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Structural Evolution of Dimethacrylate Networks Studied by Dielectric Spectroscopy

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ABSTRACT: In this work, the structural heterogeneity of copolymers formed by photopolymerizations of diethylene glycol dimethacrylate (DEGDMA) and poly(ethylene glycol 600) dimethacrylate (PEG600DMA) has been characterized as a function of double bond conversion and cross-linking density (as measured by comonomer composition) by dielectric analysis (DEA). The heterogeneity has been characterized by a distribution parameter which represents the breadth of the polymer relaxation spectrum. It was found that the distribution parameter as measured by DEA matched well with those estimated previously by dynamic mechanical analysis. In addition to obtaining fundamental structural information from the α-transition (or glass transition) region, β-transitions (or secondary transitions) were studied in the poly(DEGDMA-*co*-PEG600DMA) networks studied. These secondary transitions are observed as a result of unreacted pendant as well as monomeric double bonds that are present in the samples. The heights of the damping factor peaks at the secondary transitions increase as the cross-linking density of the copolymer is increased (by increasing the DEGDMA composition). Further, the peak height decreases as the conversion increases in a given sample, strongly suggesting that the residual unsaturation in the copolymer network is responsible for the β-transition. Evidence is also presented that precludes the possibility that the initiator or its fragments cause the secondary transitions.

Introduction

Cross-linked polymers formed by photocuring multifunctional monomers are finding use in a wide variety of applications[1−6] ranging from dental materials to microelectronics. Tailoring these materials for the various applications is a significant challenge and requires a fundamental understanding of the formation−structure−property relationships. While these network polymers have very desirable properties, the network structure formed by photopolymerizing multifunctional monomers is extremely heterogeneous.[1,6−11] It has been of significant interest to characterize this structural heterogeneity by using various experimental techniques[6−13] as well as to develop a theoretical understanding of these heterogeneities.[14−20] It has been noted in the literature[9−11] that both very highly cross-linked polymer-rich regions, known as microgels, and "pools of unreacted monomer" are found in the same network. Such a range of environments is reflected in the mechanical response of the materials as wide glass transition regions.[10,12,13] Therefore, by examining the glass transitions and the distribution of relaxation times, the distribution of mobilities (or microenvironments) can be characterized. In our earlier work,[13] dynamic mechanical analyses (DMA) performed on photopolymerized cross-linked polymers have been described. From these analyses, parameters that describe cross-linking density and the heterogeneity of polymer networks have been inferred. The structural heterogeneity was characterized by performing frequency scans over a limited frequency range at various temperatures (above and below T_g) and, subsequently, performing time−temperature superpositions to construct a master curve of the modulus relaxation. While this technique is widely used, the validity of the superposition principle and the limited frequency range of the DMA make it imperative that we obtain evidence that will supplement information gleaned from DMA. In the study described in this manuscript, dielectric spectroscopy is used to corroborate our earlier results obtained from DMA. More importantly, significant evidence that both microgel regions and pools of unreacted monomer coexist in the same network has been obtained by dielectric spectroscopy.

Dielectric Analysis. Dielectric analysis[21−27] (DEA) exploits the presence of permanent dipoles in the chemical structure of the polymers being examined. The dipoles in a network can contribute to molecular or segmental moments which result in molecular configurations or conformations. Such polymers that exhibit dipole moments are said to be "dielectrically active". Measuring the polarization induced in these polymers due to an applied electric field is a very useful method for probing polymer structure. These measurements involve applying an electric field across a polymer film and examining the current response. By performance of static measurements (i.e., applying time-invariant electric fields), the equilibrium structure of the polymers can be probed. However, more interesting information regarding the polymer chain dynamics and distribution of relaxation times can be gleaned by performing dynamic measurements.

