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The volume shrinkage, thermal and sorption behaviour of polydiacrylates

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Crosslinked polymers of ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate and poly(ethylene glycol (400)) diacrylate were prepared by photopolymerization using 2,2-dimethoxy-2-phenylacetophenone as the initiator at a light intensity of 2 mW cm^{-2}. Volume shrinkage on polymerization was recorded. The most highly crosslinked networks exhibited the maximum volume shrinkage. Thermal stability was directly related to the high crosslinking density. The presence of heterogeneities in the network structure was ascertained using thermomechanical analysis. Dynamic and equilibrium swelling studies were used to study further the crosslinked structure of these polymers.

(Keywords: diacrylate networks; volume shrinkage; swelling behaviour)

INTRODUCTION

Bulk homopolymerizations of multifunctional monomers result in the formation of highly crosslinked polymers whose properties depend, among other factors, on the type and distance between the functional groups of the monomers. These materials are used extensively in the coatings, films and food packaging industries[1], as biomaterials[2,3] and in information technology[4]. For example, crosslinked dimethacrylates have long been investigated for use in the preparation of denture bases, crowns and bridges, orthodontic appliances and artificial teeth[3,5].

In information technology, crosslinked polyacrylates are investigated for possible applications as optical-fibre coatings, aspherical lenses and information storage systems[4] such as compact discs (CD) and laser video discs (LVD). In CDs and LVDs, the information is stored in binary code in a series of pits arranged in a spiral track. A scanning laser light spot focused with the help of an aspherical lens traverses the spiral track and accesses the encoded information. Methods for the bulk manufacture of aspherical lenses and information storage systems include *in situ* rapid polymerization techniques such as the Philips 2p process. This involves the crosslinking photopolymerization of the monomer in contact with a mould that possesses the shape or contains the information to be replicated.

Owing to the nature of the 2p process and the manner in which information is stored on the material, the polymer needs to have certain properties, which include[6]: (i) low volume shrinkage on polymerization so that incorrect transfer of shape or information is avoided; (ii) good thermal and dimensional stability to ensure the stability of the pit patterns; (iii) minimum presence of heterogeneities so that low birefringence is exhibited; and (iv) low moisture absorption to prevent warpage of the material under normal conditions.

These properties of the dimethacrylate polymers have been investigated previously because of their possible applications as dental materials[7] and as information storage systems[6]. The volume shrinkage on polymerization of poly(ethylene glycol) dimethacrylates containing one to four ethylene glycol (EG) units was reported to be between 10 and 15%, with the most highly crosslinked materials exhibiting greater shrinkage[6]. Also, the dimethacrylate polymers exhibited glass transition temperatures between 250 and 280°C, indicating fairly high dimensional stability.

The presence of multiple transitions in poly(triethylene glycol dimethacrylate) (PTrEGDMA) networks was reported by Wilson and coworkers[8,9]. These multiple transitions indicated the heterogeneous nature of the crosslinked material and were assigned to: (i) the glass transition of the less densely linked regions in the material (ii) the transition due to further reaction of double bonds; and (iii) the glassy–rubbery transition of the highly crosslinked regions in the material. Verification of the presence of these spatial inhomogeneities in ethylene glycol dimethacrylate polymers was provided by Allen *et al.*[10], who used nuclear magnetic resonance spectroscopy to identify and assay residual unsaturation in the network and to differentiate between constrained and unconstrained monomer molecules.

Evidence of inhomogeneities can also be obtained by measuring the concentration of trapped radicals in the polymers. Trapped radicals are surrounded by 'dead' polymer chains and are therefore inaccessible for further reaction. The presence of trapped radicals indicates the presence of regions more crosslinked than the surrounding environment in the materials. Electron spin resonance

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spectroscopy has been used to measure the trapped-radical concentration in polydimethacrylates[11] and polydiacrylates[12].

An indication of the crosslinked structure of the polymers can be obtained by performing an analysis of the dynamic and equilibrium swelling behaviour of the polymers in various solvents. Previous studies from our group have reported on such an analysis of crosslinked dimethacrylate polymers[6]. The molecular weight between crosslinks was calculated using equilibrium swelling data and rubber elasticity theory, leading to the conclusion that only two or three repeating units were present between crosslinks in these networks. Results from this study also showed that, as the amount of crosslinking was increased, the isobutanol, methanol, xylene or methyl ethyl ketone absorbed decreased. Turner *et al.*[5] reported that in poly(methyl methacrylate-*co*-TrEGDMA) copolymers, the amount of water absorbed increased as the amount of crosslinking was increased, probably because of phase separation, which is possible in dimethacrylate copolymers[13].

