(ethylene glycol).

IR spectra of these multifunctional acrylates are very similar to each other. Disappearance of the $C = C$ peak at 1630, 1420, 950, and 810 cm^{-1}
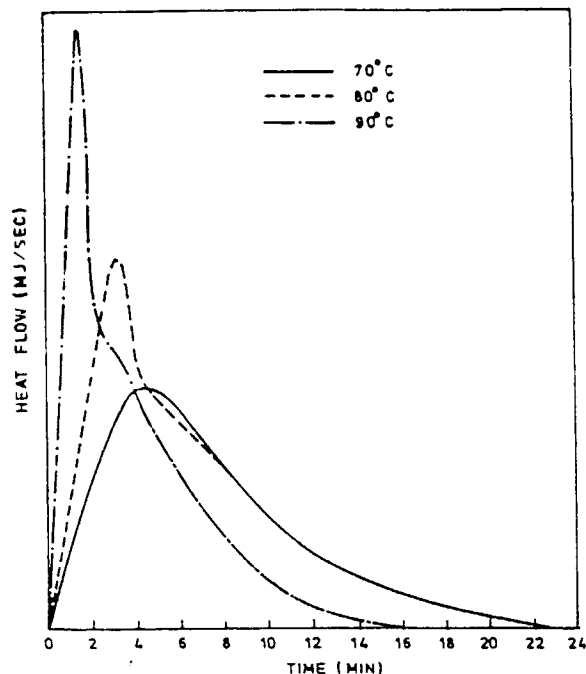
in the spectra of polyacrylates confirm the cross-linking.

A complete assignment of proton signals of multifunctional monomers in chloroform was achieved by homonuclear decouplings and inspection of the chemical shift. Because of the similarity in the structures, only the ^{1}H-NMR spectrum of DEGDA is shown in Figure 1.

A number of methods have been reported in the literature for determining reaction kinetics by DSC. We applied the Friedman method of kinetic analysis[9] to DSC measurements of curing of different multifunctional acrylates. To describe the kinetics of free-radical bulk polymerization, the following rate equation was used:

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{RT} + n \ln (1 - \alpha)$$

Figure 4 DSC thermograms of DEGDA crosslinking at different temperatures.

Table II Curing Characteristics of DEGDA with 1.0% (w/w) ABCVA Obtained from Isothermal DSC at Different Temperatures

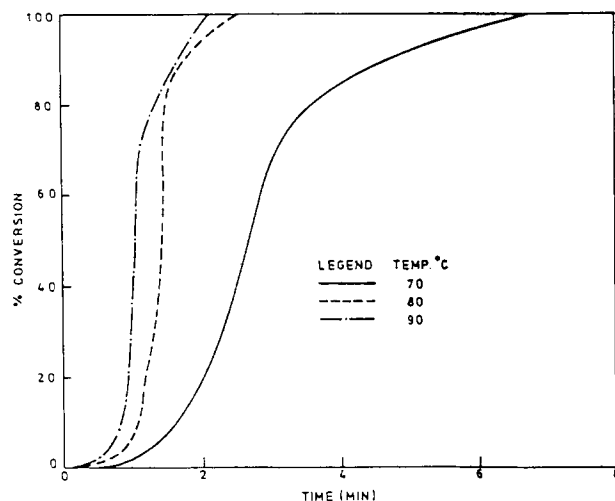| Temperature (°C)	Completion Time (min)	Heat of Polymerization (J/g)
70	7.50	498.16
80	2.59	527.09
90	2.14	563.04

Figure 5 Percentage conversion vs. time plot of DEGDA crosslinking at different temperatures.

where α is the fractional conversion ($\alpha = \Delta H_0 / \Delta H$, ΔH_0, and ΔH are the partial and total heat values, respectively); t, time; A, the preexponential factor; E, the apparent activation energy; R, the universal gas constant; T, the absolute temperature; and n, the order of the reaction. DSC curves at different heating rates (2, 5, 15, 20, and 30°C/min) for diethylene glycoldiacrylate (DEGDA) are shown in Figure 2. The values have been corrected for base line and show only the deviations from the base line. The results obtained from the DSC thermograms are given in Table I. The conversion profiles are shown in Figure 3. As shown in Figure 3, the peak exotherm temperature (T_p) varies in a predictable manner with the heating rate. Similarly, both polymerization initiation temperature (T_i) and completion temperature (T_f) also increase with the increase of the rate of heating.[10,11]

