Polymers for information storage systems: 4. Thermal and compressive properties of polyacrylates and polymethacrylates

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Trimethylolpropane trimethacrylate, glyceryl trimethacrylate, pentaerythritol tetraacrylate and dipentaerythritol monohydroxypentaacrylate were polymerized by ultra-violet irradiation in the presence of 2,2-dimethoxy-2-phenylacetophenone as a photoinitiator. The polymerization reactions and some of the polymers' physical properties were studied to determine the possible use of these monomers as lacquers for laser video disc production. Thermal analysis and compressive creep experiments were performed to investigate the crosslinked structure of these networks.

(Keywords: methacrylates; ultra-violet polymerization; creep behaviour; acrylates)

INTRODUCTION

Laser video discs (LVD) are one of the more promising information storage methods. The LVD is similar to its audio analogue, the compact disc, in that it holds digital information that is read by a laser. LVD have easier access and higher storage capacity than compact discs. Three basic types of LVD systems exist[1]: read only, write once and reversible. The polymers investigated in this project were for use in read-only discs.

Three methods of production of read-only LVD are used[1]: photopolymerization, injection moulding and injection–compression moulding. The Philips 2p photopolymerization process begins with the formation of a glass master disc, which is then used to make a number of metal discs. The metal discs are coated with a thin layer of a monomer or a mixture of monomers, called the lacquer, to form the replicate or final disc. A small amount of photoinitiator is added to the monomer to allow it to polymerize under ultra-violet (u.v.) light. The monomer is then covered with a clear substrate that allows u.v. transmission. A mode of production described by Johnson and Thomas[1] uses the monomer as both the coating and the substrate. Once the substrate is in place, the disc is exposed to high-intensity u.v. light for a few seconds to polymerize the coating. After this step is finished, the coating and substrate are separated from the master disc. A reflective material and then a protective layer are put on the coated layer.

The polymers used in these applications must have low light adsorption and low light scattering loss in the wavelength region of the laser; the laser beam must reach the detector with sufficient intensity. Birefringence must be at a low level to keep the detection efficiency adequate.

The copying process itself requires certain physical properties. The lacquer must be of low viscosity to allow the layer to spread quickly over the master disc. Volume change upon polymerization should be minimized to keep the integrity of the impressions (pits) in the lacquer. The polymer must be easily released from the mould, and the lacquer layer upon polymerization should adhere to the substrate layer. Finally, the surface hardness and dimensional stability should be high. Softer surfaces lead to deformation in the pit patterns[1]. The polymer should have good thermal stability and a glass transition temperature higher[2] than 90°C. Finally, moisture and chemical absorption of the material must be low to prevent warping and/or degradation of the polymer.

High surface hardness, low moisture absorption and high glass transition temperatures are related to a high degree of crosslinking in the polymer, that is a very small molecular weight between consecutive crosslinks. Unfortunately, a high degree of crosslinking increases the volume shrinkage upon polymerization. Poly(methyl methacrylate) (PMMA) was the material originally used for the lacquer and substrate[3]. It was chosen mainly because of its optical qualities, which are better than those of polycarbonates. Unfortunately, PMMA absorbs water, causing the layer to warp. With two-sided discs the warping is mostly eliminated, but this can still cause problems. In addition, PMMA undergoes a 20% volume shrinkage upon polymerization[4]. Therefore, a better polymer for the lacquer layer is needed.

Kloosterboer and collaborators[5,6] have researched diacrylates and triacrylates for use as the lacquer. They determined that these were preferred monomers because of their high rate of polymerization. LVD of very good quality were made from these monomers as single-component systems and as mixtures. Some properties of the lacquers were given[5,6]. They also found that 2,2-dimethoxy-2-phenylacetophenone (DMPA) was an optimum photoinitiator.

