PII: S0032-3861(97)00585-5

Polymer Vol. 39 No. 12, pp. 2507–2513, 1998
© 1998 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/98/$19.00+0.00

A study of the evolution of mechanical properties and structural heterogeneity of polymer networks formed by photopolymerizations of multifunctional (meth)acrylates

Anandkumar R. Kannurpatti[b], **Jay W. Anseth**[a] **and Christopher N. Bowman**[a,*]
[a]Department of Chemical Engineering, University of Colorado, Boulder, CO 80309-0424, USA
[b]E. I. duPont de Nemours and Co., Wilmington, DE 19880-0356, USA
(Received 1 May 1997; revised 30 June 1997)

A study of the mechanical properties and the structural heterogeneity of crosslinked polymers formed by photopolymerization of multifunctional monomers is described. By using living radical polymerizations, networks with no trapped carbon radicals have been synthesized. These crosslinked networks, which have no trapped free radicals can be heated without inducing further reaction and crosslinking. This feature makes the living radical polymerizations very useful in the characterization of structure and properties during and after the polymerization. In this work, living radical polymerizations have been used to study the mechanical properties of networks formed by homo- and copolymerization of diethyleneglycol dimethacrylate (DEGDMA) and poly(ethyleneglycol 600) dimethacrylate (PEG600DMA) with *n*-octyl methacrylate (OcMA) using dynamic mechanical analysis. Further, an acrylate copolymer system consisting of *n*-heptyl acrylate (HepA) and diethylene glycol diacrylate (DEGDA) has also been examined. The glass transition temperature of the copolymers was characterized as a function of composition as well as size of crosslinking agent in these copolymers. By performing frequency scan experiments, the distribution of relaxation times of the crosslinked polymers were characterized. From such analyses, the structural heterogeneity as measured by the width of the distribution of relaxation times of the networks was characterized as a function of the comonomer composition in the copolymers. Evidence that the dependence of the glass transition temperature on the crosslinking density is not straightforward is presented. Also, the results indicate that the structural heterogeneity of the materials increases as the crosslinking density of the copolymer is increased. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: living radical photopolymerizations; dynamic mechanical analysis; mechanical properties)

INTRODUCTION

Highly crosslinked networks formed by photopolymerization of multifunctional monomers are very useful materials. These high strength polymer networks have found use in a wide variety of applications such as dental restorative materials[1,2], optical discs, contact lenses and optical communication devices[3–5]. To ensure the effective use of these materials and to tailor them for a particular application, a good understanding of the relationship between the structure and the properties of the polymers is essential. However, while polymerizing these networks using conventional initiators, radicals become entrapped in highly crosslinked regions[3,6–8]. The presence of these trapped radicals makes it very difficult to heat the network without facilitating further reaction and crosslinking. Because measurement of properties as a function of temperature is required to obtain glass transition temperatures as well as to draw conclusions regarding the structural heterogeneity of these networks, characterization of these crosslinked polymers has been difficult. In this paper, a recently introduced[7,8] technique using 'iniferters' (i.e. living radical polymerizations) to enable the study of the evolution of the structure and properties is utilized to examine (meth)acrylate networks.

The formation of microgels (very highly crosslinked regions of extremely restricted segmental mobility) is the primary cause of structural heterogeneity in networks[3,6,9,10] formed by curing multifunctional monomers. It has also been observed by researchers[11,12] that in the same polymer network one may find unreacted monomer pools. Therefore, a diverse distribution of microenvironments is present in these crosslinked polymers. This heterogeneity of environments leads to a wide distribution of mobilities (or relaxation times) of the polymer segments.

The distribution of relaxation times in the various microregions of the polymers is reflected in the mechanical behaviour of these crosslinked materials and has been used in the past by several researchers as a measure of the structural heterogeneity[11,13–16]. However, in order to study the mechanical behaviour, a sample that will not chemically change over a range of temperatures is required. The presence of trapped radicals, which are widely observed in crosslinked polymers formed by

---

[*] To whom correspondence should be addressed

photocuring multifunctional monomers, makes the polymers change chemically (increases double bond conversion and hence, crosslinking density) when they are heated. By using living radical polymerizations[7,8], it has been possible to avoid radical trapping and, therefore, synthesize a network that does not undergo further reaction upon heating. Calorimetric and electron spin resonance spectroscopy studies have shown that no trapped radicals are present in networks synthesized by these living radical polymerizations[8].

In this work, poly(methacrylates) and poly(acrylates) formed by copolymerizing a mono(meth)acrylate and a di(meth)acrylate are examined for their glass transition behaviour as well as structural heterogeneity by performing dynamic mechanical analysis on samples polymerized by living radical polymerizations. These characterizations are performed as a function of crosslinking agent composition, molecular weight (or size), and type.