A straight line is obtained by plotting ln $d\alpha/dt$ vs. $1/T$ (Arrhenius plot) having an intercept A and slope E/R. Values for average E and average A obtained from the Arrhenius plot are 108.8 kJ/mol and 5.34×10^{12} s^{-1}. The order of the reaction was calculated from the ln $d\alpha/dt$ vs. ln $(1 - \alpha)$ plot.[12] The crosslinking reaction is of first order and the value of the specific rate constant obtained from the intercept of the plot is 0.923 s^{-1}. The rate of polymerization (R_p) was calculated for 20-60% and 2-8% conversion. Values of R_p are given in Table II. Calculated values do not have the error more than ±1.0%.

It is significant that the intensity of the exothermic gel effect and rate of polymerization decrease with the lowering of the heating rate. These are attributed to the fact that termination in a highly viscous medium are predominantly diffusion-controlled and any increase in the rate of reaction temperature may be reflected in the lowering of the viscosity of the reaction medium which will lead toward facile completion of the reaction and network formation. This is also supported by the fact that the onset of the gel effect is delayed due to the lowering of the heating rates.

Isothermal DSC measurements were carried out at 70, 80, and 90°C and analyzed as described above. Figure 4 displays the observed rate of cure as a function of time at different temperatures. Values of the heat of polymerization with the time of completion of polymerization are given in Table II. A conversion time plot is given in Figure 5. An activation energy of 89.0 kcal/mol and a frequency factor of 6.23 s^{-1} were obtained by plotting ln $d\alpha/dt$ vs. $1/T$, the Arrhenius plot.

DSC measurements were obtained at 10°C/min to study the effect of the structural changes on crosslinking kinetics. Values of the heat of polymerization at 10°C/min and activation energy for DEGDA, triethylene glycol diacrylate (TEGDA),

Table III   Kinetic Parameters for Curing of Different Multifunctional Acrylates with 1.0% (w/w) ABCVA Obtained from DSC Thermograms 10°C/min Heating Rate

Monomer	ΔH_p (J/g)	E (kJ/mol)	$R_p'' \times 10^3$ (s^{-1})	t_{gel} (min)
DEGDA	646.5	106.8	15.50	1.30
TEGDA	584.4	105.3	10.98	1.57
TTGDA	572.6	90.3	6.32	2.00
PEGDA				
(Mol. wt. = 600)	160.2	66.5	7.90	2.60

For ΔH_p, R_p'', t_{gel}, and E, see Table II for explanation.
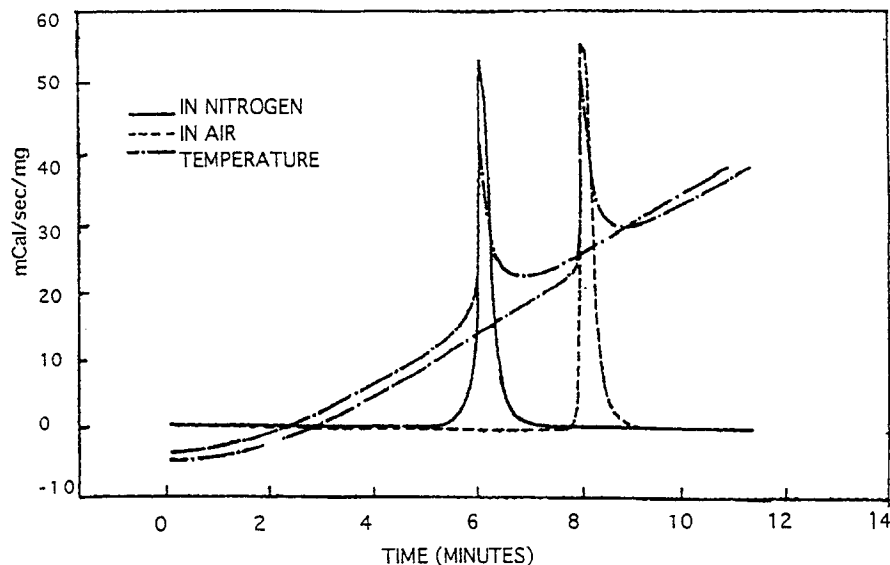
Figure 6 DSC thermograms of crosslinking of DEGDA at 10°C/min heating rate in different atmospheres.