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Bowman *et al.*[2] tested several multiethylene glycol dimethacrylates as lacquers for LVD, as well as several different photoinitiators. They found that DMPA was the only satisfactory photoinitiator. All polymerized dimethacrylates had highly crosslinked structures with high glass transition temperatures. The dimethacrylates were very reactive to u.v. light at room temperatures with the DMPA present. Volume shrinkage during these polymerizations was fairly low compared to PMMA.

In light of the results obtained before in our laboratory, the goal of this research was to determine if multimethacrylates with three or more double bonds achieve a higher degree of crosslinking. Two trimethacrylates, a tetraacrylate and a pentaacrylate were studied as possible LVD materials. The objectives of this research were: (i) to polymerize successfully the monomers in question by exposure to ultra-violet light; (ii) to analyse thermal and mechanical properties of the polymers and to relate their thermal and mechanical properties to the crosslinked structure; and (iii) to determine if these monomers can be used as lacquers in the 2p photopolymerization process.

EXPERIMENTAL

Polymer preparation

Four monomers were used in this study. Trimethylolpropane trimethacrylate (TrMPTrMA; mol. wt 338.4, density 1.06 g cm^{-3}, 100% pure, inhibited with 175 ppm methyl ether of hydroquinone) and glyceryl trimethacrylate (GlyTrMA; mol. wt 297.33, 100% pure, inhibited with 100 ppm hydroquinone) were supplied by Aldrich Chemical Co., Milwaukee, WI. Before polymerization, the inhibitors were removed by passing them through a Dehibit-100 column (Polysciences Inc., Warrington, PA). Pentaerythritol tetraacrylate (PETeA, known as Sartomer 295; mol. wt 352.34, density 1.18 g cm^{-3}, 85% purity) and dipentaerythritol monohydroxypentaacrylate (DPEMHPeA, known as Sartomer 399; mol. wt 524.34, density 1.17 g cm^{-3}, 60% purity) were supplied by Sartomer, West Chester, PA. Any possible inhibitors were removed using a Dehibit-100 column as well.

2,2-Dimethoxy-2-phenylacetophenone (DMPA) was added to the monomers as a photoinitiator at approximately 1 wt%. For polymer preparation, a thin layer of the monomer was poured into flat-bottomed aluminium pans. These pans were placed in a nitrogen atmosphere and irradiated with 366 nm u.v. light at an intensity of approximately 10 mW cm^{-2}. The total exposure time was 1 h at temperatures ranging from 27 to 35°C. The resulting thin crosslinked polymer films were then stored in a desiccator until testing.

The shrinkage during polymerization was followed by placing the monomer/photoinitiator solution in n.m.r. tubes. The u.v. intensities were 0.5 to 1 mW cm^{-2}, and the total exposure time was again 1 h. The volume change *versus* time was measured as the change in height of the solution in the n.m.r. tubes.

Polymer characterization

Polymer samples were tested in a differential scanning calorimeter (model 990, E.I. duPont de Nemours, Wilmington, DE) to determine their glass transition temperature and other thermal characteristics. The d.s.c. was operated under a flow of nitrogen gas and at a scanning rate of 10°C min^{-1}.

Compressive creep experiments under different temperatures were carried out in a thermomechanical analyser (model TMS2, Perkin-Elmer, Norwalk, CT). The instrument was used in penetration mode with a probe of diameter 0.89 mm and a scanning speed of 10°C min^{-1}. Polymer samples were cut to the size of the probe. A load was placed on the probe assembly to provide a known compressive stress to the polymer, defined as the load divided by the cross-sectional probe tip area. Temperature and sample thickness were measured as a function of time. The compressive strain, $\varepsilon(T)$, was measured as the ratio of thickness change divided by the initial thickness.

The same equipment was also used to measure the time dependence of the compressive strain on the polymer under a constant stress at a specific temperature. In these experiments the load was applied and the temperature increased at 80°C min^{-1} to the desired temperature. The load was applied before raising the temperature in order to obtain meaningful data; therefore, the initial thickness was measured at 25°C. A typical response included a period of expansion during the temperature increase, followed by the compressive behaviour when the temperature approached its final value.

