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 cm³ 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 cm² 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 crosslinked polymeric networks. The crosslinks in these cases are the carbon atoms from where the ethylene glycol bridges originate. Thus, the molecular weight between crosslinks, Mₓ, should be the size of the ethylene glycol bridge between to CH₂=CH(CH₃)= structures. Consequently the degree of crosslinking should be progressively increasing from PTeEGDMA to PTrEGDMA, PDEGDMA and PEGDMA.