While the physical properties, and thermal and sorption behaviour of dimethacrylate polymers have been thoroughly investigated, there have not been many such reports for diacrylate polymers. In this contribution, we report on our investigation of the effect of varying monomer chain length and hence crosslink density on the volume shrinkage on polymerization, the thermal stability, the glass transition temperature and solvent sorption behaviour of the photopolymerized materials. This information is essential in the evaluation of these polymers as alternative materials in information technology applications.

EXPERIMENTAL

Ethylene glycol diacrylate (EGDA, 70% pure, *MW*= 170.16; Aldrich Chemical Co., Milwaukee, WI), diethylene glycol diacrylate (DEGDA, *MW*=214.22), triethylene glycol diacrylate (TrEGDA, *MW*=258.27), tetraethylene glycol diacrylate (TeEGDA, *MW*=302.32) and poly-(ethylene glycol (400)) diacrylate (PEG(400)DA, *MW*= 522.58; last four all Polysciences Inc., Warrington, PA) were used as received.

U.v. photopolymerizations were carried out using 1 wt% of 2,2-dimethoxy-2-phenylacetophenone (DMPA) as a photoinitiator, added to the monomer at least 24 h prior to use to ensure complete dissolution and placed in a closed amber bottle at 4°C. Approximately 2–3 g of mixture was placed in between two glass plates, which were separated by 0.5 mm spacers. The mixture was then placed in a glovebox having a continuous nitrogen purge and allowed to equilibrate for 15–20 min. Polymerization was initiated with u.v. light (model Ultracure 100, EFOS, Mississaugua, Ontario, Canada) of intensity 2 mW cm^{-2} for 20–30 min at temperatures ranging from 24 to 28°C. The polymers were then subjected to post-preparation thermal treatment at 110–130°C/68 mmHg overnight. The samples were stored in a desiccator until use.

The thermal stability of the materials was studied using a thermogravimetric analyser (model TGA 2950, TA Instruments, Wilmington, DE). In these experiments, 5–10 mg of the polymer were placed in the t.g.a. sample pan and allowed to equilibrate at room temperature. The weight of the sample was recorded as the temperature was ramped at a rate of 5°C min^{-1} from room temperature to 400°C. A continuous nitrogen purge was used in these experiments.

The temperature-dependent transitions of the polymer were studied using a thermomechanical analyser (model TMA 2940, TA Instruments, Wilmington, DE). In these experiments, the polymer samples were placed under a quartz probe and the vertical dimension (thickness) was measured as the temperature was increased at a rate of 5°C min^{-1}. PTrEGDA, PTeEGDA and PPEG(400)DA samples were first cooled to −50°C and then heated to 300°C, while the remaining were heated from 25°C to 300°C under a continuous nitrogen purge.

For studying the sorption behaviour, the polymers were first cut into 1 cm × 1 cm squares having a thickness of about 0.5 mm, and their exact dimensions and weight were measured. The samples were then placed in acetone, methyl ethyl ketone (MEK), methyl isopropyl ketone (MiPK), isopropyl alcohol (iPrOH), t-butyl alcohol (tBuOH) or water at 32 ± 2°C. The weight of the samples was recorded every 30–40 min for 5 h and then twice every day until equilibrium was attained.

RESULTS AND DISCUSSION

By using monomers with different numbers of ethylene glycol (EG) units between the two acryl groups, we were able to vary the crosslinking density in the prepared polymers. Here we report on the volume shrinkage on polymerization, and the thermal and sorption behaviour of polymers with different crosslinking densities. These results are useful in evaluating the materials for possible applications as information storage systems.