RESULTS AND DISCUSSION

Characterization of the crosslinked structure

All of the monomers polymerized under the conditions described before formed clear, hard crosslinked polymers. Some polymer samples were slightly yellow, characteristic of the initiator. The yellowing seemed to be a function of u.v. exposure time. GlyTrMA did not polymerize as the other samples but formed a two-phase substance, one phase being a clear, amber-coloured solid and the other phase a white, powdery substance.

Volume changes could be estimated after 1 h polymerization in the n.m.r. tubes. The total volume shrinkage upon polymerization of TrMPTrMA was estimated to be approximately 6%. This value could be compared to that predicted by Patel *et al.*[4]. A comparison of the polymerization shrinkage values obtained here with those obtained by Bowman *et al.*[2] showed that all of the monomers of this study polymerized more slowly. Patel *et al.*[4] concluded that the change in molar volume of ester methacrylates upon polymerization was at a relatively constant value of 22.5 cm^3 mol^{-1}. The general equation calculating volume shrinkage in multimethacrylates is:

$$\frac{\Delta V}{V_m} = \frac{22.5 n \rho_m}{m} \tag{1}$$

where ρ_m is the density of the monomer (in g cm^{-3}), n is the number of reactive double bonds in the monomer, m is the molecular weight of the monomer, ΔV is the change in molar volume (in cm^3 mol^{-1}), V_m is the molar volume of the monomer (in cm^3 mol^{-1}) and $\Delta V/V_m$ is the volume shrinkage.

With a value of $n=3$ for TrMPTrMA (three double bonds available for free-radical polymerization), a volume shrinkage of 21.1% was obtained, much greater than the actual shrinkage measured. The experimentally observed lower shrinkage could be the result of an exothermic reaction, which increased the temperature of the material and caused it to expand. In addition, de Boer *et al.*[7]

