

# Polymers for information storage systems III. Crosslinked structure of polydimethacrylates

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Polymers of ethylene glycol dimethacrylate, diethylene glycol dimethacrylate, triethylene glycol dimethacrylate and tetraethylene glycol dimethacrylate were produced by photopolymerization using the photoinitiator 2,2-dimethoxy-2-phenyl-acetophenone. These polymerization reactions and the resulting materials were examined as to their feasibility for production of laser video discs using the 2p process. The volume shrinkage during polymerization, swelling characteristics, molecular weight between crosslinks and the glass transition temperature of the polymeric networks were determined and compared with the characteristics of polymers presently used in laser video disc production. The networks produced by the polymerization of these monomers were highly crosslinked with glass transition temperatures greater than 200°C. They swelled little in any of four solvents used with a maximum volume fraction of the solvent at equilibrium lower than 10%.

(Keywords: laser video discs; dimethacrylates; crosslinking; network; swelling)

## INTRODUCTION

### *Storage information systems*

The technical challenges in the area of information storage including development of devices with increased speed, decreased costs and higher information density call for improved laser video discs (LVD). LVD are similar to compact discs in that they store digital information which is read by a laser, but LVD also contain optical information.

In the last decade LVD systems have achieved great popularity in the United States and in Europe<sup>1</sup>. These discs are the size of long playing records and contain<sup>2</sup> approximately five billion bits of information per square cm. With the ability to store and easily access this volume of information, LVD could be the primary means of data storage in the future. For this reason perfecting the production process, elongating the life of the disc and lowering the costs involved in producing the disc are important areas of research.

LVD can be manufactured by a moulding process or by the Philips 2p process<sup>3-6</sup>. The Philips 2p process uses a glass master 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 a monomer or group of monomers with a small percentage of dissolved photoinitiator. This mixture is exposed to ultraviolet 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<sup>5</sup>.

The information stored on an optical disc is stored in

much the same way that information is stored on a typical long playing record. It is stored in a spiral track which consists of a series of pits which represent the digital indices 1 and 0. These pits are read from the disc with a laser whose light passes through an optical lens before being focused on the disc. The laser light is then reflected back through the objective lens and passed on to the detector. The detector is able to distinguish whether the index read was a 1 or 0 by the intensity of reflected light. The pits (approximately 0.1  $\mu\text{m}$  deeper than the spaces) reflect less light than the spaces.

### *Polydimethacrylates as polymers for LVD coatings*

At present there are significant problems in the production of the replicate. To make a high quality disc, the replicate must have certain physical properties which include<sup>5,7-10</sup>: low absorption at 630 nm; low birefringence (a measure of the homogeneity of the polymer); glass transition temperature between 90°C and 120°C; dimensional stability; thermal stability; extremely low moisture absorption; low volume change upon polymerization; a monomer with low viscosity; ability of the polymer to release from mould; and surface hardness.

In the actual production of the disc the monomers need to have low viscosity so that they can flow quickly and easily onto the mould. Low volume change upon polymerization and easy release from the mould are critical to obtain an exact replicate. A fairly high glass transition temperature, dimensional and thermal stability, low moisture absorption, and surface hardness increase the useful life of the disc. In order to obtain many of the above characteristics such as a high glass transition temperature, low moisture absorption, and surface hardness a very high degree of crosslinking of the final polymer is needed. If the system has a very low molecular weight between crosslinks (i.e. a high degree of crosslinking), then the chains tend to be immobile which leads to a high glass transition temperature and surface hardness.

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Also, the average mesh size is reduced as the crosslinking increases. This renders the polymer more hydrophobic and, at high enough degrees of crosslinking, enables the material to reject almost all water. Unfortunately, the volume change (shrinkage) upon polymerization increases as the system becomes denser (i.e., at higher crosslinking densities).

At present, materials used for LVD production include poly(methyl methacrylate) (PMMA), polycarbonates and polystyrene. PMMA is preferred over other materials because of its relatively high isotropy (low birefringence), low light absorption, high glass transition temperature and low cost. However, it has significant problems, notably high moisture absorption which may lead to warping of the disc.