In these dynamic dielectric measurements,[21] a sinusoidal field (time-dependent field) is applied across the polymer film and the current response is monitored. The response is dependent on the frequency of the applied field, just as the strain response is dependent on the frequency of the applied stress in dynamic mechanical analysis (DMA). By examination of this response, very useful information regarding the structural heterogeneity of the polymer networks can be gleaned. It should be noted that DEA is a very convenient technique to

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probe a wide range of relaxation times because it is relatively easy (compared to DMA) to scan a broader frequency range. However, it should be recalled that DEA can be used only on polymers that are dielectrically active.

Photopolymerized Networks. As discussed previously, polymer networks formed by photocuring multifunctional monomers are extremely heterogeneous. Further, these diffusion-limited polymerizations result in networks with trapped radicals and unreacted double bonds. In this work, "living" radical polymerizations are used to avoid radical trapping[13] so that DEA may be performed as a function of temperature without changing the structure of the network being analyzed. Briefly, the "living" radical polymerization mechanism provides a means to synthesize polymer networks which are structurally similar to those obtained by conventional polymerization, however, without the trapped carbon radicals. As in our previous work,[13] "living" radical photopolymerization has proven to be a very useful tool in understanding the structure and properties of network polymers.

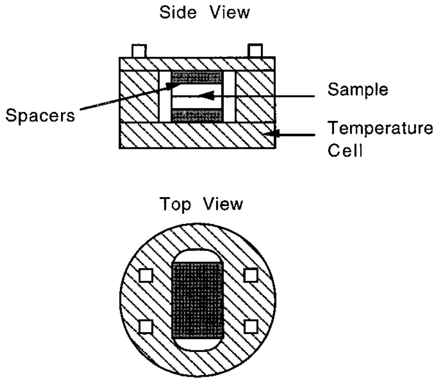
The focus of this work is to understand the structural evolution of cross-linked polymers formed by free-radical photopolymerizations as a function of double bond conversion as well as cross-linking densities. In particular, a focus of this work will be understanding the nature of secondary transitions in highly cross-linked polymers. Studies have been performed on copolymers of diethylene glycol dimethacrylate (DEGDMA) and poly(ethylene glycol 600) dimethacrylate (PEG600DMA). The dielectric spectra are analyzed to obtain distribution parameters as a function of composition of the copolymer. This information is compared to that previously obtained[13] from DMA. Further, secondary transitions (or β-transitions) are observed and characterized as a function of composition and double bond conversion.

Experimental Section

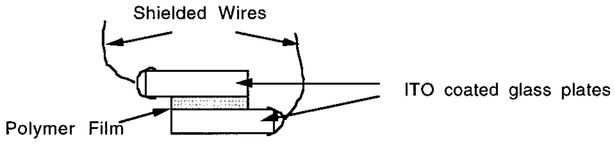
Materials. Diethylene glycol dimethacrylate (DEGDMA) and poly(ethylene glycol 600) dimethacrylate were obtained from PolySciences Inc. and used as received. *p*-Xylylene bis(*N*,*N*-diethyl dithiocarbamate) (XDT) was used to initiate "living" radical polymerizations. The mechanism of these polymerizations is described in a previous paper.[28]

Methods. Dielectric studies were performed using a 1260 Solatron impedance analyzer (Schlumberger, Hampshire, U.K.). Samples were photocured between two indium−tin oxide (ITO) coated glass plates (donated by Donnelly Applied Films, Boulder, CO) so that the cured film and the conducting faces were in intimate contact, forming a parallel plate capacitor. The samples were mounted in a custom-built cell (Boulder Nonlinear Systems, Boulder, CO) whose temperature can be controlled between −10 and +80 °C. The outside shell of the cell was grounded, and shielded cables were used to connect the terminals of the capacitor arrangement and the impedance analyzer. Schematic diagrams of the temperature cell and the parallel plate capacitor arrangement are represented in Figure 1. Data were acquired from 20 000 Hz to 1 mHz by applying a voltage whose amplitude was 1.3 ± 0.2 V depending on the sample being tested.

