

Polymers for Information Storage Systems.

II. Polymerization Kinetics for Preparation of Highly Crosslinked Polydimethacrylates

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SYNOPSIS

Polymers of ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate, and tetraethylene glycol dimethacrylate were prepared by photoinitiated polymerizations in the presence of 2,2-dimethoxy-2-phenyl-acetophenone at 27°C. The reactions led to highly crosslinked polymeric networks. The volume shrinkage observed during polymerization was a function of the number of ethylene glycol units in the dimethacrylate monomer. The kinetic rate constants of polymerization, as determined from the photopolymerization characteristics using a dilatometric technique, were again dependent on the number of ethylene glycol units in the monomer. The importance of these results on the crosslinked structure of the prepared networks is discussed.

INTRODUCTION

Among various information storage systems and devices, laser videodiscs (LVD) have attracted significant interest.^{1,2} In one of the two most important manufacturing processes of such discs, the Philips 2p process,³⁻⁹ a glass master is used to make a succession of metal discs that are used in production of the final LVD. In the 2p process the replicate, a thin polymer coating, is made by coating the metal master with a thin layer of monomer or group of monomers with a small percentage of dissolved photoinitiator. This mixture is exposed to ultraviolet (UV) light to polymerize. After the polymerization is complete, the lacquer layer and substrate are removed from the master, the replicate is coated with a reflective material and, finally, a protective layer is applied.⁵

In the present work, we investigate the kinetics of typical polymerization reactions of dimethacrylates which can be candidates for LVD materials. Some of the novel polymers that are presently considered for LVD applications include highly cross-

linked or highly branched structures which are glassy below approximately 50°C and show considerable transparency. Kloosterboer and his associates⁶ have experimented with ethylene glycol acrylates and related materials for this purpose. In addition, Gossink⁴ has discussed the relative characteristics of a variety of other polymeric materials.

In our laboratory we are experimenting with multifunctional forms of dimethacrylate monomers, i.e., methacrylates containing two double bonds. Until now these systems have been used predominantly as crosslinking agents during the copolymerization of hydrophilic monomers for the production of important biomedical polymers.¹⁰ For example, these monomers have been used as crosslinking agents for styrene^{11,12} and 2-hydroxyethyl methacrylate.¹³ Also, polydimethacrylate networks are widely used in dental applications.¹⁴⁻¹⁶

The poly(ethylene glycol dimethacrylate)s studied here have been investigated by only a few researchers before. Hubca et al.¹⁷ and Miyazaki and Horibe¹⁶ experimented with the bulk and solution polymerization of these chemicals observing that in thin layer polymerization autoacceleration occurs while the initial rate is maximum for thick layer polymerization. Dragan et al.¹⁸ investigated the kinetics of these polymerizations and determined that

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the nature of the polymerization process is independent of the number of ethylene glycol units. Kloosterboer and Litjen¹⁹ determined some of the thermal and mechanical characteristics of poly(tetraethylene glycol dimethacrylate) which was photochemically initiated. It was shown that increasing either the temperature or the light intensity caused an increase in the conversion of the double bonds. However, complete kinetic analysis of these reactions is not available.

EXPERIMENTAL

Materials

Ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), and tetraethylene glycol dimethacrylate (TeEGDMA) were obtained from Aldrich Chemical Co. (Milwaukee, WI). They were polymerized by radical polymerization initiated by UV light. In a typical experiment approximately 3 cm³ of monomer were mixed with about 5 wt % photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone. Monomers and initiator were used as received. The liquid mixture was placed in flat bottomed aluminum pans which were placed under an ultraviolet (UV) lamp (Model UVGL-58, UVP, San Gabriel, CA) and irradiated (polymerized and crosslinked) at intensities varying from 1 to 2 × 10⁻⁶ einsteins/L s (at 366 nm). Intensities were measured by a UV meter (Black-Ray ultraviolet meter, Model J221, UVP, San Gabriel, CA). Polymerization reactions were performed under a nitrogen atmosphere with temperatures from 22 to 27°C. The thin film monomer samples remained under the nitrogen atmosphere for a period of at least 12 h in order to remove dissolved oxygen from the samples. It was found that temperatures within the sample remained constant as no thermal relaxation was observed upon removal of the UV source. The above intensities, concentrations and atmospheric conditions correspond to reaction times ranging from 10 min to 1 h.