Novel polymers based on reactions of diacrylates have been considered for LVD applications. They include highly crosslinked or highly branched structures which are glassy below approximately 50°C and show considerable transparency<sup>4,6</sup>. Dimethacrylates are now considered as candidates for LVD systems although they have been most prominently used as crosslinking agents in other reactions<sup>11</sup>. For example, these monomers have been used as crosslinking agents for styrene<sup>12,13</sup> and hydroxy ethyl methacrylate<sup>14,15</sup>. Polydimethacrylate networks have been used as dental biomaterials<sup>16-20</sup>.

Some of the properties of poly(multiethylene glycol dimethacrylates) have been reported before. Hubca *et al.*<sup>21</sup> experimented with the bulk and solvent polymerization of these chemicals observing that in thin layer polymerization autoacceleration occurs while the initial rate is the maximum for thick layer polymerization. Drăgan *et al.*<sup>22</sup> studied the kinetics of these polymerizations and determined that the nature of the polymerization process is independent of the number of ethylene glycol units. Kloosterboer<sup>23,24</sup> 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<sup>25,26</sup>.

The different applications of polymers in today's audio and video industries were described by Gossink<sup>4</sup>, Pearson<sup>2</sup>, Kloosterboer *et al.*<sup>6</sup>, Arakawa<sup>7</sup> and Fujiwara<sup>27</sup> discussed the relative value of the different polymers used in LVD systems as well as describing the physical and chemical properties of these materials such as poly(methyl methacrylate), polystyrene and polycarbonates. The goals of the present work were to study the properties of several multiethylene glycol dimethacrylates and to determine their possible use as coatings for LVD systems.

## EXPERIMENTAL

### Preparation of polymers

Ethylene glycol dimethacrylate (EGDMA, MW = 198.24,  $\rho = 1.043 \text{ g/cm}^3$ ), diethylene glycol dimethacrylate (DEGDMA, MW = 242.30,  $\rho = 1.052 \text{ g/cm}^3$ ), triethylene glycol dimethacrylate (TrEGDMA, MW = 286.36,  $\rho = 1.055 \text{ g/cm}^3$ ) and tetraethylene glycol dimethacrylate (TeEGDMA, MW = 330.42,  $\rho = 1.051 \text{ g/cm}^3$ ) were the monomers of choice for the polymerization reactions. They were purchased from Aldrich Chemical Co., Milwaukee, WI and used as received.

In a typical experiment approximately 3 cm<sup>3</sup> of monomer were mixed with about 5 wt% 2,2-dimethoxy-2-phenyl-acetophenone as a photoinitiator. The liquid mixture was placed in flat-bottomed aluminium pans which were placed under an ultraviolet lamp (Model UVGL-58; UVP, San Gabriel, CA) and irradiated (polymerized and crosslinked) at intensities varying from 1 to  $2 \times 10^{-6}$  einsteins/l s (at 366 nm). Intensities were measured by a u.v. meter (Black-Ray Ultraviolet Meter, Model No. J221, UVP, San Gabriel, CA). Production of the polymer samples was achieved under atmospheric conditions and under a nitrogen atmosphere at temperatures from 22°C to 27°C. The above intensities, concentrations, and atmospheric conditions corresponded to reaction times ranging from 10 min to 1 h. The shrinkage of the samples during polymerization was measured by dilatometry, using a cathetometer to study the height change in small diameter tubes.

Upon completion of the polymerization, the thin circular polymer samples were cut into 0.5 cm<sup>2</sup> squares which were used for property measurements. All polymer samples were kept in desiccators until use.

### Characterization

The glass transition temperature was determined in a thermomechanical analyser (model TMS-2, Perkin Elmer, Norwalk, CT) with a scanning speed of 10°C/min.

Swelling studies were performed in methanol, methyl ethyl ketone, xylene, and isobutanol. In a typical experiment thin squares of the polymer samples were placed in the appropriate swelling agent and swollen at 40°C up to equilibrium. The samples were then dried, first at room temperature for three days, then at 60°C and 100 mm Hg for two days and the final weight of the dry sample was measured. From these results, the equilibrium polymer volume fraction,  $v_2$ , was measured and the crosslinked structure characteristics were determined.

## RESULTS AND DISCUSSION

### Preparation of crosslinked polymers

The dimethacrylate monomers used here were selected because of their ability to form highly crosslinked networks. These are important in achieving some of the desired properties of LVD materials such as high glass transition temperature, low moisture absorption and surface hardness. These monomers also have a relatively low viscosity and form transparent polymers, both necessary properties for better LVD lacquers.

