Polymers for information storage systems
I. Preparation and properties of highly crosslinked polydimethacrylates

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Summary

Various multiethylene glycol dimethacrylates were polymerized by UV light in the presence of 2,2-dimethoxy-2-phenyl-acetophenone as a photoinitiator. The ensuing highly crosslinked polydimethacrylates were characterized by thermomechanical analysis and swelling studies. The crosslinked structure was investigated and kinetic aspects of the reactions were analyzed.

Introduction

In recent years there has been an explosion in the development of devices and systems for the storage and handling of information. Laser video discs (LVD) are one of the most promising forms of this technology (1). Laser video discs are similar to compact discs in that they store digital information which is read by a laser, but LVD also contain optical information. They are a combination of video tape and compact discs but have greater capacity and easier access than either compact discs or video tapes.

They can be manufactured by two significantly different processes, a molding process (2) or the Philips 2p process (3-6). The later process begins with a glass master which is used to make a succession of metal discs that are used in production of the final LVD. The replicate, a thin polymer coating, is made by coating the metal master with a thin layer of a monomer or group of monomers (lacquer) 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.

At present time 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 (2,7): (i) low absorption at 630 nm; (ii) low birefringence (a measure of the homogeneity of the polymer); (iii) glass transition temperature between 90°C and 120°C; (iv) dimensional stability; (v) thermal stability; (vi) extremely low moisture absorption; (vii) low volume change upon polymerization; (viii) low viscosity monomer; (ix) ability of the polymer to release from mold; and (x) surface hardness.

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Some of the novel polymers that are presently considered for LVD applications include highly crosslinked or highly branched structures which are glassy below approximately 50°C and show considerable transparency. Kloosterboer *et al.* (6) have experimented with ethylene glycol acrylates and related materials for this purpose. In our laboratory we are experimenting with multifunctional forms of methacrylate monomers, i.e. methacrylates containing at least two double bonds.

Experimental Part

Ethylene glycol dimethacrylate (EGDMA), diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), and tetraethylene glycol dimethacrylate (TeEGDMA) were the monomers of choice for the polymerization reactions. In a typical experiment approximately 3 cm^3 of monomer were mixed with about 5 wt% photoinitiator, 2,2-dimethoxy-2-phenyl-acetophenone. The liquid mixture was placed in flat bottomed aluminum pans under an ultraviolet (UV) lamp (Model UVGL-58, UVP, San Gabriel, CA), and irradiated (polymerized and crosslinked) at intensities varying from 1 to 2 x 10^{-6} einsteins/L s (366 nm). Intensities were measured by a UV meter (Black-Ray ultraviolet meter, model No. J221, UVP, San Gabriel, CA). Production of the polymer samples was achieved both under atmospheric conditions and under a nitrogen atmosphere. Reaction temperatures ranged from 22°C to 27°C for 10 min to 1 hr. Thin circular samples of the polymers were obtained, which were cut into 0.5 cm^2 squares.

Small quantities of the monomers were also mixed with the selected photoinitiator, 2,2-dimethyl-2-phenyl-acetophenone, in NMR tubes at initiator concentrations varying from 5 to 15 wt% to study the reaction kinetics. The NMR tube was sealed at atmospheric conditions and exposed to UV intensities ranging from 0.5 to 2 x 10^{-6} einsteins/L s. The height of solution was measured throughout the experiment (dilatometry) as a way of following the volume change and percent conversion. Additional experiments were run at lower intensities (from 0.1 to 0.5 x 10^{-6} einsteins/L s) were run in order to determine the total volume shrinkage upon polymerization.

The glass transition temperature was determined in a thermomechanical analyzer (model TMS2, Perkin Elmer, Norwalk, CT) with a scanning speed of 10°C/min starting at room temperature.

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

Crosslinked Structure and Equilibrium Swelling

All polymerization reactions led to highly corsslinked polymeric networks. The crosslinks in these cases are the carbon atoms from where the ethylene glycol bridges originate. Thus, the molecular weight between crosslinks, $\overline{M}_c$, should be the size of the ethylene glycol bridge between to CH_2=$CH(CH_3)$– structures. Consequently the degree of crosslinking should be progressively increasing from PTeEGDMA to PTrEGDMA, PDEGDMA and PEGDMA.

The glass transition temperatures for PEGDMA, PDEGDMA, PTrEGDMA, and PTeEGDMA averaged 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 polymer networks.