EXPERIMENTAL

Materials

Mechanical property studies were performed on samples prepared by copolymerizations of diethyleneglycol dimethacrylate (DEGDMA) and poly(ethyleneglycol 600) dimethacrylate (PEG600DMA) with *n*-octyl methacrylate (OcMA) as well as copolymerizations of *n*-heptyl acrylate (HepA) with varying concentrations of diethyleneglycol diacrylate (DEGDA). All monomers were purchased from Polysciences Inc. and used as received. The initiator used in this study to perform living radical polymerizations, *p*-xylylene bis (N,N-diethyl dithiocarbamate) (XDT), was received from 3M. While polymerizing samples of OcMA and PEG600DMA a regular initiator such as 2,2-dimethoxy-2-phenyl acetophenone (DMPA) was used because these polymerizations typically reached nearly 100% conversion of double bonds. Thus, there were no reactive functionalities left and the mobilities in these polymers are such that radical trapping was not a problem. However, as mentioned previously, other copolymers were polymerized using XDT.

Methods

A dynamic mechanical analyzer (DMA7e, Perkin–Elmer, Norwalk, CT) was used to perform the dynamic mechanical measurements. Samples were photocured with an EFOS ultracure high intensity light source which emits light at 365 nm. The intensity of light at the sample was kept a constant at approximately 600 mW cm^{-2} (as measured by an EIT Spotcure UV Intensity meter) for all samples. An initiator concentration of 0.1 wt% was chosen and sample thicknesss of 0.9 mm or less were used to ensure that the thin film approximation was not violated. Double bond conversions were measured by monitoring the change in carbon–carbon double bond concentration using Fourier transform infrared (*FT*i.r.) spectroscopy (Magna-IR 750, Nicolet, Madison, WI).

Samples used for dynamic mechanical analysis (DMA) were thin rectangular films of 0.9 mm or less thickness and dimensions of 5 mm × 20 mm. Experiments were performed on the DMA to measure moduli and loss tangent as a function of temperature by applying a sinusoidal stress of frequency 1 Hz. These measurements were used to determine the glass transition temperature (T_g). Measurements of moduli as a function of frequency (0.01–50 Hz) were performed at several temperatures. These results were used to perform time–temperature superposition and were further analysed to quantify the degree of heterogeneity of the polymer network as described elsewhere[7,8].

RESULTS AND DISCUSSION

As described in a previous publication[8], living radical polymerizations provide a very useful method of characterizing temperature-dependent properties of highly crosslinked polymer networks. In this work, this technique has been exploited further to study various copolymer networks of (meth)acrylates. In *Figure 1* a typical DMA temperature scan as a function of temperature is depicted. The figure shows a poly(DEGDA) sample.

It can be observed from the figure that the modulus behaviour is well captured over the 200°C temperature range. If a conventional initiator (such as DMPA) were used instead of the XDT, the modulus behaviour of that particular sample could not have been probed as a result of continued reaction during the temperature scan. The storage modulus undergoes a change from a glassy state value of $\sim 10^9$ Pa to 6×10^7 Pa in the rubbery state. This change is clearly observed and the glass transition region extends over 150° in temperature. Further, from the width of the damping factor curve (or the tan δ curve) it can be observed that the glass transition region spreads over a very wide temperature range. This extended transition region is a result of the high degree of structural heterogeneity of the polymer sample studied. The broader tan δ peak implies a more heterogeneous polymer[13,15,16] with a wide distribution of relaxation times. Because the glass transition region is spread over this wide a temperature range, it is difficult to provide a specific temperature as the glass transition temperature of the material. However, in keeping with convention, this work uses the peak of the tan δ curve as the glass transition temperature (T_g) of the network.

Another important feature that should be noted while observing the modulus behaviour is the plateau in the rubbery region. This rubbery modulus value is related to the crosslinking density of the material. There have been several networks theories[17,18], which have related the modulus in the rubbery region to the crosslinking densities of crosslinked polymers. While these theories provide equations that can be used to estimate the molecular weight between the crosslinks (or the crosslinking densities), they assume a Gaussian distribution of chains. This assumption implies that for the theory to be valid there should be at least 20–30 repeat units between two crosslink

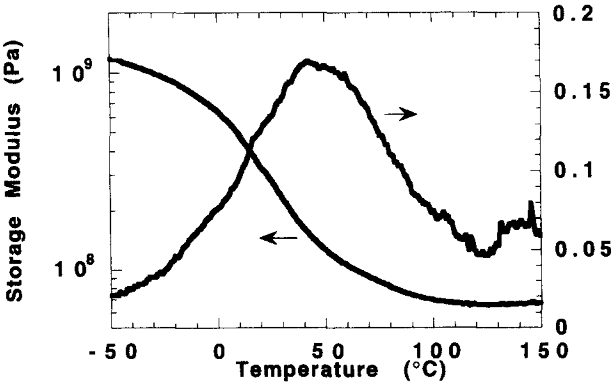

Figure 1 DMA temperature scan on a poly(DEGDA) sample polymerized with 0.1 wt% XDT using 365 nm, 600 mW cm^{-2} u.v. light