The kinetics of the reaction was followed by dilatometric studies. Small quantities of the monomers were mixed with 2,2-dimethoxy-2-phenyl-acetophenone in NMR tubes at initiator concentrations varying from 5 to 15 wt %. The tubes were exposed to UV intensities ranging from 0.5 to 2 × 10⁻⁶ einsteins/L s. The height of the polymerizing solution was measured throughout the experiment with a cathetometer and the volume change and percent

conversion were followed as a function of time. Additional experiments were run at lower intensities (from 0.1 to 0.5 × 10⁻⁶ einsteins/L s) in order to determine the total volume shrinkage upon polymerization. These experiments were followed until the polymerization reaction was complete, approximately 1 h at these intensities.

RESULTS AND DISCUSSION

Crosslinked Structure

Because of their two bonding sites, these monomers have in the past typically been used as crosslinking agents in copolymerizations.¹⁰ However, the tendency of these monomers to form highly crosslinked, glassy materials makes them a logical choice for laser video disc and other similar applications. Due to the existence of two double bonds per monomer, the ensuing polymer from all polymerization reactions was a polymeric network. Theoretically, polymeric networks of PTeEGDMA should be less crosslinked than those of PEGDMA due to the longer ethylene glycol-containing chain between two consecutive potential crosslinks (junctions).

Some investigators have reported the effects of oxygen as an inhibitor in UV-catalyzed reactions. The reported decrease²⁰ in yield due to oxygen was up to 80%. The effect of oxygen was noted in these experiments as well. Initial experiments carried out under conditions with atmospheric and dissolved oxygen revealed a significant fraction of unreacted monomer at final conversion. Further experiments with no dissolved or atmospheric oxygen had no unreacted monomer. All results are for monomers polymerized in the absence of oxygen. The polymer samples showed a slight yellowish color which appeared to be characteristic of the initiator. It has also been observed in other UV-catalyzed reactions.²¹ In early experimental studies other photoinitiators were tested such as acetophenone and 2-chlorothioxanthene-9-one. Both were found to be entirely unreactive for the monomers studied here. The initiator 2,2-dimethoxy-2-phenyl-acetophenone was used.

Both the extinction coefficient and the quantum yield were determined by identical experiments with methyl methacrylate where light intensity and initiator concentration were kept at the same level. Because the kinetic constants are known for methyl methacrylate, the extinction coefficient and the quantum yield could be determined. It was found that at the exposed wavelength of 366 nm, the ex-

tion coefficient was 32 L/mol cm and the quantum yield was found to be 1.

Volume Shrinkage during Polymerization

One of the requirements for monomers used in the production of polymers for LVD applications involving the 2p processing method is low volume change (shrinkage) upon polymerization. This is essential because replicate formation requires a close contact between the polymer and the mold. Available work on volume shrinkage of methacrylate monomers reports shrinkages as high as 21% for methyl methacrylate and as low as 8.1% for the 16-carbon methacrylate.^{22,23}

Kinetic studies were performed by following the volume change through complete conversion using a dilatometric technique. Thus, the volume shrinkage was calculated and correlated with the size of the monomer chain. The results of this study are shown in Figure 1. It is clear that, as the number of ethylene glycol units in the monomer increased, the volume shrinkage during polymerization decreased. Since the highest degree of crosslinking should cause the greatest volume shrinkage, it appears that PEGDMA is the most crosslinked while PTeEGDMA is the least crosslinked network. Similar experiments on monomethacrylates support this trend of decreasing volume shrinkage for increasing molecular weight of monomers.²² All of the dimethacrylate polymerizations carried out led to a