Copolymers of DEGDMA and PEG600DMA were photocured between the ITO glass plates using a 365 nm Ultracure Plus SS light source (EFOS) at approximately 600 mW/cm^2. The cure times were 900 s or less, and very thin films were polymerized by placing a drop of monomer mixture between the glass plates. The ITO coated sides were in intimate contact with the polymer film. The thickness of the films was approximately 20 μm. Infrared spectroscopy was performed on the tested samples to evaluate their double bond conversions.



(a) Temperature Cell with sample mounted



(b) Sample cell

Figure 1. Schematic of a (a) temperature-controlled cell and (b) a sample cell (not drawn to scale).

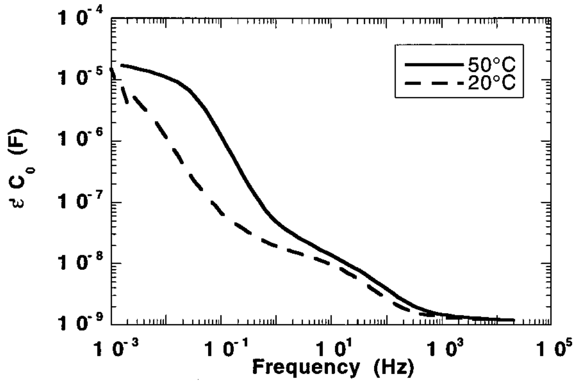


Figure 2. Product of the dielectric storage constant (ϵ') and the empty cell capacitance (C_0) as a function of frequency of the applied voltage at different temperatures.

Results and Discussion

Dielectric analysis (DEA) was performed on several copolymer samples of DEGDMA and PEG600DMA. Figure 2 shows typical dielelectric data. The storage dielectric constant (ϵ') multiplied by the capacitance of cell with air between the plates (C_0) is plotted in the figure. Because C_0 is a constant for a given capacitor geometry,[21] it was sufficient for the purposes of this study to monitor the product, $\epsilon' C_0$. Monitoring the dependence of this product on the frequency of the applied voltage allows the characterization of the distribution of relaxation times.

At high frequencies, it can be seen that the storage dielectric constant is very low because the polar groups in the polymer are not mobile at those short time scales and do not orient readily to provide a discernible change in polarization. As the frequency is decreased, the time scales increase and the most mobile groups begin to orient, inducing a polarization that is measured. Thus, an increase in the $\epsilon' C_0$ value is observed. Typically, when all the groups have responded to the voltage, the dielectric storage reaches a maximum plateau. How-

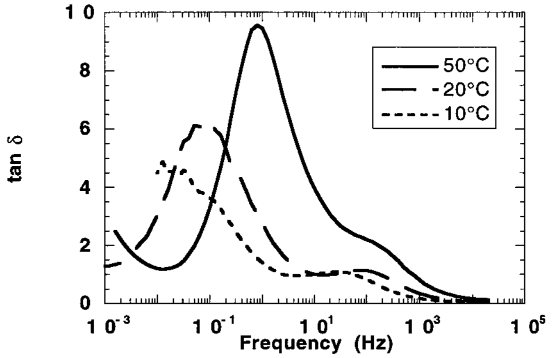


Figure 3. Loss tangent or tan δ curves for a 30/70 DEGDMA/PEG600DMA copolymer sample at 50, 20, and 10 °C.

ever, for the sample examined, it can be seen in the figure that the storage reaches an intermediate plateau at approximately 10 Hz and starts to rise further. When the frequency decreases below 0.1 Hz (in the 50 °C curve), a plateau is reached, while in the 20 °C curve, a plateau is not reached in the frequency range scanned.

To understand this behavior, it is important to note that at 20 °C the 30/70 DEGDMA/PEG600DMA copolymer sample studied is glassy, while at 50 °C it is rubbery. Therefore, when the sample is glassy, even at a frequency of 1 mHz, there are polar groups that are immobile and do not respond to the field. However, at 50 °C almost all groups are oriented by millihertz frequencies.