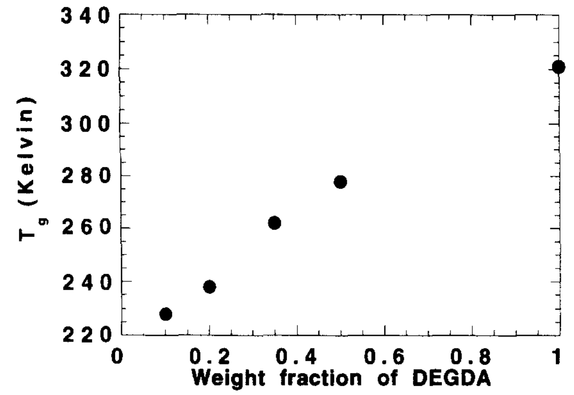

Figure 2 Glass transition temperatures of poly(HepA-co-DEGDA) samples as a function of weight fraction of diethylene glycol diacrylate

points. These assumptions may be made in the limit where the crosslinking agent concentration is low; however, in very highly crosslinked polymer networks these assumptions break down and do not provide accurate values for the crosslinking density. Further, one may consider using empirical equations such as the one proposed by Charlesworth[18] to account for the non-Gaussian distribution. However, to calculate the crosslinking density from such equations the empirical constants need to be well characterized. Therefore, in this study the plateau in the rubbery region of the modulus curve is used as a measure of the crosslinking density and actual values of the molecular weight between crosslinks are not calculated.

By performing such temperature scans on various copolymers, the T_g behaviour as a function of the comonomer composition was determined. *Figure 2* depicts the copolymers of HepA and DEGDA with varying amounts of crosslinking agent (DEGDA). It can be observed that the glass transition temperature of the copolymer increases as the crosslinking agent concentration is increased. This increase is as expected because the addition of crosslinking agent is accompanied by an increase in the crosslinking density, which decreases the mobility of the copolymer. As the mobility is decreased, the T_g of the material increases. It is rather interesting that there seems to be a nearly linear increase in the glass transition temperature of the copolymer as the weight fraction of the crosslinking agent is increased.

Similar trends are observed in copolymers of OcMA and DEGMA as well (as depicted in *Figure 3a*). As the composition of DEGDMA in the copolymer is increased, the T_g increases from approximately 249 K to 385 K. It should be noted that the polymer samples are reacted to their respective maximum conversions possible under the conditions and subsequently tested for their properties. As the composition of the crosslinker is increased, the maximum double bond conversion that the samples may attain decreases because of diffusional limitations to the polymerization process[3,11-20]. Therefore, the properties of the samples are not of the 100% polymer. Interestingly, as seen in *Figure 3b*, an increase in the T_g as the concentration of PEG600DMA increases in copolymers of OcMA and PEG600DMA is not observed over the entire range of comonomer compositions. The polymers formed by copolymerizing OcMA and PEG600DMA show a maximum in the T_g *versus* comonomer composition plot as seen in *Figure 3a* and *b*.

This anomalous behaviour in poly(OcMA-co-PEG600DMA) samples may be explained by recalling that there are two different (and at times opposing) effects that contribute to the dependence of glass transition temperature (as well as other properties) on the composition of the crosslinking agent. These effects, which have been widely discussed in the literature[21-25], are the 'copolymerization effect' and the 'crosslinking effect'. The 'copolymerization effect' is a result of merely changing the fractions and types of the monomer(s) that are copolymerized. The 'crosslinking effect' on the other hand, is the effect of the constraints caused by the crosslinks on the properties of the copolymer. Typically, an increase in crosslinks results in an increase in the T_g as the mobility of the copolymer becomes increasingly restricted. However, based on the type of crosslinking monomers, the copolymerization effect may in some cases reverse the trends expected based on the crosslinking effect[22,25].