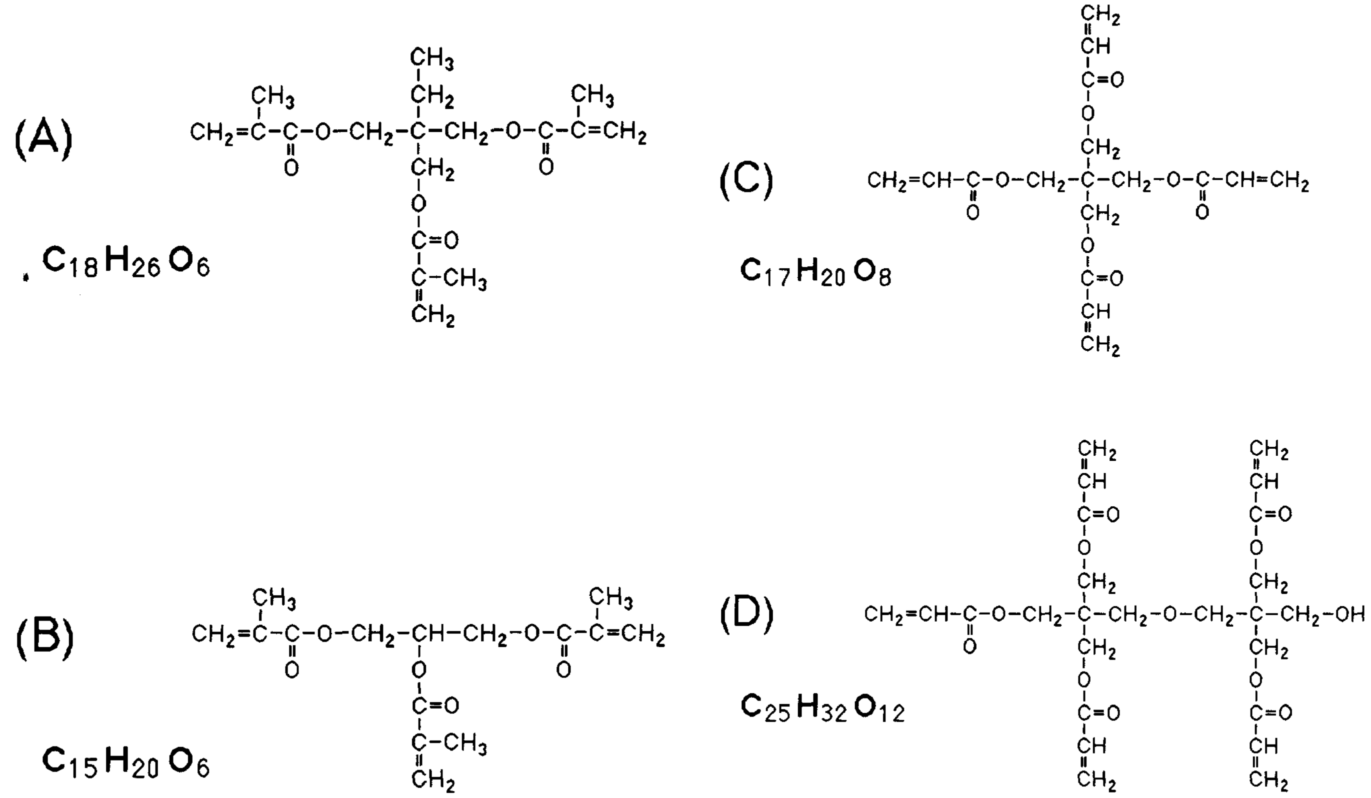

Figure 1 Structure of (A) trimethylolpropane trimethacrylate (TrMPTrMA), (B) glyceryl trimethacrylate (GlyTrMA), (C) pentaerythritol tetraacrylate (PETeA) and (D) dipentaerythritol monohydroxypentaacrylate (DPEMHPeA)

showed that vitrification of the dimethacrylate polymerization appears after 13% conversion, thus causing the shrinkage to lag behind the conversion. But the most dominant cause of the low shrinkage was low polymer conversion. If the actual shrinkage was divided by the predicted shrinkage, a relative conversion of the double bonds of 28.4% was obtained. This is not too different from conversions predicted in previous work. Kloosterboer and Lippits[5] obtained only a 33% conversion of double bonds. Miyazaki and Horibe[8] obtained an extent of polymerization of 43.3% and a crosslinking efficiency of only 1.8% when they polymerized TrMPTrMA at 90°C. This is also demonstrated by the thermograms of PTrMPTrMA obtained by us. An exothermic ramp started at 75°C, levelled off at 175°C and started falling again at 220°C.

Crosslinking is often evaluated in terms of the number-average molecular weight between consecutive crosslinks. The structural formulae of these molecules indicate that there is relatively the same number of atoms between double bonds in all groups, which is another indication of steric effects upon the polymerization. If this is true, PDPEMHPeA should especially have an extremely low conversion of double bonds, as seen in *Figure 1*.

The d.s.c. thermograms of PTrMPTrMA showed additional polymerization during the temperature scans. An inflection in the curves at a temperature of 260°C indicated a glass transition temperature, especially since this was duplicated in repeat runs. PGlyTrMA did not show the exothermic ramp whereas an inflection at approximately 150°C was indicative of the glass transition temperature. PPETeA had a glass transition around 190°C. Finally, PDPEMHPeA exhibited a glass transition near 175°C. As the glass transition temperature is a function of crosslinking, if the size of the molecule affects the extent of polymerization, and thus the degree of crosslinking, then the bulkier molecule polymers should have lower glass transition temperatures. This was shown in the present study.