Volume shrinkage

Significant volume shrinkage during polymerization is undesirable in cases where the polymers are replicated using moulds. Using the measured densities of monomers and their respective polymers, the volume shrinkage v_s was calculated using equation (1) and is presented in *Table 1*:

$$v_s = \frac{(1/\rho_m) - (1/\rho_p)}{(1/\rho_m)} \tag{1}$$

Table 1 Volume shrinkage during polymerization of diacrylate[a] and dimethacrylate[b] monomers

EG units in monomer	Monomer[c]	v_s (%)	Monomer[c]	v_s (%)
0	–	–	MMA	15.0
1	EGDA	12.7	EDGMA	15.1
2	DEGDA	11.1	DEGDMA	13.8
3	TrEGDA	11.7	TrEGDMA	12.0
4	TeEGDA	8.3	TeEGDMA	10.3
9	PEG(400)DA	8.0		–

[a] Results are averages of 6–10 measurements

[b] Results of dimethacrylate polymerizations are from Bowman *et al.*[6]

[c] Monomer abbreviations: ethylene glycol diacrylate (EGDA); diethylene glycol diacrylate (DEGDA); triethylene glycol diacrylate (TrEGDA); tetraethylene glycol diacrylate (TeEGDA); poly(ethylene glycol (400)) diacrylate (PEG(400)DA); methyl methacrylate (MMA); ethylene glycol dimethacrylate (EGDMA); diethylene glycol dimethacrylate (DEGDMA); triethylene glycol dimethacrylate (TrEGDMA); tetraethylene glycol dimethacrylate (TeEGDMA)

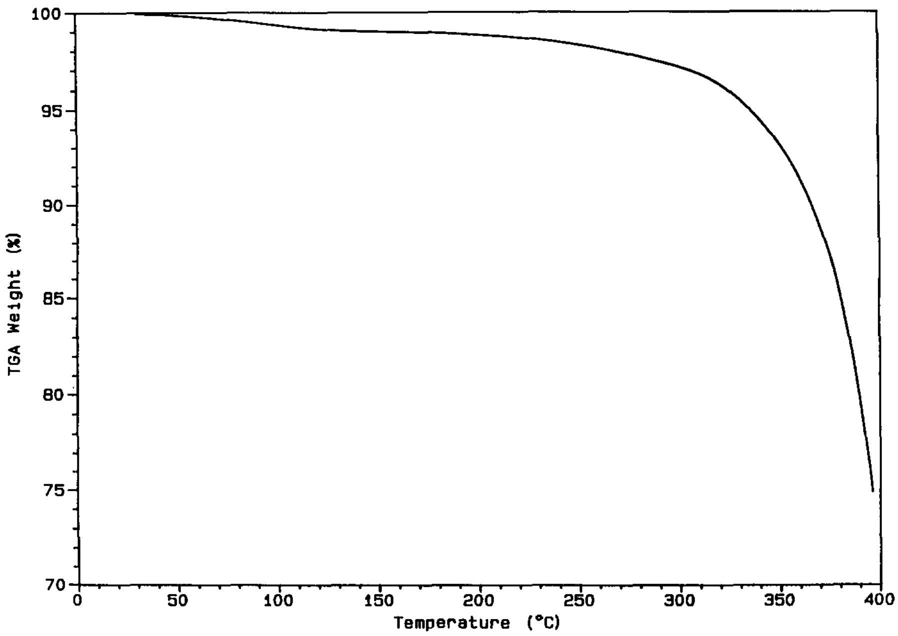

Figure 1 Thermogravimetric thermogram of PDEGDA as a function of temperature at a scanning rate of 5°C min^{-1}

Here, ρ_m is the density of the monomer and ρ_p is the density of the polymer. The densities of the monomers were determined by weighing 1 ml of the liquids. The densities of the polymers were determined by weighing samples of known dimensions. Ten measurements were made for each monomer or polymer sample and the standard deviations were less than 1%. Some polymer samples may contain small quantities of unreacted monomers, which were neglected when calculating the densities.

For comparison, *Table 1* also shows the volume shrinkage of polymerizations of the corresponding polydimethacrylates[6] as calculated from the densities. The volume shrinkage for all the diacrylate monomers was between 8 and 13%, The monomers containing a lower number of EG units between the two acryl groups exhibited the maximum volume shrinkage. As the number of EG units was increased, the volume shrinkage progressively decreased. This indicated that the monomers having shorter chain lengths formed the most highly crosslinked materials. Had EGDA been free of inerts, perhaps the volume shrinkage would have been greater than the 12.72% as was determined in this study. The diacrylates also showed less volume shrinkage than the corresponding dimethacylates. Therefore, in situations where a choice between a diacrylate and a dimethacrylate monomer is possible for an application requiring low volume shrinkage upon polymerization, the diacrylate should be preferred.