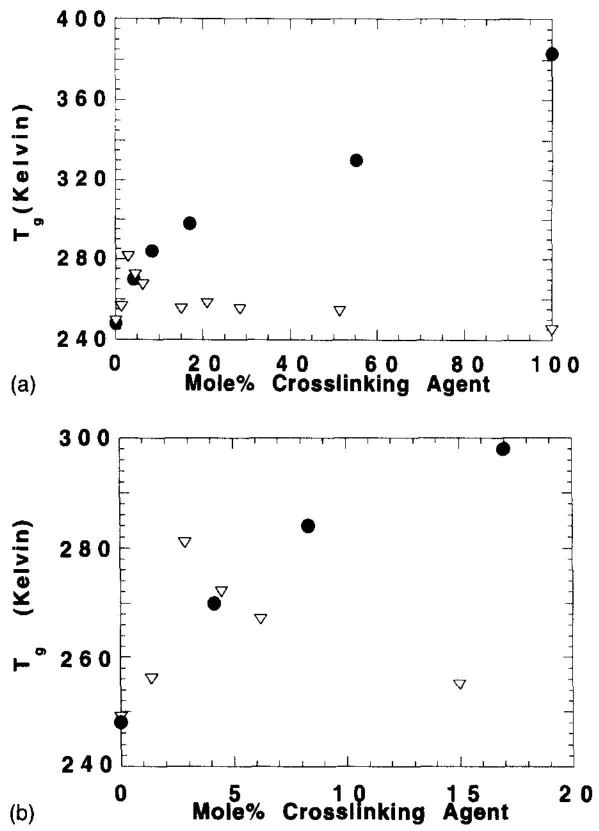

Figure 3 (a) T_g dependence on the mole% of crosslinking agent in copolymers of (●) OcMA and DEGDMA and (▽) OcMA and PEG600DMA. (b) T_g dependence on the mole% of crosslinking agent in copolymers of (●) OcMA and DEGDMA and (▽) OcMA and PEG600DMA over lower concentrations of crosslinking agent (0–20%)

Examining the T_g information in *Figure 3a* more closely, one can see that in a composition range from 0 to 10 mole% crosslinking agent (as shown in *Figure 3b*), the trends for both copolymer systems are quite similar. This similarity in trends suggests that at these low concentrations of crosslinking agent, an increase in the composition of the crosslinking agent significantly increases the crosslinking density, and this increase is nearly independent of the size of crosslinker used (DEGDMA or PEG600DMA). It appears that each mole of PEG600DMA provides more effective crosslinks than does each mole of DEGDMA as the T_g in the system crosslinked with PEG600DMA is in general slightly higher than the poly(OcMA-co-DEGDMA) samples.

Increasing the crosslinker composition beyond a certain value (10 mole%) does not contribute as significantly to the

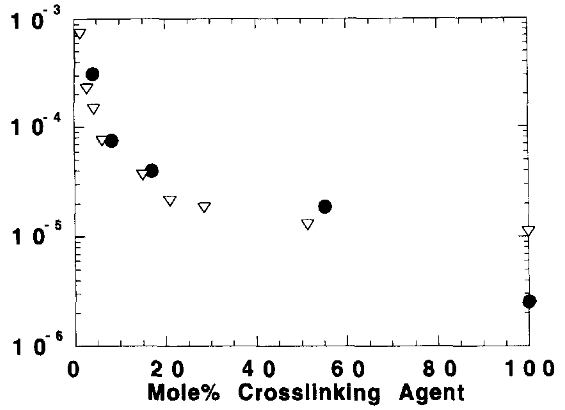

Figure 4 ζ (the inverse ratio of the modulus in the rubbery region to the temperature at which the modulus was measured) plotted as a function of the mole% of crosslinking agent in copolymers of (●) OcMA and DEGDMA as well as (▽) OcMA and PEG600DMA. ζ provides a measure of M_c, the molecular weight between crosslinks

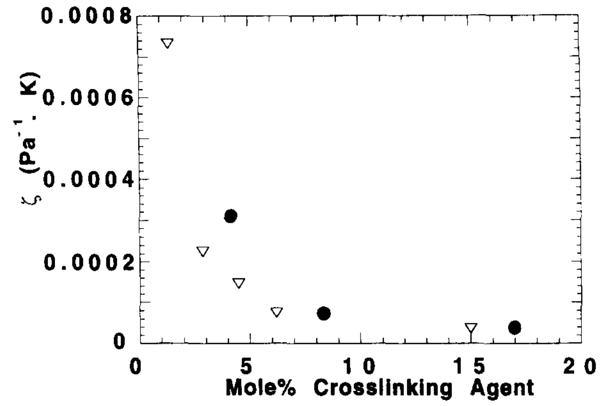

Figure 5 ζ as a function of mole% crosslinking agent in copolymers of (●) OcMA and DEGDMA as well as (▽) OcMA and PEG600DMA over lower concentrations of crosslinking agent (0–20%)

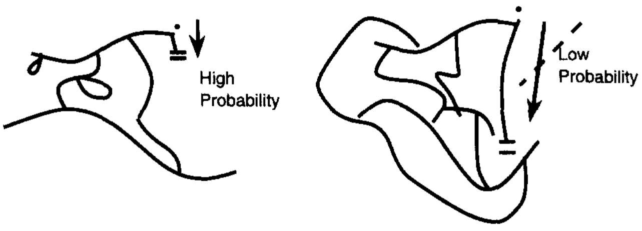

Figure 6 Cyclization is more likely when the crosslinker size is smaller. Pendant double bonds in a higher MW crosslinker are more dilute, therefore, they do not react (with the same degree of probability as in the case of a lower MW crosslinker) with the active centre that consumed the first double bond. In the figure, ● represents the propagating radicals and the arrows indicate the possible pathway for the formation of a cycle (or a loop)

reduction in mobility (by introduction of crosslinks). As a result, in the OcMA–DEGDMA system, a decrease in the slope of the T_g *versus* composition trend is observed beyond about 10% DEGDMA concentration. This effect is more pronounced in the OcMA–PEG600DMA system as a total reversal of the slope and a decrease in T_g is observed.