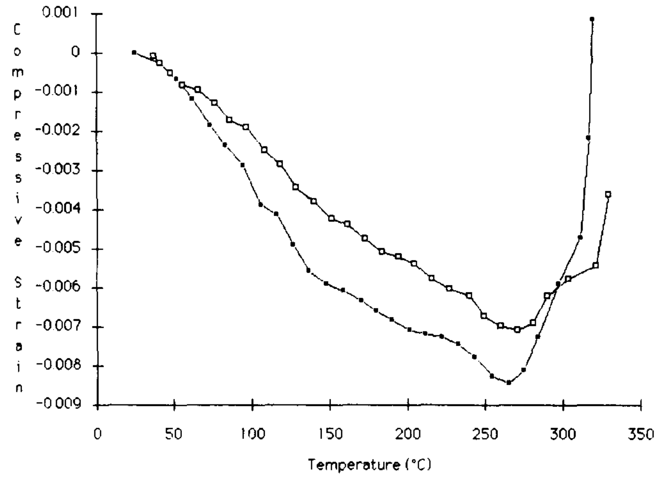

Figure 2 Compressive creep behaviour of PTrMPTrMA networks under 78.8 kPa (■) and 788 kPa (□) using a scanning rate of 10°C min^{-1}

Compressive creep behaviour

The compressive behaviour of selected crosslinked polymers was studied as a function of temperature. The temperature of each experiment was chosen to be near the estimated glass transitions of the respective polymer network. Since these runs were at varying temperatures depending on the polymer, comparison of the creep behaviour within the same material class is appropriate.

Figure 2 presents the compressive strain as a function

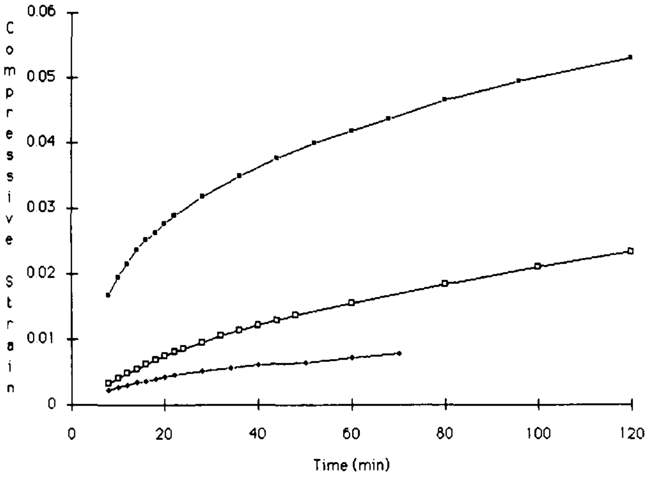

Figure 3 Isothermal compressive strain as a function of time for PTrMPTrMA networks under 50 kPa at 230°C (◆), 261°C (□) and 288°C (■)

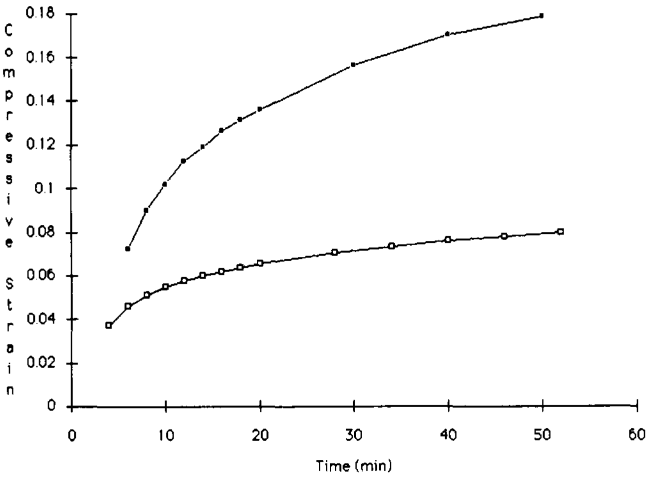

Figure 4 Isothermal compressive strain as a function of time for PGlyTrMA networks under 50 kPa at 126°C (□) and 159°C (■)