Thermal behaviour

Polymers used in the preparation of information storage systems require good thermal stability to ensure a fixed pit pattern at normal temperatures of operation. The thermal stability of polydiacrylates was examined usng thermogravimetric analysis. A typical thermogram is shown in *Figure 1* where the percentage weight loss of a PDEGDA sample is plotted as a function of temperature. PDEGDA did not lose weight significantly until a temperature greater than 250°C was attained. The slight loss in weight between 100 and 200°C could be the result of the degradation of the unreacted monomer. Previous work on the kinetic behaviour of diacrylate photopolymerizations[14] has shown that unreacted monomer may be present in the crosslinked polymers being investigated here.

A comparison of the thermal stability for all the polydiacrylates is given in *Figure 2*, which shows the weight-loss profiles for all polymers in the 300 to 400°C temperature range. These profiles indicated that the loosely crosslinked PPEG(400)DA was the least thermally stable at temperatures near 400°C, while the more tightly crosslinked PEGDA was the most stable. Weight-loss data for each polymer are given in *Table 2*. At a temperature of 300°C the weight of samples decreased by 1.7–2.7%, and at 350°C the decrease was between 5 and 10%. At 300°C PTrEGDA and PTeEGDA showed the maximum thermal stability, while at 350°C PTrEGDA exhibited the least weight loss. The thermal degradation of the inerts present in PEGDA and of the unreacted monomer in PDEGDA may have contributed significantly to the weight loss at 300 and 350°C. This may be the reason why these polymers, which have a higher crosslink density than PTrEGDA, appeared to be less thermally stable at those temperatures.

A characterization of inhomogeneities in the polymer structure is necessary since low birefringence is usually required in information technology applications. Some evidence of the presence of heterogeneities was obtained by performing t.m.a. analysis. A typical result from such an experiment is shown in *Figure 3*, which shows the percentage dimensional change recorded for a post-preparation thermally treated PTeEGDA sample. Multiple transitions were observed, which point to the heterogeneity of the crosslinked polymers. These heterogeneities could be due to the presence of heavily

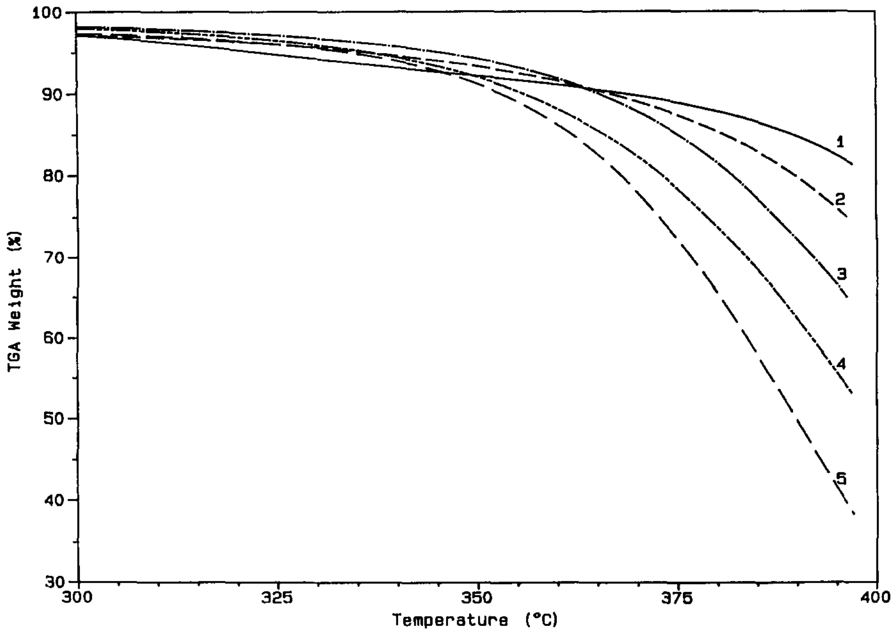

Figure 2 Weight loss as a percentage of the initial weight of various polydiacrylates over a temperature range of 300–400°C. The scanning rate used in these experiments was 5°C min^{-1}. Profiles shown for: PEGDA, curve 1; PDEGDA, curve 2; PTrEGDA, curve 3; PTeEGDA, curve 4; and PPEG(400)DA, curve 5