tetraethylene glycol diacrylate (TTGDA), and poly(ethylene glycol)diacrylate (PEGDA-600) are given in Table III. Activation energy values for the crosslinking of the multifunctional monomers were calculated by taking the DSC measurements at four heating rates, 5, 10, 15, and 20°C/min, and plotting the Arrhenius plot, ln $d\alpha/dt$ vs. $1/T$. The rate of polymerization for 20–60% conversion and gel time values were calculated for 10°C/min and are also given in Table III.[13]

The enthalpy of polymerization of these acrylates decreased as the number of alkyl groups (methyl)
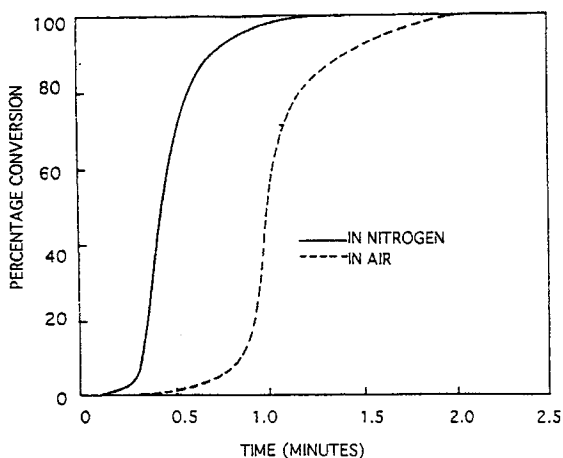

Figure 7 Percentage conversion vs. time plot of DEGDA crosslinking at 10°C/min heating rate in different atmospheres.

increased. Among the four straight-chain monomers, the maximum heat of polymerization was found in case of DEGDA due to a very sharp conversion scanned by gelling as evident from Table III. It has been observed that as the number of alkyl group increases in the monomer backbone chain the activation energy and the rate of polymerization decreases but the gel time increases. Because of the increase, the alkyl group enhances the mobility of the polymer chains and decreases the intensity of the gel effect. This may be attributed to stearic hinderances.[14]

Oxygen is an efficient inhibitor of radical polymerization. It reacts rapidly with the growing radicals which are converted into relatively unreactive peroxy radicals as follows:

$$O_2 + Mn^{\bullet} \rightarrow MnO_2^{\bullet}$$

$$MnO_2^{\bullet} + M^{\bullet} \rightarrow MnO_2M$$
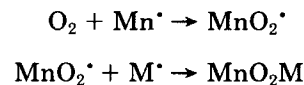
If sufficient oxygen is present, polymerization will be suppressed by continuous oxidation. At low temperature, the peroxy radicals are static and the reaction is slow and oxygen acts as an inhibitor. But at high temperature, the above reaction becomes faster and oxygen accelerates curing.[15,16] The effect of atmosphere was studied on crosslinking of DEGDA with ABCVA (1.0% w/w) initiator. DSC runs were carried out in the atmosphere of air and

Table IV Effect of Atmosphere on Crosslinking of DEGDA with 1.0% Concentration (w/w) of ABCVA at 10°C/Min Heating Rate Studied by DSC

Atmosphere	t_i (min)	T_i (°C)	ΔH_p (J/g)	t (min)
Air	7.65	92.0	626.1	1.46
Nitrogen	5.10	73.3	646.5	2.00

For ΔH_p and T_i, see Table II. t = total time taken for completion of reaction; t_i = time of initiation.

nitrogen with the flow rate of 50 mL/min at 10°C/min, showed in Figure 6. A conversion time plot is given in Figure 7. Data are presented in Table IV. These results corresponded well with the theory of oxygen inhibition. It is evident from the figure that in a nitrogen atmosphere reaction starts at 63°C, while in air, the reaction starts at 96°C. At high temperature, the reaction in air was quite fast, while in the presence of nitrogen, the reaction was initially slow compared to that in the presence of air. The induction period in the presence of oxygen was 7.6 min, while in presence of nitrogen, it was 5.04 min. These results agree very well with the oxygen inhibition theory.