The intermediate plateau that is observed is an indication of a secondary transition (or β-transition). This secondary transition is likely caused by the presence of unreacted groups (both monomeric and pendant), which are found in regions of higher mobilities. As a result, these groups respond at higher frequencies because they have shorter relaxation times. It is possible that this peak is caused by other polar species, such as the initiator or its fragments, present in the polymer. This possibility is clarified in subsequent results presented in this paper.

Figure 3 shows loss tangent (or tan δ) curves for the same copolymer at various temperatures above and below the T_g. The peak or shoulder that is observed at higher frequencies is the β-transition and the larger peak that is observed at lower frequencies is the glass transition or the α-transition. It can be seen that as the temperature increases, the glass transition peak becomes narrower and larger and is shifted to higher frequencies. This behavior is expected because as more thermal energy is provided to the sample, the mobility of the segments increases and more polar groups are oriented in shorter time scales or at higher frequencies.

If the dielectric storage constant is analyzed, the distribution of relaxation times can be characterized by a distribution parameter, β, like the parameter[13,21] obtained from DMA. A stretched exponential function of the form,

$$\epsilon' = \epsilon'_0 \exp[(\omega_0/\omega)^{\beta}] \tag{1}$$

is used to fit the dielectric storage constant. Here, ω is the frequency of the applied field. β is a distribution parameter that characterizes the distribution of mobilities (or relaxation times) in the system. The distribution parameter, β, can take a value between 0 and 1. A value close to zero implies a very heterogeneous polymer, and a value close to 1 implies a homogeneous polymer with a narrow distribution of relaxation times.

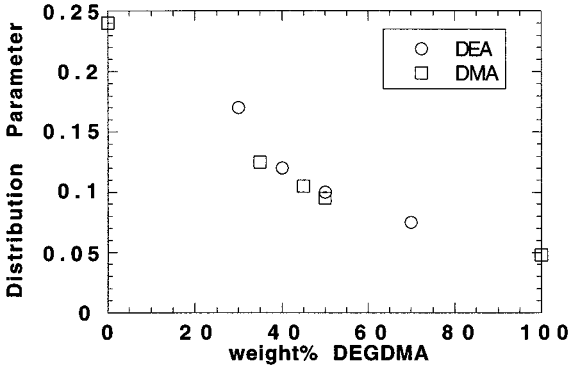


Figure 4. Comparison of distribution parameters, β, obtained by DEA and DMA for copolymers of DEGDMA and PEG600DMA, as a function of weight percent of DEGDMA. DMA data were from ref 13.

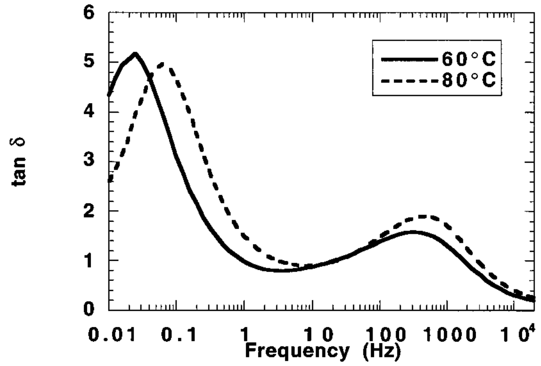


Figure 5. Loss tangent curves for a 50/50 DEGDMA/PEG600DMA copolymer as a function of frequency of applied voltage at 60 and 80 °C.

Performing this analysis allowed the comparison of the distribution parameters obtained by DEA and DMA. Figure 4 compares values obtained by these two techniques for the copolymers of DEGDMA and PEG600DMA. As can be seen in the figure, the values obtained by DEA are in very good agreement with the values obtained by DMA. It can also be seen that as the cross-linking density of the copolymer is increased by increasing the concentration of DEGDMA in the copolymer, the heterogeneity of the network increases. Therefore, it appears that DMA and DEA examine the same environments. As was observed by DMA,[13] the value of the distribution parameter decreased as the DEGDMA concentration was increased.