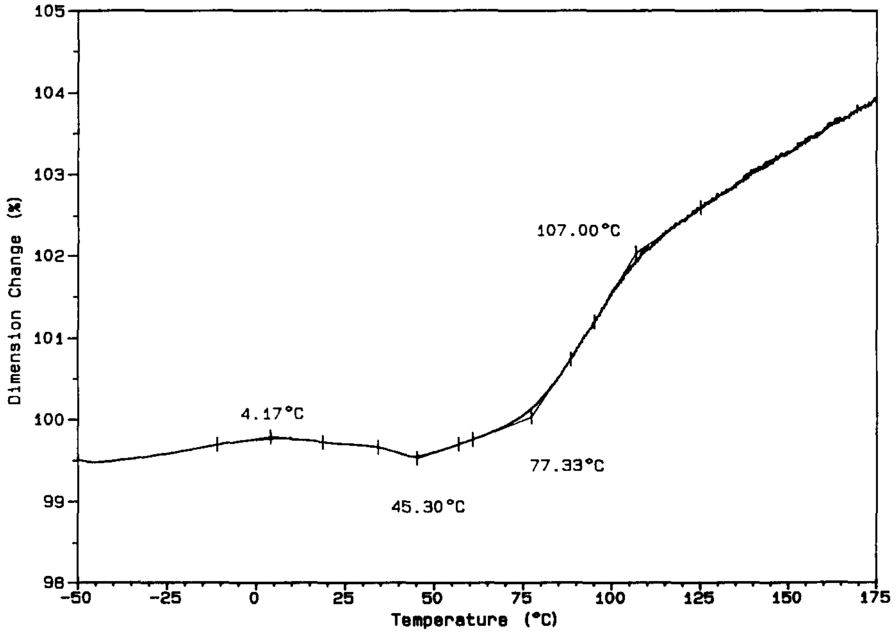

Figure 3 Dimensional change of a PTeEGDA sample as a function of temperature at a scanning rate of 5°C min^{-1}. Transitions are indicated on the thermogram

Table 2 Percentage weight loss for polydiacrylates at 300 and 350°C[a]

Polymer	Weight loss (%) at 300°C	Weight loss (%) at 350°C
PEGDA	2.64 ± 0.16	7.46 ± 0.30
PDEGDA	2.75 ± 0.19	6.90 ± 0.34
PTrEGDA	1.77 ± 0.09	5.20 ± 0.31
PTeEGDA	1.69 ± 0.34	7.10 ± 1.39
PPEG(400)DA	2.62 ± 0.37	9.46 ± 1.04

[a] Monomer abbreviations as in *Table 1*. Results are averages of 3–4 measurements

crosslinked regions in a less densely crosslinked environment or to radicals surrounded by dead polymer chains.

The thermogram shows transitions at around 4, 45, 77 and 107°C. The glass transition temperature T_g was assigned to the highest temperature where a transition showing an upturn in the percentage dimension change was consistently observed in all replicates. For PTeEGDA the transition at about 45°C was consistently observed and assigned the glass transition. The transition seen at 107°C showed an inflection point, which could

Table 3 Polydiacrylate and swelling-agent solubility parameters[a]

Polymer	δ ((cal cm^{-3})$^{1/2}$)	Swelling agent	δ ((cal cm^{-3})$^{1/2}$)
PEGDA	9.01	Methyl isopropyl ketone (MiPK)	8.5
PDEGDA	9.13	Methyl ethyl ketone (MEK)	9.3
PTrEGDA	9.26	Acetone	9.9
PTeEGDA	9.25	t-Butyl alcohol (tBuOH)	10.6
PPEG(400)DA	8.31	Isopropyl alcohol (iPrOH)	11.5
		Water	23.4

[a] Monomer abbreviations as in *Table 1*. The polymer solubility parameters were calculated using group contribution theories[16]. The swelling-agent solubility parameters were obtained from the literature[17]

be due to volume shrinkage caused by further reaction of trapped radicals, or by monomer depletion, again pointing to the presence of heterogeneities.

In an effort to discern further the heterogeneous structure of diacrylate polymers, the effect of thermal treatment on the polymer was examined. It was observed that, for four thermally untreated PDEGDA samples, the average T_g was recorded as 58 ± 2°C. However, in the case of nine post-preparation thermally treated samples, the T_g was 105 ± 4°C. Such an increase in T_g upon thermal treatment has also been observed for other multifunctional acrylates[15]. This increase of T_g on thermal treatment could be due to volume relaxation, to the depletion of unreacted monomer, thereby decreasing the plasticizing effect of the monomer on T_g, to additional reaction caused by the thermal mobility imparted to the trapped radicals, or to the formation of crosslinks during the thermal treatment. Decker and Moussa[12] have previously demonstrated that thermal treatment can cause the trapped radicals to become mobile and permit additional reactions.