To examine this effect further, in *Figure 4* the absolute temperature (at which that modulus was measured) divided by the rubbery modulus is plotted for both the copolymer systems. This ratio, ζ, is inversely related to the crosslinking density of the copolymer and directly proportional to the molecular weight between crosslinks (M_c) in the copolymer network[16–18]. In *Figure 4*, one can see that as the mole fraction of the crosslinking agent is increased within a copolymer system, ζ decreases (i.e. M_c decreases and the crosslinking density increases). This decrease in the molecular weight between crosslinks or increase in crosslinking density is expected because an increase in the crosslinking agent concentration will contribute to the formation of an increased number of 'effective' crosslinks. However, it can also be observed that after approximately 10–20 mole% crosslinking agent there is only a marginal decrease in the measure of M_c. This behaviour suggests that the number of effective crosslinks added (that contribute towards a decrease in M_c) when the concentration of the crosslinking agent is increased beyond 20 mole% is marginal. This observation, when applied to the T_g trends shown in *Figure 3*, would imply that the 'crosslinking effect' which dominates at low concentrations of crosslinker becomes less dominant at the higher concentrations of the crosslinker. Further, the 'copolymerization effect' seems to dominate at higher concentrations, especially in copolymers of OcMA and PEG600DMA.

Figure 5 plots ζ, the measure of M_c, in the lower concentration limit (less than 20 mole%) of the crosslinker. It can be clearly seen that until crosslinker concentrations of about 10 mole%, the poly(OcMa-co-DEGDMA) samples have a higher M_c than the poly(OcMA-co-PEG600DMA) samples, thus leading to the slightly higher T_g values observed for OcMA/PEG600DMA copolymers.

This observation is counter-intuitive as DEGDMA is a lower molecular weight crosslinking agent compared to PEG600DMA and one may expect the M_c to be lower when DEGDMA is used to produce crosslinks. To explain this behaviour, it should be recalled that the rubbery modulus provides a measure of the number of effective crosslinks and a small size crosslinking agent such as DEGDMA may be more susceptible to form cycles (or loops, as represented in *Figure 6*) during polymerization. This cyclization is not observed as much when PEG600DMA is used as the crosslinker (at least in lower concentrations of dimethacrylate) and as a result the measure of M_c is lower (or the number of 'effective' crosslinks is higher). These observations regarding the homogeneity are consistent with observations made by other researchers by simulations[26,27] and explain the higher T_g values observed in the copolymers of OcMA and PEG600DMA at very low concentrations of crosslinking agent (see *Figure 3*).

As mentioned previously, the network structure that evolves during these photopolymerizations of multifunctional monomers is quite complex. The formation of microgels and the presence of crosslinks and primary as well as secondary cycles (or loops) in the polymer contributes to the evolution of a very heterogeneous structure. This inhomogeneity manifests itself as a wide distribution of relaxation times because there exists a very broad distribution of mobilities in the polymer matrix. Qualitatively, the heterogeneity can be observed by examining the width of the tan δ peak[13,15,16]. Physically, this width provides a measure of the range of mobilities that exist within the polymer. In *Figure 7*, the tan δ peak width at half its height is plotted as a function of the glass transition temperatures of poly(HepA-co-DEGDA) samples and poly(OcMA-co-DEGDMA) samples.

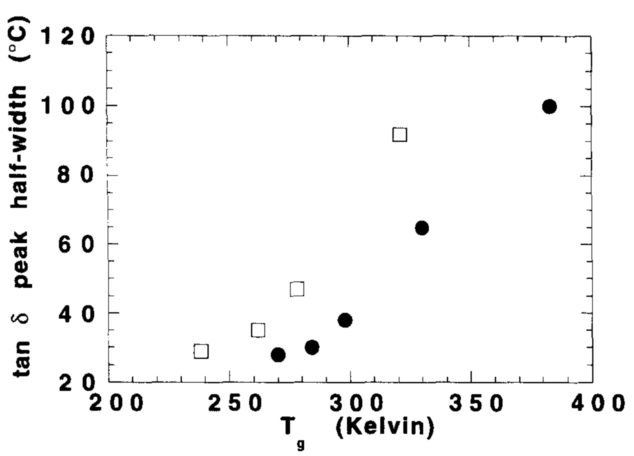

Figure 7 Width of the damping factor (at half peak height) as a function of the T_g of copolymers (□) HepA and DEGDA, and (●) OcMA and DEGDMA

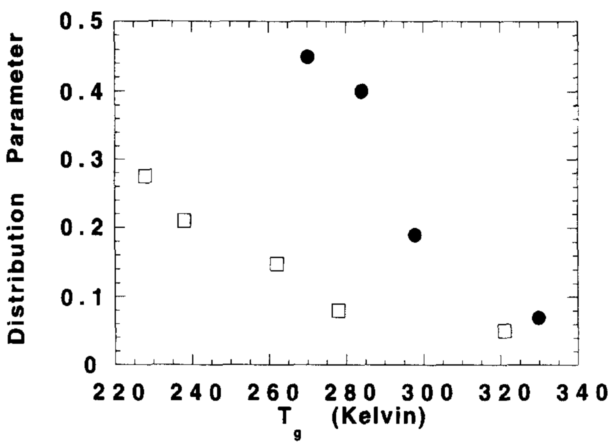

Figure 8 Distribution parameter that provides a measure of the heterogeneity of the material for the copolymers (□) HepA and DEGDA, and (●) OcMA and DEGDMA