of temperature for a PTrMPTrMA sample tested at a scanning speed of 10°C min^{-1}. Data are presented for two different initial applied stresses of 78.8 and 788 kPa. Below the glass transition temperature, the small expansion of the glassy polymers (negative compressive strain) was partially counterbalanced by the compressive process, which was more important for the sample under a stress of 788 kPa. Above the glass transition temperature of 260°C, a significant net compression at the higher stress was observed. Isothermal compressive creep studies were performed with various samples. Studies with PTrMPTrMA samples are shown in *Figure 3* for temperatures of 230, 261 and 288°C. At 230°C, a temperature that is 30°C below the glass transition temperature, there was only a small compressive strain. As the temperature increased above the glass transition temperature, the compressive strain increased significantly.

A similar isothermal compressive behaviour was observed for the samples of PGlyTrMA (*Figure 4*), PPETeA (*Figure 5*) and PDPEMHPeA (*Figure 6*). To analyse and compare the polymer behaviour, the compliance J was calculated for each polymer network as the ratio of the strain and stress, ε and σ, respectively. A relation between J and the time t of isothermal compressive creep exists for polymers at or slightly above their glass transition temperature, known as the Nutting equation:

$$J=\psi t^n \tag{2}$$

The exponent n of the relation reflects the degree of crosslinking in the polymer network and can be determined from a linear regression of the logarithms of the J and t values calculated from the data. Generally, large values of n describe a highly crosslinked material, whereas low values of n describe highly elastic materials. For the same material, one might expect the value for n to decrease as the material becomes more elastic.

Figures 7–10 show typical plots of the compliance as a function of time. The n values reported in *Table 1* were calculated based on a linear regression of the data points collected below 60 min.

The values of n for the PTrMPTrMA are, in general, larger than those for the other polymers, thus indicating a higher degree of crosslinking. This agrees with the previously reported high glass transition temperatures. The assumption that the exponent n would fall as temperature rose did not hold for the PGlyTrMA or the

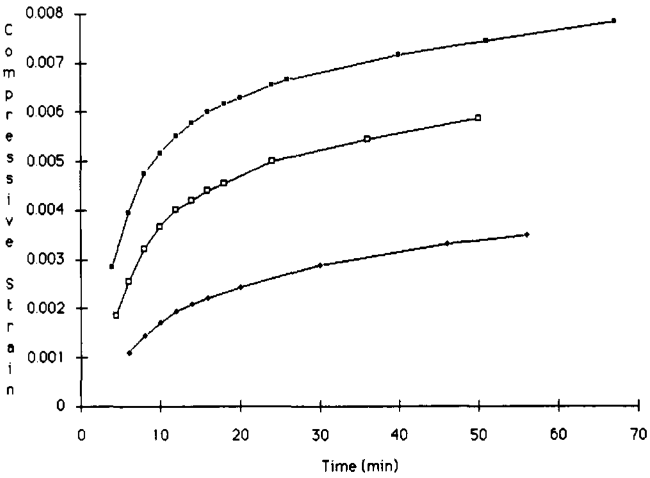

Figure 5 Isothermal compressive strain as a function of time for PPETeA networks under 50 kPa at 165°C (◆), 200°C (□) and 219°C (■)