Using DEA, more interesting features such as secondary transitions that provide a fundamental understanding of the polymer structure are observed. Secondary peaks and shoulders have been previously noted[10−13] in the ethylene glycol dimethacrylate network systems examined in this work. However, it has been fairly difficult to characterize these secondary peaks using other techniques such as DMA.

Figure 5 plots tan δ of a 50/50 DEGDMA/PEG600DMA copolymer as a function of frequency at two temperatures. A large peak is seen at low frequencies in each curve. This peak is the glass transition peak of the sample. The second, smaller peak observed at around 1000 Hz is the secondary transition peak that may be caused by other polar groups that are found in more mobile environments. Typically, pendant polar groups and other polar moieties in the network possess higher

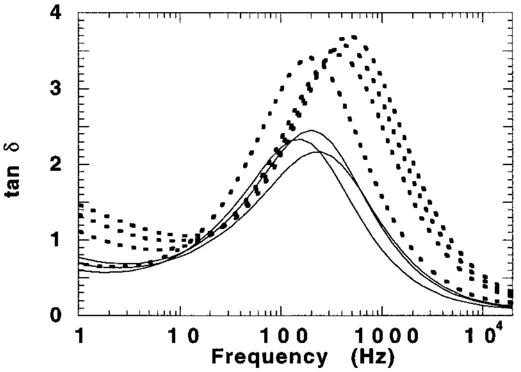


Figure 6. Secondary (or β-) transition peaks in the loss tangent curves of 50/50 DEGDMA/PEG600DMA samples polymerized with 0.1 wt % (dashed line) and 1.0 wt % (solid line) initiator (XDT). Curves at various temperatures are shown in the figure.

mobilities than polar groups that are part of the segments (or polymer backbone). The groups that are along the segments need longer times to respond to the field because they require cooperative rearrangements to orient with the field. Pendant unreacted functional groups, pendant initiator fragments, and unreacted monomeric and initiator species constitute the candidates that may be responsible for the secondary peak observed in this system.

To understand the origin of the secondary transition peak, further experiments were performed. The initiator concentration was varied an order of magnitude without varying the composition of the copolymer. Performing DEA on such samples, it was hoped to understand the effect the initiator concentration had on the secondary transition. Figure 6 shows the secondary transition peaks of 50/50 DEGDMA/PEG600DMA samples polymerized with 0.1 and 1.0 wt % XDT (initiator) at various temperatures. If the initiator is the cause of the secondary peak, the tan δ peak would be larger for the sample that has a higher concentration of initiator. However, in examining the data, just the opposite effect is observed; *i.e.*, the peak is larger for the sample that has a lower concentration of initiator. These experiments show that the initiator does not contribute to the secondary transition peak, suggesting that the unreacted methacrylates (pendant as well as monomeric) are responsible for the transition at high frequencies.

Interestingly, the data in Figure 6 also provide some direct evidence that it is the unreacted functional groups that are responsible for the secondary transition peak. At lower initiator concentrations, the final double bond conversions are typically lower than those achieved at higher initiator concentrations (refer to Table 1). This decrease in conversion at lower initiator concentrations will be observed as an increased secondary peak in the tan δ curve if the secondary peak was caused by unreacted functionalities. Such an increase in the peak is observed, suggesting strongly that the peak is caused by the unreacted double bonds (pendant or monomeric).

It is important to characterize this secondary peak because the presence of a secondary transition at a much higher frequency implies a very high degree of structural heterogeneity in the copolymer networks examined. Physically, the presence of multiple transitions at distinct average relaxation times implies the presence of two unique distributions of environments with varying mobilities.