It can be observed (by using the information in *Figures 2 and 3*) that as the composition of DEGD(M)A is increased in the copolymer, the glass transition temperature of the copolymer is increased. As the glass transition temperature increases, in *Figure 7* it can be seen that the peak width of the damping factor increases. This increase suggests that the width of the distribution of relaxation times (or mobilities) increases as the glass transition temperature is increased by adding more crosslinking agent to the system. In other words, the degree of structural heterogeneity of the copolymers increases with increasing crosslinking agent composition (or crosslinking density). It appears that for a given glass transition temperature, the acrylate copolymer is more heterogeneous than the methacrylate. However, it should be remembered that the acrylate copolymer has to reach a higher crosslinking density than the methacrylate counterpart to attain the same T_g because of the differences in the backbone polymers.

To characterize this distribution of mobilities quantitatively, i.e. the heterogeneity of the polymers, frequency domain experiments at various temperatures are performed on the DMA. From such experiments, a distribution parameter that describes the heterogeneity of the polymer networks can be extracted[7,8]. This analysis involves using the stretched exponential function (or Kohlrausch–Williams–Watts exponential), $E_0\exp[-(t/\tau)^{\beta}]$, in the glassy region to obtain the distribution parameter β (a complete description of the analysis appears in ref. 8). The distribution parameter obtained from this analysis can take a value between 0 and 1. A value close to 1 implies a very homogeneous polymer with a uniform distribution of mobilities, while a value close to 0 implies a very heterogeneous polymer with a wide distribution of mobilities or environments.

In *Figure 8*, distribution parameters for copolymers of HepA and DEGDA as well as for copolymers of OcMA and DEGDMA are plotted as a function of glass transition temperature. It can be observed that as the T_g of the materials increases, the value of the distribution parameter decreases. This decrease indicates that the heterogeneity of the copolymer increases as the T_g of the material is increased by increasing the crosslinking density of the material. As discussed before, it can be observed that the poly(OcMA-co-DEGDMA) copolymers appear to be more homogeneous than the poly(HepA-co-DEGDA) samples for a given T_g. However, the degree of crosslinking that is required to obtain a given T_g in acrylate copolymers is higher than in methacrylate copolymers (as the presence of the methyl group in the methacrylate increases the stiffness of the backbone, increasing the T_g).

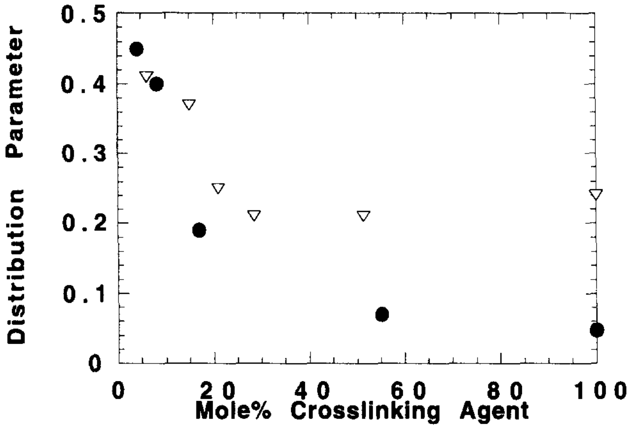

Figure 9 Distribution parameter as a function of mole% crosslinking agent in copolymers (●) OcMA and DEGDMA as well as (▽) OcMA and PEG600DMA

While it may appear that the heterogeneity of the network structure increases with the glass transition temperature of the copolymer, it should be noted that this may not always be the case. As discussed previously, in a copolymer system such as OcMA and PEG600DMA, the T_g dependence on the crosslinking agent concentration or the crosslinking density is not straightforward. However, the heterogeneity is directly related to the crosslinking density of the copolymer. This relationship is expected as the heterogeneity in these polymers is determined by the complexities during the photopolymerization. The presence of an increased number of multifunctional monomers contributes to an increase in the microgel formation, increased differences in the reactivity of the various double bonds and increased formation of cycles and/or crosslinks. All of these changes during the formation of these networks influence the final structure and heterogeneity of the network.

These influences contribute to increasing the range (with respect to the time scales of the mobilities) of microenvironments found in the three-dimensional crosslinked structure. Several investigators[3,6–8,11–13,26,27] have noted that as a result of these crosslinking photopolymerizations, environments that have very low mobilities (like the microgels) as well as regions of very high mobility (which contain unreacted monomer) co-exist in the polymer networks formed.