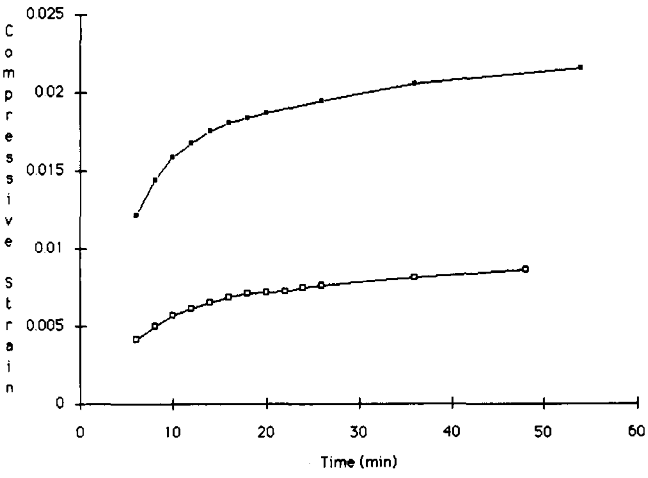

Figure 6 Isothermal compressive strain as a function of time for PDPEMHPeA networks under 50 kPa at 189°C (□) and 209°C (■)

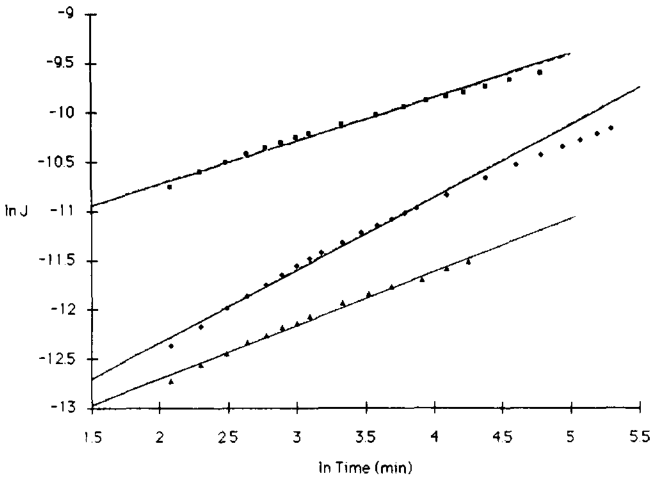

Figure 7 Time-dependent creep compliance of PTrMPTrMA networks at 230°C (▲), 261°C (◆) and 288°C (■)

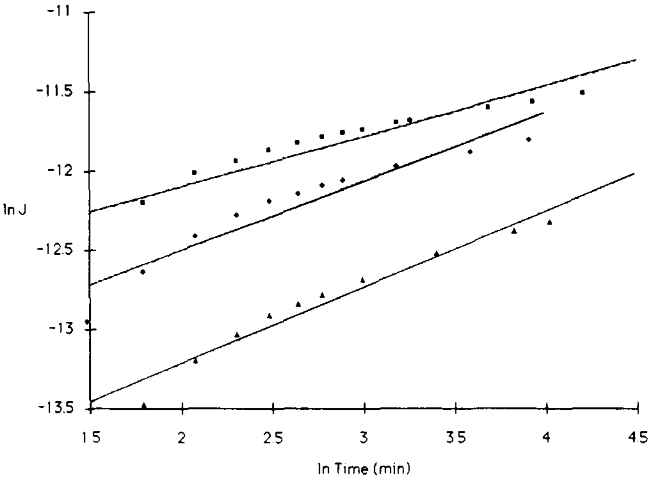

Figure 9 Time-dependent creep compliance of PPETeA networks at 165°C (▲), 200°C (◆) and 219°C (■)

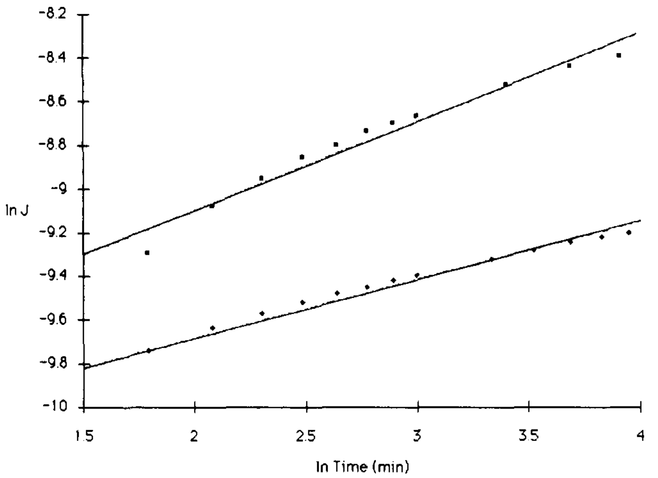

Figure 8 Time-dependent creep compliance of PGlyTrMA networks at 126°C (◆) and 159°C (■)