The most important quality about these monomers was their ability to go through radical polymerization initiated by u.v. light. Some investigators have reported the effects of oxygen as an inhibitor in u.v. catalysed reactions. The reported decrease in yield was up to five times<sup>28</sup>. This decrease was observed as some dimethacrylate monomer remained when the reaction was performed under atmospheric conditions. Under a nitrogen atmosphere there was no visible unreacted monomer after a much shorter time.

The glass transition temperatures for PEGDMA, PDEGDMA, PTrEGDMA and PTeEGDMA were 271°C, 250°C, 248°C and 279°C, respectively. These extremely high glass transition temperatures are indicative of the high crosslinking density of these polymers. The glass transition temperature of PMMA (the polymer

currently used in LVD manufacture) is 105°C. Thus, with the new polymers, an increased thermal stability of the replicate is achieved.

In general, the glass transition temperatures should decrease with increasing number of ethylene glycol groups because the mobility of the chains will be greater. This is observed with all polymer networks, excluding PTeEGDMA. One possible explanation for this result is that as the chain between crosslinks becomes larger, a very slight degree of alignment of chains occurs that reduces their mobility. This alignment may occur in the longer chains as they have a longer ethylene glycol structure.

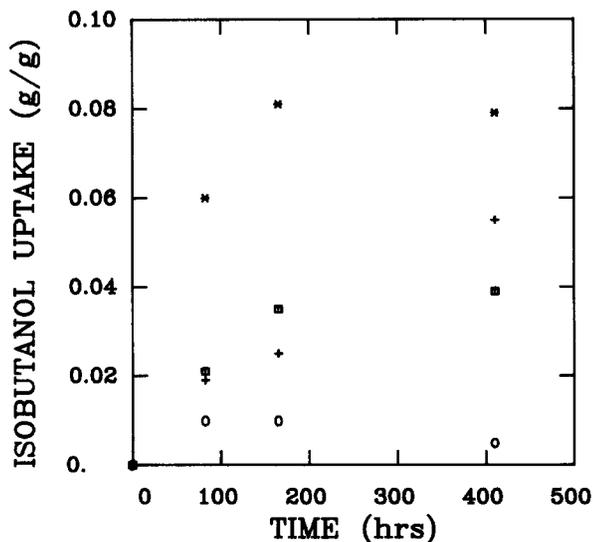
*Volume shrinkage*

Low volume change upon polymerization is essential because, during replicate formation, the transfer of the exact detail of the pits requires a close contact between the polymer and mould. If the polymer has a large volume contraction it pulls away from the mould and causes incorrect transfer of data. The only available data on volume shrinkage of methacrylate monomers reports shrinkages of as high as 21% for methyl methacrylate and as low as 8.1% for the 16 carbon methacrylate<sup>29</sup>.

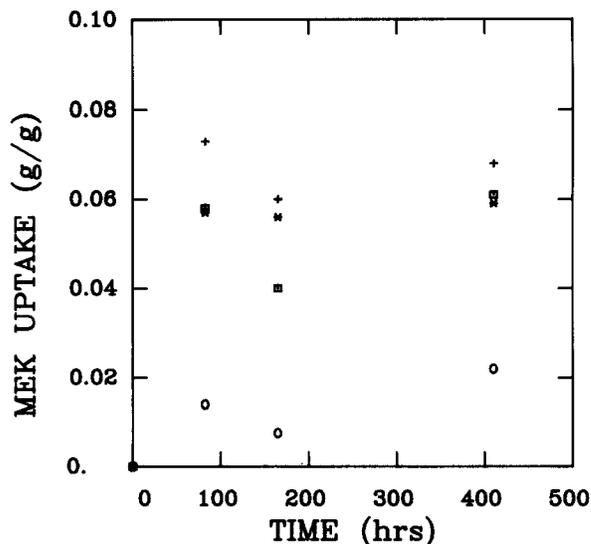
Volume shrinkage studies were done by following the polymerization volume change through complete conversion using a dilatometric technique involving small diameter tubes and a cathetometer. The results are shown in Table 1. It is clear that as the number of ethylene glycol units increases the volume shrinkage decreases. The highest degree of crosslinking should cause the greatest volume shrinkage. Because of this trend, it would