To understand the dependence of this structural heterogeneity as measured by DMA on the crosslinking agent composition and size or molecular weight (MW), experiments were performed in samples of OcMA (MW $\sim 198\ \text{g mole}^{-1}$) copolymerized with DEGDMA (MW $\sim 242\ \text{g mole}^{-1}$) and PEG600DMA (MW $\sim 748\ \text{g mole}^{-1}$). *Figure 9* plots the distribution parameter of the copolymers of OcMA with DEGDMA and PEG600DMA as a function of the mole% of crosslinking agent used. It can be observed that as the composition of the dimethacrylate is increased, the distribution parameter decreases or the structural heterogeneity of the copolymer increases. Examining *Figure 9*, it may be observed that the degree of heterogeneity within each copolymer system appears to increase (or the distribution parameter decreases) as the concentration of crosslinking agent is increased. This increase continues until a certain degree of heterogeneity is achieved, beyond which no significant change in the distribution parameter is observed. This limit in the distribution parameter seems to be higher in the case of OcMA/PEG600DMA copolymers. This observation may be explained by examining the reasons for the heterogeneity.

During these polymerizations, the dimethacrylate is susceptible to cyclization which results in an increase in the rate of microgelation and therefore, leads to increased heterogeneity. By using a higher MW dimethacrylate (such as PEG600DMA), the tendency to form cycles as opposed to crosslinks can be decreased[26,27]. Therefore, copolymerizing OcMA with PEG600DMA results in a more homogeneous copolymer network than copolymerizing OcMA with DEGDMA.

To examine the trends in the degree of heterogeneity further, in *Figure 10* the distribution parameter is plotted as a function of ζ, which is a measure of the molecular weight between crosslinks (M_c). As the M_c decreases (the crosslinking density increases), the heterogeneity of the copolymer increases. Also, at the same crosslinking density it appears that the OcMA–PEG600DMA copolymers are more homogeneous than the OcMA–DEGDMA copolymers. This observation confirms that using a larger MW crosslinking agent, the heterogeneity of the copolymer can be decreased and still maintain the same molecular weight between crosslinks. However, it should be noted that at the same M_c, the glass transition temperatures and strength can be vastly different depending on the nature of the monomer(s) polymerized. Further, it can be seen from the figure that the structural heterogeneity of the HepA–DEGDA copolymers becomes comparable to that of the OcMA–DEGDMA copolymers as the crosslinking density is increased. It appears that at intermediate crosslinking densities the acrylate copolymers are more homogeneous than the OcMA–DEGDMA copolymers. Therefore, the heterogeneity of the polymer structure is dependent on the monomer type as well.

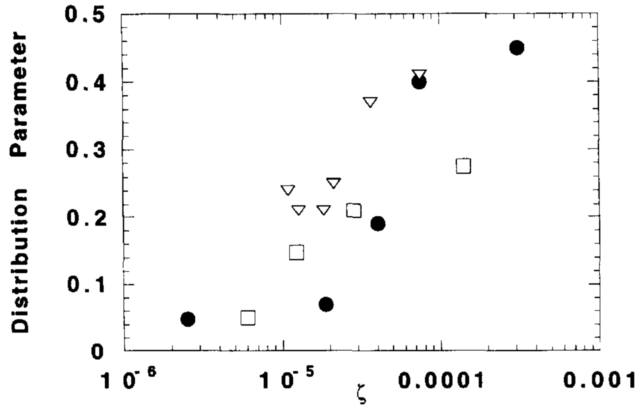

Figure 10 Distribution parameter as a function of ζ, which is a measure of the molecular weight between crosslinks for copolymers of (●) OcMA and DEGDMA as well as (▽) OcMA and PEG600DMA, and (□) HepA and DEGDA

CONCLUSIONS

In this work, an overall perspective of the inter-relationship between the polymerization conditions, mechanical properties and the structural heterogeneity of photopolymerized (meth)acrylate networks has been provided. The dependence of glass transition temperatures as well as degree of inhomogeneity on the crosslinking density has been examined in selected copolymer systems. The crosslinking density was varied by varying the composition as well as size of the crosslinking agent. Interesting behaviour has been observed when examining the OcMA copolymers of DEGDMA and PEG600DMA. Copolymers of OcMA and DEGDMA as well as HepA and DEGDA exhibit typical T_g behaviour as a function of mole fraction of crosslinking agent. As crosslinking agent composition increases, the T_g of the material increases. However, when OcMA is copolymerized with PEG600DMA, an increase in T_g is observed only for low concentrations of the crosslinker. Continued increase of the PEG600DMA concentration results in a decrease in the glass transition temperature of the copolymers. This decrease is attributed to the 'copolymerization effect'. It should be remembered that the decrease in T_g is not an effect of residual unsaturation in the system because copolymers of PEG600DMA and OcMA reach double bond conversions close to 100%. Further, even in the DEGDMA copolymers it appears that the crosslinking effect is dominant only for low concentrations of the crosslinker. However, at higher concentrations of DEGDMA the 'copolymerization effect' and the effect of residual unsaturation cannot be separated. As a result, in those copolymers it is not clear what mechanism dominates at higher concentrations of crosslinker.