It is well known that polymer molecular weight and polymer concentration in the reaction medium as well as polymerization rate can be controlled by the type and concentration of the initiator used.[17,18] In the present study, it was assumed that the autoacceleration effect may be correlated with the type of initiator. The course of bulk polymerization of DEGDA with different initiators as ABCVA, AIBN,
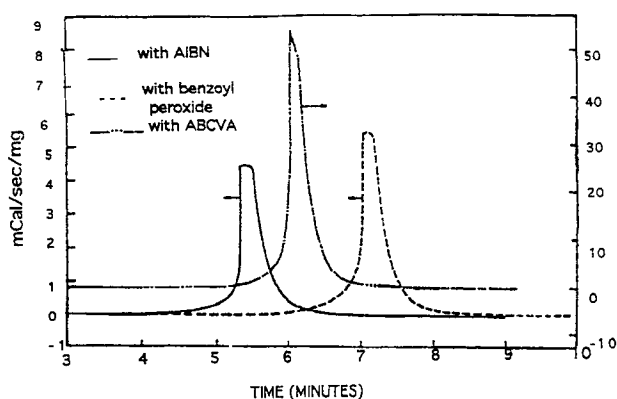
Figure 8 DSC thermograms of DEGDA at 10°C/min heating rate with 1.0% (w/w) concentration of different initiators.
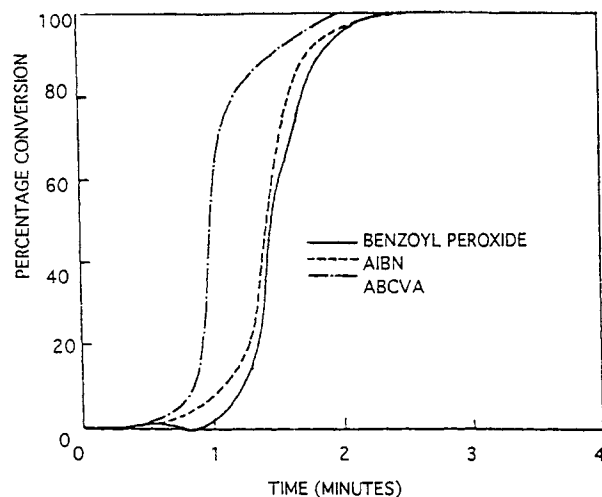
Figure 9 Conversion vs. time plot of DEGDA crosslinking at 10°C/min heating rate with 1.0% (w/w) concentration of different initiators.

and BPO with 1.0% (w/w) concentration was studied. DSC thermograms and conversion vs. time plots are given in Figure 8 and 9, and the data are given in Table V. The rate of the polymerization reaction varied with the different types of initiators as evident from the figure and data. It has been further observed that ABCVA is the most efficient initiator among all initiators used for this study.

CONCLUSION

Dynamic differential scanning calorimetry (DSC) is a useful method to follow the kinetics of the non-isothermal bulk polymerization of multifunctional acrylate monomers. Using this technique, the nature of the reaction, rate of the reaction, and other kinetic parameters have been evaluated. A reaction window

Table V Effect of Initiators on Crosslinking of DEGDA at 10°C/Min Heating Rate with 1.0% Concentration of Different Initiators; Values Obtained from DSC Thermograms

Initiator	ΔH_p (J/g)	T_i (°C)	t (min)
ABCVA	646.5	73.3	2.00
AIBN	621.5	58.63	3.00
BPO	624.4	61.86	2.79

For ΔH_p, T_i, and t, see Table IV.

profile has been proposed to predict the entire course of reaction. DSC curves of nonisothermal bulk polymerization of these multifunctional acrylate monomers indicated that the heat of polymerization, activation energy, and rate of polymerization decreases with the increase in the number of alkyl group in the monomer chain. Oxygen inhibition of acrylate polymerization is manifested by a delay in the onset of an exotherm under air atmosphere. ABCVA was found to be the most efficient initiators among BPO, AIBN, and ABCVA.

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