**Table 1** Average volume shrinkage during polymerization reactions

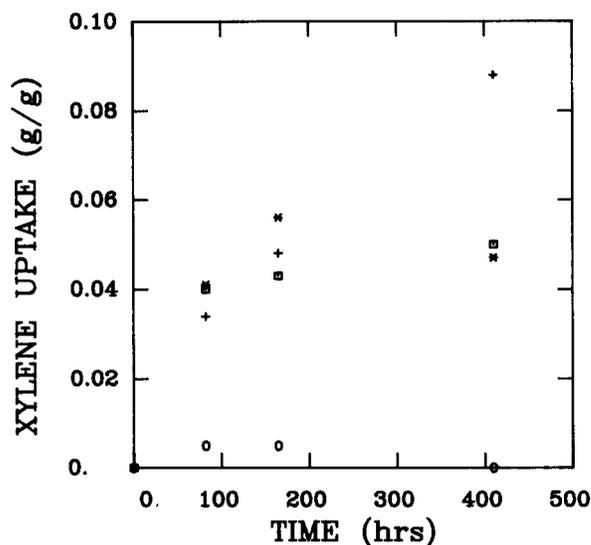
Monomer	Average Volume Shrinkage (%)
MMA	15.0
EGDMA	15.1
DEGDMA	13.8
TrEGDMA	12.0
TeEGDMA	10.3



**Figure 1** Isobutanol uptake in polydimethacrylate networks at 40°C. Swelling studies for PEGDMA (○), PDEGDMA (□), PTrEGDMA (+) and PTeEGDMA (\*)



**Figure 2** Methyl ethyl ketone uptake in polydimethacrylate networks at 40°C. Swelling studies for PEGDMA (○), PDEGDMA (□), PTrEGDMA (+) and PTeEGDMA (\*)



**Figure 3** Xylene uptake in polydimethacrylate networks at 40°C. Swelling studies for PEGDMA (○), PDEGDMA (□), PTrEGDMA (+) and PTeEGDMA (\*)

appear that PEGDMA is the most crosslinked while PTeEGDMA is the least crosslinked.

*Swelling characteristics*

The experimental studies of swelling agent uptake into the crosslinked polymers as a function of time at 40°C can be used to evaluate the crosslinked structure of the novel polymers as well as the diffusive characteristics of these materials. Figures 1-4 show weight uptake of four swelling agents (methanol, isobutanol, methyl ethyl ketone (MEK), and xylene) for the four polymeric networks studied here. The data are expressed in g of swelling agent per g of dry polymer plotted against time.

The equilibrium values of the four different polymers in the four different swelling agents are presented in Table 2. These data show that the crosslinked networks are not affected by these swelling agents indicating the high crosslinking density of these systems. Again, it

Table 2 Equilibrium swelling analysis of polydimethacrylates at 40°C

Polymer	Swelling agent	Equilibrium uptake g/g	Equilibrium polymer volume fraction, $v_2$	Flory interaction parameter, $\chi_1$	Mol. wt. $\bar{M}_c$
PEGDMA	Xylene	0.0050	0.992	2.046	225
	Methanol	0.0354	0.947	0.772	
	MEK	0.0231	0.966	1.280	
	Isobutanol	0.0100	0.985	0.401	
PDEGDMA	Xylene	0.0663	0.914	1.478	325
	Methanol	0.0346	0.949	0.972	
	MEK	0.0667	0.908	0.972	
	Isobutanol	0.0386	0.945	0.341	
PTrEGDMA	Xylene	0.0817	0.894	1.176	375
	Methanol	0.0730	0.896	1.119	
	MEK	0.0769	0.893	0.742	
	Isobutanol	0.0052	0.925	0.349	
PTeEGDMA	Xylene	0.0796	0.900	0.989	400
	Methanol	0.0338	0.951	1.233	
	MEK	0.0650	0.911	0.632	
	Isobutanol	0.0793	0.894	0.376	