The average glass transition temperatures for each of the other polymers were: 75°C for PEGDA, 85°C for PTrEGDA and 43°C for PTeEGDA. It was difficult to determine the T_g for PPEG(400)DA because transitions were observed over a wide range and were not consistently seen at specific temperatures. PPEG(400)DA was rubbery when prepared at room temperature and hence its T_g was below 25°C. Since a T_g between 90 and 120°C is required of polymers used in the preparation of information storage systems, only PDEGDA ($T_g = 105$°C) would be suitable for these applications.

An analysis of the glass transition temperatures shows that, as the number of EG units in the monomer was increased, the T_g for the polymer decreased. The longer monomer chains lead to the formation of a network with a lower crosslinking density and hence greater chain flexibility. An increase in the number of EG units between crosslinks causes an increase in the free volume of the material, therefore causing it to become rubbery at a lower temperature than a more tightly crosslinked network. PEGDA exhibited a T_g lower than that of PDEGDA owing to the presence of 30% inerts, which acted as plasticizers.

Sorption behaviour

The equilibrium and dynamic swelling behaviour of the crosslinked polymers can provide additional information on their structure. In situations where enough swelling agent is absorbed and the polymer forms a gel, rubber elasticity theory can be used to estimate the molecular weight, and therefore the molecular distance between crosslinks.

To ensure the selection of swelling agents thermodynamically compatible with the polymers, first the polymer solubility parameters were calculated using the group contribution method of Hoftyzer and van Krevelen[16]. Then, swelling agents having solubility parameters obtained from Grulke[17] in the range of the predicted values for the polymers (see *Table 3*) were selected for use. Water was also used because the moisture absorption characteristics of the polymer need to be known if they are to be considered as materials for information storage systems, aspherical lenses and optical-fibre coatings.

The typical dynamic swelling behaviour of polydiacrylates in MEK is shown in *Figure 4*, where the change in the ratio of the mass of the polymer at any time, M_t, to the initial dry mass of the polymer, M_0, is plotted as a function of time. The less highly crosslinked polymers such as PTeEGDA and PPEG(400)DA showed a rapid swelling-agent uptake rate as compared with the other polymers. Similar behaviour was also observed in MiPK and acetone, as polymer and swelling-agent solubility parameters were similar and hence the polymer–swelling agent mixtures were thermodynamically compatible. Therefore, the lower crosslinking density in these polymers allowed for a greater distance between crosslink points and allowed the swelling-agent molecules to diffuse through. For the polymers with a greater crosslinking density, the distance between crosslinks (or mesh size) was probably too small for the solvent to diffuse through.

Assuming an unperturbed polymer chain conformation between crosslink points, the mesh size ξ was calculated using equation (2)[18]:

$$\xi = (C_\infty n)^{1/2} l \qquad (2)$$

Here, C_∞ is the characteristic ratio, n is the number of bonds between the two crosslink points and l is the bond length (1.54 Å for C–C bonds). A value of $C_\infty = 7$ is typical for poly(isopropyl acrylate) and polymethylene[18], and was used in the mesh size calculations. Since limiting

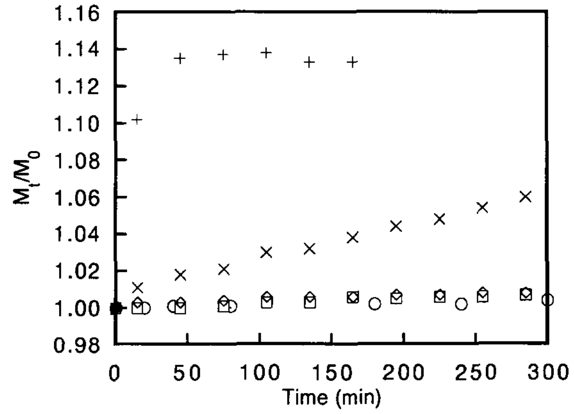

Figure 4 Dynamic swelling of polydiacrylates in methyl ethyl ketone at 32°C. Swelling studies for: (○) PEGDA; (□) PDEGDA; (◇) PTrEDGA; (×) PTeEGDA; and (+) PPEG(400)DA