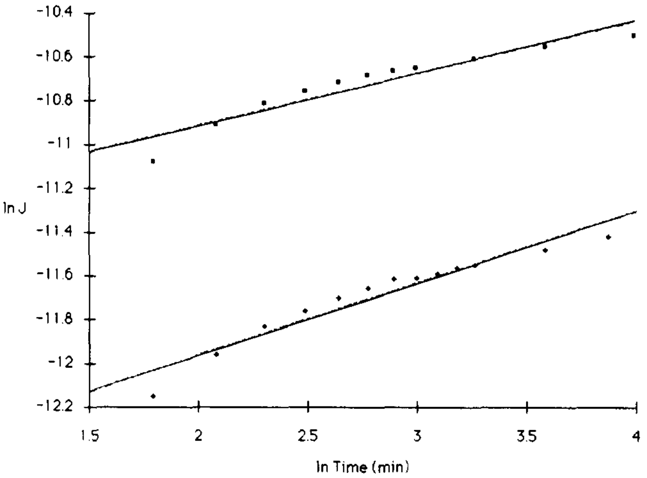

Figure 10 Time-dependent creep compliance of PDPEMHPeA networks at 188°C (◆) and 209°C (■)

PTrMPTrMA networks. The n values of the three studies at 261°C for PTrMPTrMA were approximately equal, indicating that the data are reproducible. However, the relation of n to crosslink density probably holds. Once again, excluding the PGlyTrMA, the value of n seems to be related to the size of the monomer.

The TrMPTrMA is the best candidate as a homomonomer in the 2p process. It clearly had physical properties superior to those of the other monomers tested. Unfortunately, it has a high percentage of unreacted double bonds, which could lead to further polymerization under conditions of extreme heat. It also has a viscosity somewhat above what is desired for the 2p process[5].

CONCLUSIONS

In conclusion, the TrMPTrMA, PETeA and DPEMHPeA polymerized under u.v. light to form hard, clear polymers. GlyTrMA formed a two-phase polymer, part amber-coloured, part white powder, which limits its usefulness in this application.

Differential scanning calorimetry and compressive creep experiments were used to characterize the polymers. The crosslink density was analysed from data of the glass transition temperatures and the behaviour of compressive strain *versus* time. PTrMPTrMA gave results indicating a high degree of crosslinking; PGlyTrMA, PPETeA and PDPEMHPeA were inferior in degree of crosslinking to the PTrMPTrMA. The TrMPTrMA might be a candidate for use in the Philips 2p process. The PETeA and DPEMHPeA may be useful in a mixture with lower-molecular-weight monomers.

Table 1 Analysis of compressive creep experiments using Nutting's equation

Material	T (°C)	Stress (kPa)	ψ	n
PTrMPTrMA	230	788	1.03×10^{-6}	0.544
	261	788	1.52×10^{-6}	0.713
	261	788	1.00×10^{-6}	0.738
	261	394	4.06×10^{-6}	0.614
	288	788	9.23×10^{-6}	0.437
PGlyTrMA	126	788	3.62×10^{-5}	0.270
	159	788	5.00×10^{-5}	0.404
PPETeA	165	788	6.97×10^{-7}	0.481
	200	788	1.55×10^{-6}	0.437
	219	788	2.94×10^{-6}	0.318
PDPEMHPeA	188	788	3.29×10^{-6}	0.331
	209	788	1.12×10^{-5}	0.241

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