Table 1. Double Bond Conversions As Measured by FTIR Spectroscopy of the Various Copolymer Samples Studied[a]

DEGDMA: PEG600DMA in the monomer mixture	XDT concentration (wt%)	measured double bond conversion (%)	estimated unreacted monomer fraction (%)	estimated pendant double bond fraction (%)
30:70	1.0	24	58	18
30:70	1.0	62	14	24
30:70	1.0	77	5	18
50:50	1.0	70	9	21
50:50	0.1	47	28	25
70:30	1.0	50	25	25

[a] Table also shows estimated unreacted pendant double bond fraction as well as monomer fraction.

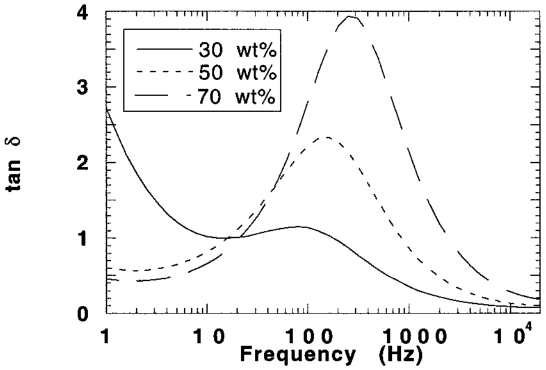


Figure 7. Secondary transition tan δ peaks for copolymers of PEG600DMA and DEGDMA. Legend shows weight percent of DEGDMA in the monomer mixture.

To characterize the secondary transition or the β-transition as a function of cross-linking density, copolymers of varying compositions of DEGDMA and PEG600DMA were examined. Figure 7 plots the secondary transition peaks for various samples at temperatures which are in the glassy region of the polymers. It can be observed that as the composition of DEGDMA in the sample is increased, the peak maximum increases. This observation is consistent with the fact that the maximum attainable conversion in these copolymers decrease as the composition of DEGDMA is increased. As shown in Table 1, it was found by infrared spectroscopy that the double bond conversion of the copolymers decreased as the composition of DEGDMA was increased.

Further, as the composition of DEGDMA is increased, the peaks are slightly shifted to the right (i.e., to higher frequencies). This shift suggests that at lower conversions the unreacted functionalities find themselves in higher mobility regions. Further, the fact that a second peak is observed implies that the network has distinct, high mobility regions or “monomer pools”. Similar observations have been made by other researchers employing solid-state NMR techniques.[9−11]

To confirm the observations regarding the conversion dependence of the secondary transition peak, DEA was performed on samples of 30/70 DEGDMA/PEG600DMA at various conversions or polymerization times (refer to Table 1). It can be observed in Figure 8, that the secondary peak is the dominant peak at lower conversions or polymerization times. As the cure time is increased, more double bonds react into the backbone of the network, and the secondary peak decreases. At high conversions, it can be observed that the secondary peak almost becomes a shoulder of the α-transition peak. These observations confirm that the secondary transition is caused by the unreacted pendant as well

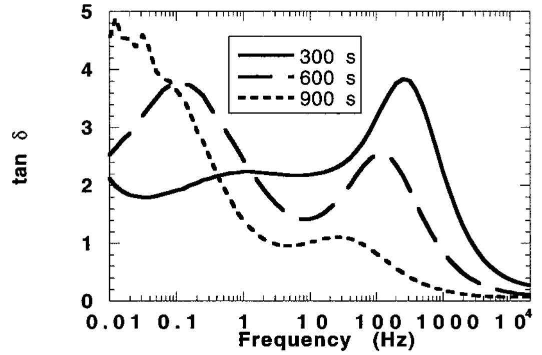


Figure 8. Tan δ peaks for 30/70 DEGDMA/PEG600DMA samples cured to varying times. Legend indicates cure times.