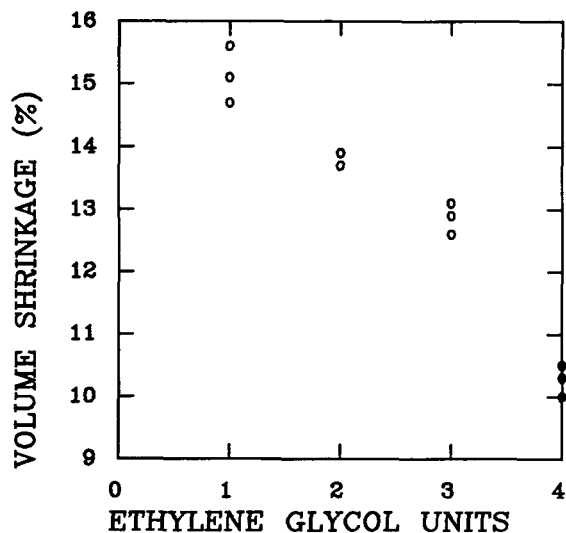


Figure 1 Percentage of volume shrinkage during polymerization of dimethacrylate monomers at 24°C as a function of the number of ethylene glycol units in the monomer structure.

lower volume shrinkage than polymerization of poly(methyl methacrylate) (PMMA), currently used for LVD manufacture.

Kinetics

The investigation of the polymerization kinetics was done using dilatometric techniques at room temperature. In the classical photopolymerization theory the rate of polymerization is expressed as a function of the volume shrinkage^{24,25} by

$$R_p = \frac{\Delta V}{V[1/\rho_m - 1/\rho_p]M\Delta t} \quad (1)$$

where R_p is the rate of polymerization, V is the volume of the system, ρ_m is the monomer density, ρ_p is the polymer density, M is the molecular weight of the monomer, and Δt is the elapsed time for the volume change, ΔV , to occur.

Therefore, in a typical experiment the change of volume as a function of time was recorded and the polymerization rate was calculated using the above equation. Then, to determine the kinetic constants for the reaction, the rate of reaction, R_p , is²⁴

$$R_p = k_p[M](R_i/2k_t)^{1/2} \quad (2)$$

where k_p is the rate constant for propagation, k_t is the rate constant for termination, $[M]$ is the monomer concentration, and R_i is the rate of initiation which, for a photopolymerization, can be expressed as²⁴

$$R_i = 2\phi I_0[1 - e^{-\epsilon(A)b}] \quad (3)$$

where ϕ is the quantum yield of the initiator, ϵ is the extinction coefficient of the initiator, b is the thickness of the reaction vessel, and I_0 is the incident light intensity in terms of light quanta per unit volume and time. The energy per mole of light quanta (also referred to as an einstein) is equal to $Nh\nu$, where N is Avogadro's number, h is Planck's constant, and ν is the frequency of the incident light. Finally, the rate becomes²⁴⁻²⁶

$$R_p = \frac{k_p}{k_t^{1/2}} [M] [\phi I_0 (1 - e^{-\epsilon(A)b})]^{1/2}$$

Thus, the kinetic constant to be determined from this analysis is $k_p/k_t^{1/2}$, but, to determine this constant, ϵ and ϕ must be known for the initiator.

As previously mentioned, both of these values were determined from the known value of $k_p/k_t^{1/2}$

at zero percent conversion of methyl methacrylate. This value at 24°C is approximately 0.06 (L/mol s)^{1/2}. At 366 nm $\phi \sim 1$ and $\epsilon = 32$ L/mol cm.

Using these values of ϕ and ϵ , the kinetic constants for the polymerization reactions of EGDMA, DEGDMA, TrEGDMA, and TeEGDMA, $k = k_p/k_t^{1/2}$, were calculated and shown in Figure 2. It appears from these results that the product of rate constants, $k_p/k_t^{1/2}$, increased as the number of ethylene glycol units increased. The rate constant for TeEGDMA was more than twice that of EGDMA and nearly six times greater than the rate constant for MMA reaction. The rate constant for EGDMA was approximately three times greater than that for MMA. This increased reactivity could reduce production time up to six times if these rate constants were maintained at the higher intensities used in production.