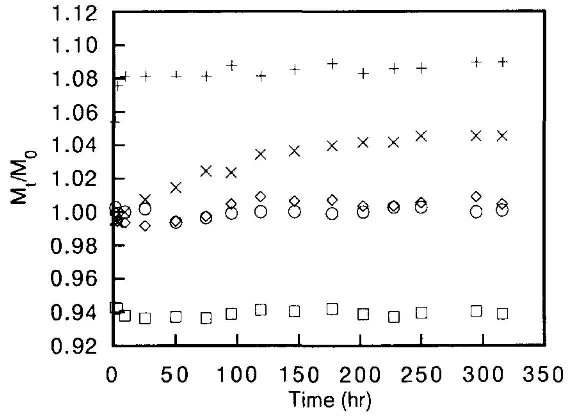

Figure 5 Swelling behaviour of polydiacrylates in isopropyl alcohol at 32°C. Swelling studies for: (○) PEGDA; (□) PDEGDA; (◇) PTrEDGA; (×) PTeEGDA; and (+) PPEG(400)DA

conversions were greater than 90%[14] for each of the monomers used in this study, it was assumed that one repeating unit was present between crosslinks. The calculated mesh sizes were: 10.8 Å for PEGDA, 12.9 Å for PDEGDA, 14.7 Å for PTrEGDA, 16.3 Å for PTeEDGA and 22.7 Å for PPEG(400)DA.

The calculated values were overestimates because polymer chains in glassy polymers would not be in their unperturbed conformations. Additionally, the presence of physical entanglements and microgel regions in the polymer matrix decreased the area available for the diffusion of the swelling agent. Since the swelling-agent hydrodynamic diameters are typically in the range of the actual mesh sizes, it is possible that the polymers were so highly crosslinked that they would always have low swelling-agent uptake even when a thermodynamically compatible swelling agent was used.

A typical plot showing the swelling behaviour of the selected polymers in iPrOH is shown in *Figure 5*. PTrEGDA and PPEG(400)DA exhibited a rapid swelling-agent uptake rate whereas PEGDA and PTrEGDA did not absorb as much solvent, and PDEGDA lost about 6% of its original weight. Similar results were observed when tBuOH was used as a swelling agent. Here too, the low crosslinking density (larger mesh size) of PTrEGDA and PPEG(400)DA allowed for swelling-agent transport. Hydrogen bonding between the alcohol hydrogen atom and the EG units of the polymer may also have contributed positively to the solvent uptake. The solubility parameters of alcohols are somewhat different from those of the polydiacrylate networks, indicating low tendency for swelling.

PDEGDA samples decreased in mass and equilibrated at about 94–95% of their initial weight when placed in iPrOH and tBuOH. This loss of weight could be caused by the diffusion of unreacted monomer present in the crosslinked network into the solvent. This hypothesis is supported by previous results from our group[14], which have shown that, when a light intensity of 2 mW cm^{-2} is used to initiate the polymerizations, DEGDA only attains 94% limiting conversion. Even after the monomer has diffused out, no solvent uptake is possible because of the small mesh size in this polymer. These results allowed us to identify solvents that may be used to extract the unreacted monomer from the crosslinked polyacrylates.

The equilibrium swelling-agent uptake can be characterized by the equilibrium polymer volume fraction v_2, which was calculated using equation (3) and is reported in *Table 4*:

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

Here, M is the mass, ρ is the density and the subscripts s and p stand for solvent and polymer, respectively.

As the monomer chain length was decreased and the crosslinking density of the polymer increased, v_2 increased. As the crosslinking density increased, the amount of swelling agent absorbed decreased. Higher v_2 values for each polymer were observed in MiPK than in MEK or acetone. This might be because of either the larger size of MiPK molecules as compared with that of acetone or the thermodynamic incompatibility of the MiPK–polymer mixture, or a combination of both factors. Water did not swell the polymers appreciably, as indicated by the high v_2 values in *Table 4*. As the crosslinking density of the polymers was increased, the amount of water absorbed decreased. This is contrary to a previous report[5] in which the investigators found an increase in the water absorbed as the amount of crosslinking in poly(MMA-*co*-TrEGDMA) copolymers was increased. Low moisture absorption is a favourable characteristic if the polymers are to be used in applications where warpage due to moisture absorption is undesirable.

CONCLUSIONS

Diacrylate monomers polymerized rapidly at room temperature when a light intensity of 2 mW cm^{-2} was used for photoinitiation. The volume shrinkage was greatest for the monomers with shorter chain lengths, as they formed the most highly crosslinked networks. In general, the volume shrinkage was between 8 and 13% for the diacrylate monomers, less than that reported for the corresponding dimethacrylate monomers.