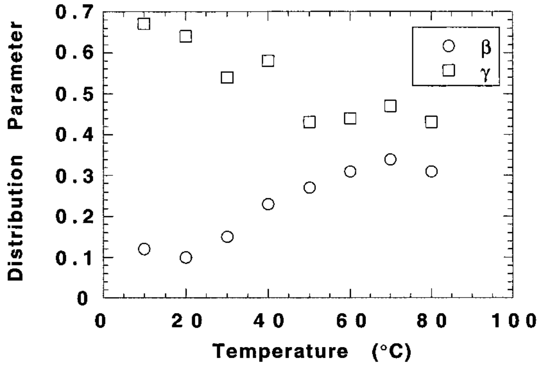


Figure 9. Distribution parameters, β and γ, for the α- and the β-transition processes, respectively, as a function of temperature in a 50/50 DEGDMA/PEG600DMA copolymer sample. The T_g of the polymer is approximately 40 °C.

as monomeric double bonds. The shift in the peak maximum frequency to lower frequencies in the high conversion samples suggests (as before) that the unreacted species find themselves in more restricting (low mobility) environments as the conversion increases.

From these experiments, which varied initiator concentration, composition of the copolymer and conversion of the copolymer, it has been clarified that the secondary peak is caused by the unreacted double bonds (pendant and monomeric). In Table 1, estimated unreacted as well as pendant double bond fractions in the copolymers are also presented. It can be seen that the secondary peak correlates very well with the pendant as well as the unreacted monomer compositions. It has also been noted that the unreacted species seem to be in environments that have generally higher mobility while, as indicated by the lower frequency at which the α-transition is observed, the polymer-rich regions are regions of low or very restricted mobility. It is also interesting to understand the effect of temperature on the network mobilities or the distribution of relaxation times. Because DEA provides the capability of scanning a wider frequency range than DMA, the distribution parameter can be characterized as a function of temperature more conveniently.

In Figure 9, distribution parameters, β and γ, that describe the distribution of mobilities in the two transition regions (α- and β-transitions, respectively) are plotted for the 50/50 copolymer of DEGDMA and PEG600DMA. γ is obtained by performing a stretched exponential fit to the secondary transition. When the temperature is low and the sample is glassy, the β values are low and approximately constant at about 0.1. As the temperature is increased beyond the glass transition temperature of the sample ($T_g \sim 40$ °C), the β value increases. This observation suggests that the distribution of polymer segmental mobilities becomes increasingly homogeneous. This feature may be as expected because the segmental orientation requires cooperative motion, and it becomes increasingly easier as the temperature increases for segments in various environments to rearrange. Similar observations have been made by Torkelson and co-workers[27,29] while examining linear polymers.

In observing the β-transition distribution parameter, γ, it can be seen that an opposite effect takes place. The distribution of mobilites seems to become increasingly heterogeneous as the temperature is increased. This increase is caused because the β-transition process becomes increasingly coupled to the α-transition process. In other words, the rearrangement of the side chains or unreacted groups becomes coupled with the cooperative motions that reorient the segments of the polymer network at higher temperatures (when the segments of the network have a higher mobility because of the increased thermal energy). Thus, it becomes harder to define two distinct transitions as the two distributions mold into a single average distribution.

Conclusions

In this work, dielectric analyses (DEA) have been performed on copolymers of DEGDMA and PEG600DMA using "living" radical polymerizations. Using these tools, information critical to the understanding of the structural evolution of network polymers has been gleaned. It was shown that as the cross-linking density of the polymer network increases (by increasing DEGDMA composition as well as by increasing the double bond conversion), the structural heterogeneity of the system also increases.

In addition, fundamental information regarding the network structural heterogeneity and mobilities was obtained. Secondary transition peaks were readily observed in these cross-linked polymers, and it was clearly shown that these transitions are a result of the unreacted double bonds. Results have been presented to describe the dependence of the structural heterogeneity of both reacted and unreacted functional groups on temperature. Uniquely, it has been observed that as the temperature increases, these microenvironments surrounding the reacted and unreated functional groups appear to merge and become equally heterogeneous.