These dimethacrylate monomers appear to show autoacceleration since the rate of polymerization increased as conversion increased. Because of autoacceleration it was important to use initial volume change per unit time when computing rate constants. Thus, the kinetic constants calculated are only accurate for initial rates. The kinetics of polymerization can be analyzed for all samples studied here as shown in Figures 3–6. It is evident from the figures that, for all of the polymerization reactions, at some point as conversion increased so did the rate of reaction. Typically, autoacceleration began between 25 and 35% conversion. This is near the

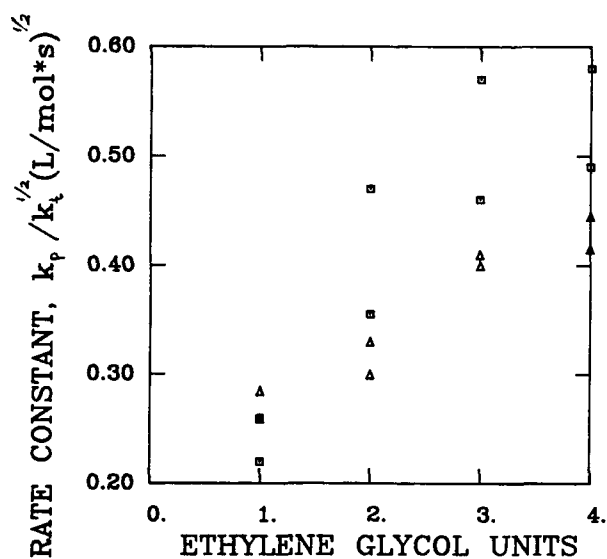


Figure 2 Overall polymerization rate constant $k_p/k_t^{1/2}$ for dimethacrylate monomers reacted at 24°C (Δ) and 27°C (□) as a function of the number of ethylene glycol units in the monomer structure.

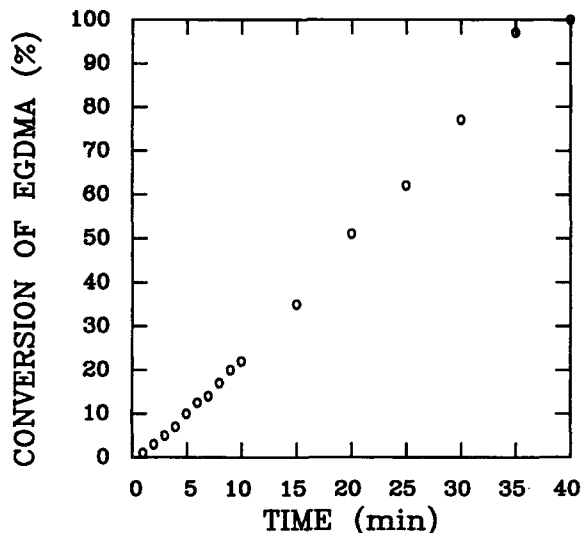


Figure 3 Conversion during bulk polymerization of EGDMA at 24°C indicating a slight autoacceleration effect.

theoretical gel point of 33% conversion for tetra-functional monomers, assuming equal reactivity of functional groups. This is the defining characteristic of autoacceleration reactions. This phenomenon will drastically reduce production times for reactions of this type.

From these figures, the conversion X was related to volume change^{25,26} by

$$X = \Delta V \rho_p / V (\rho_p - \rho_m) \quad (4)$$

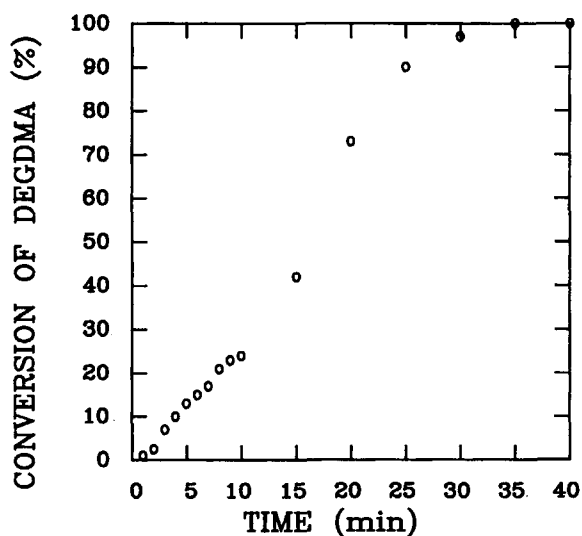


Figure 4 Conversion during bulk polymerization of DEGDMA at 24°C indicating a significant autoacceleration effect.