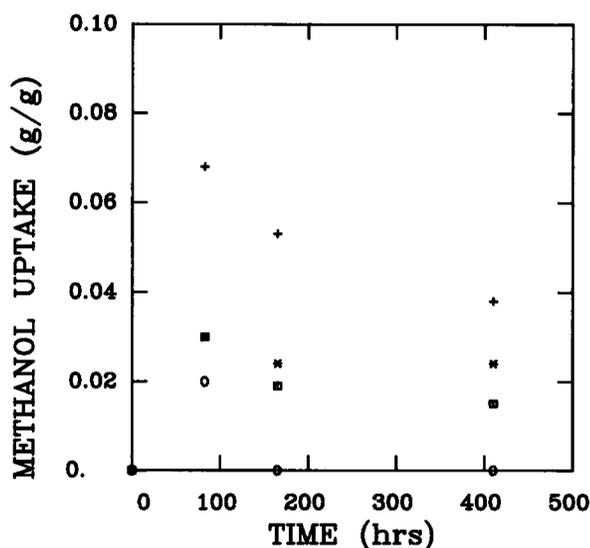


Figure 4 Methanol uptake in polydimethacrylate networks at 40°C. Swelling studies for PEGDMA (○), PDEGDMA (□), PTrEGDMA (+) and PTeEGDMA (\*)

appears that PEGDMA is more crosslinked than the other three polymers. This would agree with recent simulations<sup>10,30</sup>.

The equilibrium swelling data could be used to calculate the molecular weight between crosslinks,  $\bar{M}_c$ . A non-Gaussian chain distribution equation was used<sup>31</sup>.

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} \frac{(\bar{v}/V_1)[\ln(1-v_2) + v_2 + \chi_1 v_2^2] \left[1 - \frac{1}{N} v_2^{2/3}\right]^3}{\left(v_2^{1/3} - \frac{v_2}{2}\right) \left(1 + \frac{v_2^{1/3}}{N}\right)^2} \quad (1)$$

Here  $\bar{M}_n = 75\,000$  as discussed before<sup>32</sup> for similar systems,  $\bar{v}$  is the specific volume of the polymer (equal to the reciprocal of its density),  $V_1$  is the molar volume of the swelling agent,  $\chi_1$  is the Flory polymer-swelling agent interaction parameter, and  $v_2$  is the polymer volume fraction. The term  $N$  is defined as:

$$N = 2\bar{M}_c/M_r \quad (2)$$

where  $M_r$  is the molecular weight of the repeating unit.

For the calculations in this work, the specific volume of the polymers prepared was calculated from the corresponding densities of 1.229 g/cm<sup>3</sup> for PEGDMA, 1.221 g/cm<sup>3</sup> for PDEGDMA, 1.211 g/cm<sup>3</sup> for PTrEGDMA, and 1.175 g/cm<sup>3</sup> for PTeEGDMA. The values of the molar volume of the swelling agent were 40.4, 89.6, 122.2 and 92.5 cm<sup>3</sup>/mol for methanol, methyl ethyl ketone, xylene and isobutanol, respectively. For the calculation of the equilibrium polymer volume fraction,  $v_2$ , the following equation was used.

$$v_2 = \frac{M_p/\rho_p}{(M_p/\rho_p) + (M_s/\rho_s)} \quad (3)$$

where  $M_p$  is the dry polymer weight,  $\rho_p$  is the polymer density,  $M_s$  is the mass of swelling agent at equilibrium and  $\rho_s$  is the swelling agent density. Finally, the values of the  $\chi_1$  factor which are reported in Table 2 were calculated by Brannon-Peppas<sup>33</sup> using the theory of Mikos and Peppas<sup>34</sup>.

The results of these calculations using equations (1) and (2) are shown in Table 2. It is concluded that there are only two to three repeating units between crosslinks in the networks produced here. At this degree of crosslinking, equation (1) is at its limit of applicability and the calculations should only be considered approximate. The high degree of crosslinking inferred by the data of  $\bar{M}_c$  of Table 2 supports the conclusions drawn from the glass transition temperature and volume shrinkage experiments. It appears that the number of repeating units between crosslinks is fairly constant while the molecular weight between crosslinks rises as the number of ethylene glycol groups in the monomer rises.

High degrees of crosslinking should provide stable LVDs and other information systems, both thermally due to the high glass transition temperature and mechanically due to a nearly zero water absorption and a hard solid surface.

## CONCLUSIONS

It is concluded that PEGDMA, PDEGDMA, PTrEGDMA and PTeEGDMA produce highly crosslinked structures (two to three repeating units between

crosslinks) with the molecular weight between crosslinks increasing from PEGDMA to PTEGDMA. The dimethacrylate monomers are highly reactive to u.v. light at room temperature. The volume shrinkage observed during the polymerization reactions is low relative to MMA and decreases with increasing size of the monomer. Finally, the glass transition temperatures for these polymers are extremely high, assuring thermal stability.

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