The polymers were thermally stable up to a temperature of 300°C. The networks with a high crosslinking density were more stable than those with a lower crosslink density at higher temperatures. Results from thermomechanical analysis demonstrated the heterogeneous nature of the crosslinked materials. These heterogeneities could be due to the presence of microgel regions, unreacted monomer, or trapped radicals. The

Table 4 Equilibrium volume fractions v_2 of polydiacrylates in swelling agents at 32 ± 2°C[a]

Polymer	MiPK	MEK	Acetone	tBuOH	iPrOH	Water
PEGDA	0.985	0.982	0.965	0.997	0.998	0.943
PDEGDA	0.980	0.941	0.837	–[b]	–[b]	0.936
PTrEGDA	0.982	0.881	0.870	0.969	0.993	0.944
PTeEGDA	0.906	0.873	0.848	0.965	0.934	0.902
PPEG(400)DA	n.d.[c]	n.d.	n.d.	0.877	0.878	n.d.

[a] Monomer abbreviations as in *Table 1*. Results are averages of 2 3 samples

[b] PDEGDA lost weight in tBuOH and iPrOH and hence volume fractions were not calculated

[c] No data

glass transition temperature for PDEGDA was 105°C and decreased with a decrease in the crosslinking density.

The sorption behaviour of the materials indicated that the most highly crosslinked samples absorbed the least amount of swelling agent. Moisture absorption was less than 15% even for the materials with a lower crosslinking density such as PPEG(400)DA. PDEGDA samples decreased in weight when isopropyl alcohol and t-butyl alcohol were used as swelling agents, possibly because of the extraction of unreacted monomer from the material. These alcohols can be used in solvent extraction of leachable monomer from crosslinked acrylates if required.

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REFERENCES

1 Salim, M. S. in 'Radiation Curing in Polymers II' (Ed. D. R. Randell), Royal Society of Chemistry, Cambridge, UK, 1991, p. 3

2 Peppas, N. A. and Langer, R. *Science* 1994, **263**, 1715

3 Bowen, R. L. *J. Dent. Res.* 1970, **49**, 810

4 Kloosterboer, J. G. *Adv. Polym. Sci.* 1988, **84**, 1

5 Turner, D. T., Haque, Z. U., Kalachandra, S. and Wilson, T. W. in 'Crosslinked Polymers: Chemistry, Properties, and Applications' (Eds R. A. Dickie, S. S. Labana and R. S. Bauer), ACS Symp. Ser., Vol. 367, American Chemical Society, Washington, DC, 1988, p. 427

6 Bowman, C. N., Carver, A. L., Kennett, S. N., Williams, M. M. and Peppas, N. A. *Polymer* 1990, **31**, 135

7 Ruyter, I. E. and Oysaed, H. *CRC Crit. Rev. Biocompatibility* 1988, **40**, 247

8 Wilson, T. W. and Turner, D. T. *Polym. Mater. Sci. Eng. Proc.* 1988, **59**, 413

9 Wilson, T. W. *J. Appl. Polym. Sci.* 1990, **40**, 1195

10 Allen, P. E. M., Bennett, D. J., Hagias, S., Hounslow, A. M., Ross, G. S., Simon, G. P., Williams, D. R. G. and Williams, E. H. *Eur. Polym. J.* 1989, **25**, 785

11 Zhu, S., Tian, Y., Hamielec, A. E. and Eaton, D. R. *Polymer* 1990, **31**, 154

12 Decker, C. and Moussa, K. *J. Polym. Sci., Polym. Chem. Edn.* 1987, **25**, 739

13 Simon, G. P., Allen, P. E. M. and Williams, D. R. G. *Polymer* 1991, **32**, 2577

14 Kurdikar, D. L. and Peppas, N. A. *Polymer* 1994, **35**, 1004

15 Anseth, K. S., Bowman, C. N. and Peppas, N. A. *Polym. Bull.* 1993, **31**, 229

16 van Krevelen, D. W. 'Properties of Polymers', Elsevier, Amsterdam, 1990

17 Grulke, E. A. in 'Polymer Handbook' (Eds. J. Brandrup and E. H. Immergut), Wiley, New York, 1989, p. VII/519

18 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Wiley, New York, 1969