The degree of structural heterogeneity that is inherent in these crosslinked polymers because of the presence of microgels and loosely crosslinked regions (and even unreacted monomers) requires more understanding. The heterogeneity depends strongly on the crosslinking density of the system and the nature of the crosslinking monomers as has been demonstrated by the studies presented here on the acrylate and methacrylate copolymers. Depending on the monomer size and type, the resultant polymer may have features such as crosslinks and primary or secondary cycles that contribute to the heterogeneity of the materials. These heterogeneities affect the structure and the performance of the crosslinked network formed. In this paper, it has been demonstrated that in increasing the crosslinking density, the polymer network is made more heterogeneous. Further, it appears that by increasing the size of the crosslinking agent, the network structure may be made more homogeneous. However, in obtaining a more homogeneous network it is possible that some of the properties (strength or T_g) of the polymer may be sacrificed. Therefore, in choosing the composition and size of the crosslinking agent for a specific application, it is important to consider the effect these polymerization conditions have on the final structure and properties of the material.

ACKNOWLEDGEMENTS

The authors would also like to thank DuPont and 3M for their financial support and, NSF for its support through a Presidential Faculty Fellowship to CNB (CTS-9453369) and the equipment grant for the FTIR (CTS-9500477).

REFERENCES

1. Ruyter, I. E. and Oysaed, H., *CRC Critical Rev. in Biocompatability*, 1988, **4**, 247.
2. Smith, L. T. and Powers, J. M., *Int. J. Prosthodont.*, 1991, **4**, 445.
3. Kloosterboer, J. G., *Adv. Polym. Sci.*, 1988, **84**, 1.
4. Fouassaier, J. P. and Rabek, J. F. (ed.), *Radiation Curing in Polymer Science and Technology*, Volume IV: *Practical Aspects and Applications*. Elsevier, New York, 1993.
5. Zwiers, R. J. M. and Dortrant, G. C. M., *Applied Optics*, 1985, **24**, 4483.
6. Anseth, K. S., Anderson, K. J. and Bowman, C. N., *Macromol. Chem. Phys.*, 1996, **197**, 833.
7. Kannurpatti, A. R., Anderson, K. J., Anseth, J. W. and Bowman, C. N., *Polymeric Materials Science and Engineering*, 1996, **74**, 100.
8. Kannurpatti, A. R., Anderson, K. J., Anseth, J. W. and Bowman, C. N., *J. Polym. Sci. Part B: Polym. Phys.*, 1997, **35**, 2297.
9. Matsumoto, A., Ando, H. and Oiwa, M., *Eur. Polym. J.*, 1989, **25**, 185.
10. Bastide, J. and Liebler, L., *Macromolecules*, 1988, **21**, 2647.
11. Simon, G. P., Allen, P. E. M., Bennett, D. J., Williams, D. R. G. and Williams, E. H., *Macromolecules*, 1989, **22**, 3555.
12. Cook, W.D., *Polymer*, 1992, **33**, 2152.
13. Simon, G. P., Allen, P. E. M. and Williams, D. R. G., *Polymer*, 1991, **32**, 2577.
14. Wilson, T. W., *J. Appl. Polym. Sci.*, 1990, **40**, 1195.
15. Allen, P. E. M., Clayton, A. B. and Williams, D. R. G., *Eur. Polym. J.*, 1994, **30**, 427.
16. Matsuoka, S., *Relaxation Phenomena in Polymers*. Hanser Publishers, New York, 1992.
17. Treloar, L. R. G., *The Physics of Rubber Elasticity*. Oxford University Press, London, 1958.
18. Charlesworth, J. M., *Polym. Eng. Sci.*, 1988, **28**, 230.
19. Anseth, K. S., Wang, C. M. and Bowman, C. N., *Polymer*, 1994, **35**, 3243.
20. Anseth, K. S., Wang, C. M. and Bowman, C. N., *Macromolecules*, 1994, **27**, 650.
21. Fox, T. G. and Loshaek, S., *J. Polym. Sci.*, 1955, **15**, 371.
22. Loshaek, S., *J. Polym. Sci.*, 1955, **15**, 391.
23. Kanig, G., *J. Polym. Sci., Part C*, 1957, **1967**, 16.
24. Chompff, A. J., *Polymer Networks: Structure and Mechanical Properties*, ed. A. J. Chompff and S. Newman. Plenum Press, New York, 1971, p. 145.
25. Bicerano, J., Sammler, R. L., Carriere, C. J. and Seitz, J. T., *J. Polym. Sci., Part B*, 1996, **34**, 2247.
26. Anseth, K. S. and Bowman, C. N., *J. Polym. Sci., Part B*, 1995, **33**, 3243.
27. Bowman, C. N. and Anseth, K. S., *Macromol. Symp.*, 1995, **93**, 269.