Equilibrium swelling studies were used to verify the highly crosslinked nature of these networks. All networks prepared were swollen to equilibrium at 25°C in xylene, methyl ethyl ketone and methanol and their equilibrium polymer volume fraction, v_2, was determined (see Table 1). The data show very high values of v_2, indicative of a highly crosslinked system. In the case of xylene and MEK swelling, PTeEGDMA was always the most swellable of the four networks, therefore the least crosslinked. The data of methanol swelling are less reliable because methanol is almost incompatible with these polymer structures.

Table 1
Equilibrium Swelling of Polymer Networks
in Various Swelling Agents

Swelling Agent	Polymer Network	Equil. Polymer Vol. Fraction, v_2
Xylene	PEGDMA	0.992
	PDEGDMA	0.914
	PTrEGDMA	0.894
	PTeEGDMA	0.900
Methyl ethyl ketone	PEGDMA	0.966
	PDEGDMA	0.908
	PTrEGDMA	0.893
	PTeEGDMA	0.911
Methanol	PEGDMA	0.947
	PDEGDMA	0.949
	PTrEGDMA	0.896
	PTeEGDMA	0.951

One of the prerequisites for coatings in LVD applications is low volume change upon polymerization. This is essential because during replicate formation the transfer of the exact detail of the pits requires a close contact between the polymer and the mold. If the polymer has a large volume contraction it will pull away from the mold and cause incorrect transfer of data.

Volume shrinkage was determined by following volume change through complete conversion using a dilatometric technique involving NMR tubes and a cathetometer. The results of this study are shown in Table 2. 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 is clear that PEGDMA is the most crosslinked while PTeEGDMA is the least crosslinked network.

Table 2
Average Volume Shrinkage During Polymerization Reaction

Monomer	Volume Shrinkage During Polymerization (%)
EGDMA	15.1
DEGDMA	13.8
TrEGDMA	12.8
TeEGDMA	10.3

The investigation of the kinetics of the various polymerization reactions was done using dilatometric techniques at room temperature. According to the classical photopolymerization theory the rate of polymerization is expressed as a function of the volume shrinkage by

$$R_p = \frac{\Delta V}{V \left[\dfrac{1}{\rho_m} - \dfrac{1}{\rho_p} \right] M \, \Delta t} \tag{1}$$

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.
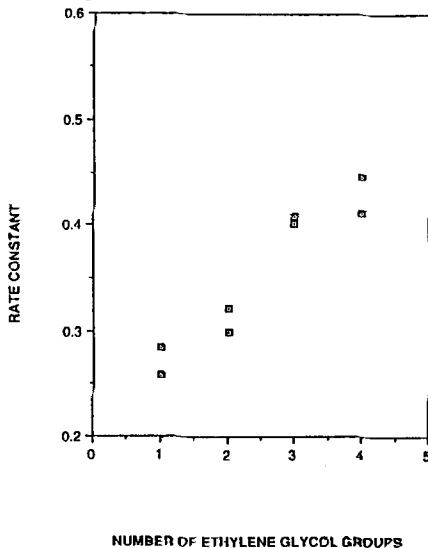

Figure 1. Rate constant of polymerization reactions of MEGDMA monomers as a function of the number of ethylene glycol groups in the monomer, at 24°C.

Therefore, in a typical experiment the change of volume as a function of time was recorded and then translated into a polymerization rate using the above equation. The volume shrinkage as a function of time was monitored, and the rate of polymerization was calculated from equation (1). After the rate was known for two initiator concentrations and two UV intensities, it was possible to calculate both ϕ and ϵ because the value of $k_p/k_t^{1/2}$ is known. The results indicated that ϕ was approximately 1 while ϵ was found to be 32 L/mol s. The determined values of the kinetic constant for the polymerization reactions of EGDMA, DEGDMA, TrEGDMA, and TeEGDMA are shown in Figure 1. It appears from these results that the rate of polymerization is greater as the number of ethylene glycol units increases. This rate constant for TeEGDMA is more than twice that of EGDMA and it is also significantly greater than the rate constant for PMMA (the polymer currently used in LVD production) which is only 1/6 the rate constant for TeEGDMA. The rate constant for EGDMA is also greater than that for PMMA. This increased reactivity could reduce production time up to 6 times if these rate constants are maintained at the higher intensities used in production.

Acknowledgments

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