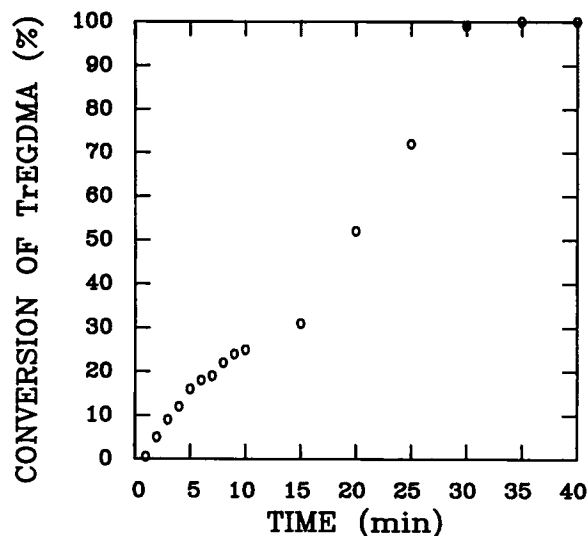


Figure 5 Conversion during bulk polymerization of TrEGDMA at 24°C indicating a significant autoacceleration effect.

Overall activation energies and preexponential constants, k_0 , were calculated and are shown in Table I for DEGDMA through TeEGDMA. Experimental error was too large to allow for an estimation of these parameters for EGDMA. These activation energies represent the activation energy of propagation minus half of the activation energy of termination. The activation energies ranged from 11 to 14 kcal/mol and decreased from DEGDMA to TeEGDMA implying that increased temperature

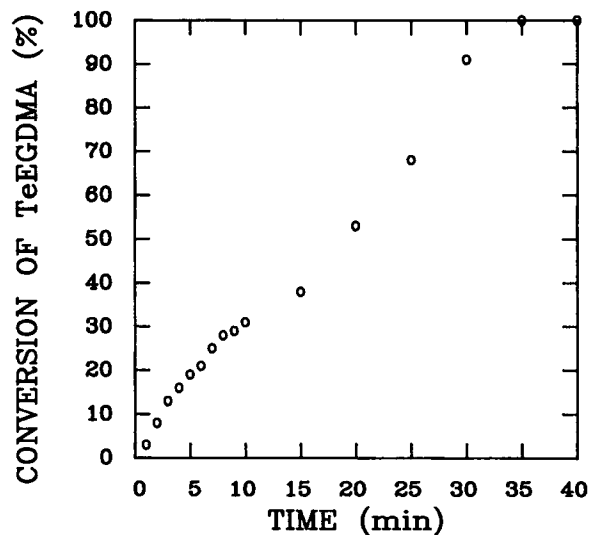


Figure 6 Conversion during bulk polymerization of TeEGDMA at 24°C indicating a significant autoacceleration effect.

Table I Activation Energy and Preexponential Terms of Kinetic Constants

Monomer	Activation Energy ΔE (kcal/mol)	k_0 (L/mol s) ^{1/2}
DEGDMA	14 ± 1	7 × 10 ⁹ ± 1 × 10 ⁹
TrEGDMA	12 ± 1	2 × 10 ⁸ ± 3 × 10 ⁷
TeEGDMA	11 ± 1	5 × 10 ⁷ ± 7 × 10 ⁶

will favor DEGDMA production. These results are of the same magnitude as the studies of Moore et al.²⁷ with other related diacrylates and dimethacrylates.

CONCLUSIONS

This work demonstrated that dimethacrylate monomers such as EGDMA, DEGDMA, TrEGDMA, and TeEGDMA were reactive to UV light under atmospheric conditions or in a nitrogen atmosphere. The volume shrinkage during these polymerization reactions ranged from 10 to 16% and decreased as the number of ethylene glycol groups increased. The polymerization rate term, $k = k_p/k_t^{1/2}$, increased with the number of ethylene glycol groups. It appears from these results that, in the areas of volume shrinkage and polymerization rates, the ethylene glycol dimethacrylates are significant improvements over methyl methacrylate.

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