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References and Notes

(1) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(2) Peter Pappas, S., Ed. *Radiation Curing Science and Technology*; Plenum Press: New York, 1992.
(3) Fouassier, J. P.; Rabek, J. F., Eds. *Radiation Curing in Polymer Science and Technology, Volume IV: Practical Aspects and Applications*; Elsevier: New York, 1993.
(4) Turner, D. T.; Haque, Z. U.; Kalachandra, S.; Wilson, T. W. *ACS Symp. Ser.* **1988**, *367*, 427.
(5) Smith, L. T.; Powers, J. M. *Int. J. Prosthodont.* **91**, *4*, 445.

(6) Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Adv. Polym. Sci.* **1995**, *122*, 177.
(7) Anseth, K. S.; Rothenberg, M. D.; Bowman, C. N. *Macromolecules* **1994**, *27*, 2890.
(8) Kloosterboer, J. G.; Lijten, G. F. C. M.; Greidanus, F. J. A. M. *Polym. Rep.* **1986**, *27*, 269.
(9) Simon, G. P.; Allen, P. E. M.; Bennett, D. J.; Williams, D. R. G.; Williams, E. H. *Macromolecules* **1989**, *22*, 3555.
(10) Simon, G. P.; Allen, P. M.; Williams, D. R. G. *Polymer* **1991,** *32*, 2577.
(11) Allen, P. E. M.; Simon, G. P.; Williams, D. R. G.; Williams, E. H. *Macromolecules* **1989**, *22*, 809.
(12) Wilson, T. W. *J. Appl. Polym. Sci.* **1990**, *40*, 1195.
(13) (a) Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2297. (b) Kannurpatti, A. R.; Anseth, J. W.; Bowman, C. N. *Polymer* **1998**, *39*, 2507.
(14) Dusek, K. In *Polymer Networks: Structure and Mechanical Properties*; *Proceedings of the ACS Symposium on Highly Cross-Linked Polymer Networks*; Chompff, A. J., Newman, S.,Eds.; Plenum Press: New York, 1970; p 245.
(15) (a) Dusek, K. *J. Polym. Sci., Symp.* **1975**, *53*, 57. (b) Dusek, K. *J. Polym. Sci., Symp.* **1975**, *53*, 75.
(16) Dusek, K.; Somvarsky, J. In *Synthesis, Characterization and Theory of Polymer Networks and Gels*; Aharoni, S. M., Ed.; Plenum Press: New York, 1992; p 283.
(17) Tobita, H.; Hamielec, A. *Macromolecules* **1989**, *22*, 3098.
(18) Boots, H.; Pandey, R. *Polym. Bull.* **1984**, *11*, 415.
(19) Bowman, C. N.; Peppas, N. A. *Chem. Eng. Sci.* **1992**, *47*, 1411.
(20) (a) Anseth, K. S.; Bowman, C. N. *Chem. Emg. Sci.* **1994**, *49*, 2207. (b) Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part B* **1995**, *33*, 3243.
(21) Fava, R. A., Ed. *Methods of Experimental Physics: Polymers, Part C: Physical Properties*; Academic Press: New York, 1980.
(22) Schönhals, A.; Schlosser, E. *Colloid Polym. Sci.* **1989**, *267*, 125.
(23) Richert, R. *Chem. Phys. Lett.* **1992**, *199*, 355.
(24) Diaz-Calleja, R.; Riande, E.; Guzman, J. *J. Polym. Sci., Part B* **1991**, *29*, 93.
(25) Mangion, M. B. M.; Johari, G. P. *J. Polym. Sci., Part B* **1989**, *28*, 1621.
(26) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Polym. Mater. Sci. Eng.* **1993**, *69*, 1.
(27) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1993**, *26*, 5943.
(28) Kannurpatti, A. R.; Lu, S.; Bunker, G. M.; Bowman, C. N *Macromolecules* **1996**, *29*, 7310.
(29) Dhinojwala, A.; Wong, G. K.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 7395.

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