Exploiting the Heterogeneity of Cross-Linked Photopolymers To Create High-T_g Polymers from Polymerizations Performed at Ambient Conditions

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Received March 29, 2001; Revised Manuscript Received August 27, 2001

ABSTRACT: There has been a significant debate related to whether a material with a high glass transition temperature can be obtained from a polymerization performed at a significantly lower temperature (e.g., ambient temperature). To investigate this issue and understand the factors that play a role in determining the relationship between glass transition temperature (T_g) and cure temperature (T_{cure}), three model systems with different degrees of heterogeneities were studied: triethylene glycol dimethacrylate (TEGDMA), diethylene glycol dimethacrylate (DEGDMA) (more heterogeneous), and styrene−divinylbenzene copolymer (St-*co*-DVB) (more homogeneous). These systems were photopolymerized in a temperature cell while simultaneously monitoring the sample temperature with the T_{cure} varying from 25 to 95 °C. The polymerization rate and final double-bond conversion were monitored using near-infrared (NIR) spectroscopy. The T_g of the exact sample cured within the NIR was subsequently measured using dynamic mechanical analysis (DMA). Since this work utilized living radical photopolymerizations, the traditional issues associated with characterizing chain polymerizations (specifically, trapped radicals that persist after cure) were eliminated. It was found that the differences between T_g and T_{cure} were significantly greater for the more heterogeneous multi(EG)DMA system than for the less heterogeneous St-*co*-DVB system with the $T_g - T_{cure}$ being as large as 100 °C. Therefore, heterogeneous networks with broad distributions of relaxation times like DEGDMA exhibit unique cure behavior and facilitate obtaining a higher T_g as a function of T_{cure} than is possible in a comparable, more homogeneous network.

Introduction

Highly cross-linked polymers formed by the photopolymerization of multifunctional monomers are becoming increasingly important materials in many areas such as coatings[1] and biomaterials.[2] Typically, during the bulk polymerization of multifunctional monomers, the development of a 3-D network restricts the mobility of polymer segments, and the subsequent decrease in free volume causes several orders of magnitude decrease in the system mobility. Consequently, a series of phenomena occur, such as autoacceleration, autodeceleration, reaction−diffusion-controlled termination,[3,4] trapped radicals, and limited ultimate double-bond conversion. Since the kinetics and network formation of cross-linking systems are quite complex, a thorough understanding of polymer network structure and mechanical property evolution is still being pursued. The relationship between cure temperature (T_{cure}) and glass transition temperature (T_g) of the polymer is especially important since there is significant debate about whether a high-T_g material can be obtained from a monomer cured at a low temperature (e.g., ambient temperature). The investigation of this problem is also important for many practical applications.

Many researchers have investigated the relationship between T_g and material properties for thermosetting systems. Gillham and co-workers[5−7] studied the isothermal curing of a series of thermosetting systems and developed conversion−temperature−property diagrams for several systems. For a tetrafunctional aromatic diamine−difunctional epoxy system, they found that the T_g vs conversion relationship is independent of cure path,[8] and T_g did not exceed T_{cure} by more than 30 °C. For thermally cured epoxy systems, it is generally observed that T_g does not exceed T_{cure} by more than 40 °C, with the empirical range being 15−35 °C.[9] In addition, Wise and co-workers investigated the effect of T_{cure} on the T_g for the diaminodiphenylmethane (DDM)/diglycidyl ether of the bisphenol A (DGEBA) system.[10] It was found that when the samples were polymerized below the T_g of the fully cured material, the measured T_g was only 15−20 °C above T_{cure}. For the aniline/DGEBA system, the difference was approximately 10 °C.

Unlike the step-growth polymerizations described above, less research has been conducted on the T_g−T_{cure} relationship for chain-growth polymerizations. The reason is that there are several significant problems in characterizing high-T_g polymers, resulting from radical chain polymerizations. One problem is that trapped radicals generally persist in the partially cured networks due to vitrification. When a sample is heated during mechanical testing, additional polymerization is induced as a result of the increased mobility of the trapped radicals and unreacted monomer units. Therefore, the glass transition temperature of the “as-cured” network cannot be measured due to the postpolymerization that occurs upon heating. Another difficulty that often arises is the significant temperature increase caused by the exothermic reaction that occurs during

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10.1021/ma010542g CCC: $20.00

free radical polymerizations. As a result, a cure temperature that is much higher than the initial cure temperature may be realized, particularly in rapid polymerizations. All these problems cause the results of the research reported in this area to be less reliable than that for step-growth systems.

Though these limitations exist, some investigations of chain polymerizations have been conducted. Cook and co-workers investigated the cure kinetics of dimethacrylate-based vinyl ester resins by scanning and isothermal DSC and DMA.[11] For these materials, the difference between the T_g and the isothermal T_{cure} was approximately 11 °C (measured by DSC). Since the samples were not completely reacted, reinitiation of cure during DMA testing was observed.

Kloosterboer and Lijten discussed the effect of T_{cure} on the mechanical properties of 1,6-hexanediol diacrylate.[12] By photocuring the samples at room temperature, a difference between T_g and T_{cure} of 70 °C was achieved. However, with the use of a conventional initiator (2,2-dimethoxy-α-phenylacetophenone, DMPA), a measurable amount of free radicals remain trapped in the cross-linked network. Therefore, when the sample is heated above the T_{cure} during mechanical testing, additional polymerization is induced as a result of the increased mobilities of the trapped radicals and unreacted monomer units. The authors noted this effect and measured an increase in conversion upon heating using FTIR.

To avoid the possibility of additional polymerization during mechanical analysis, living radical photopolymerizations are used in this work to create partially cured networks that contain no trapped radicals. Initiators, such as *p*-xylylene bis(*N*,*N*-diethyl dithiocarbamate) (XDT), photocleave in the presence of ultraviolet light into carbon-based initiating radicals and sulfur-based dithiocarbamate radicals that will terminate with carbon radicals already present in the network. Photopolymerizations with these systems have been used successfully to eliminate trapped radicals in other dimethacrylate networks and allow for mechanical characterization as a function of both temperature and double-bond conversion.[13−15] Furthermore, polymerizations initiated by these compounds proceed at a much slower rate than conventional free radical polymerizations, thus decreasing the rate of heat evolution during cure.

To investigate whether a material with a high T_g can be obtained from a monomer cured at a low temperature (e.g., ambient temperature) and to understand the factors which dictate the relationship between T_g and T_{cure}, three systems with different degrees of heterogeneity are compared here. One system is a styrene (St)−divinylbenzene (DVB) copolymer, a typical mono/divinyl system. A second one is triethylene glycol dimethacrylate (TEGDMA) homopolymer, a multifunctional methacrylate monomer that forms a cross-linked, highly heterogeneous network. Because of its high refractive index, low specific gravity, and good impact resistance, TEGDMA has been used in various applications such as optical[16] and dental[17] materials. The third system is diethylene glycol dimethacrylate (DEGDMA), an even more heterogeneous, more cross-linked system than TEGDMA. The photopolymerizaton kinetics of these systems and the effect of heterogeneity on the relationship between T_{cure} and T_g were investigated using near-IR spectroscopy and dynamic mechanical analysis (DMA).

Materials and Methods

Materials. Three model systems were studied and compared in this work: triethylene glycol dimethacrylate (TEGDMA, Polysciences Inc., Warrington, PA), diethylene glycol dimethacrylate (DEGDMA, Polysciences Inc., Warrington, PA), and a mixture of styrene (St, Aldrich Chemical Co. Inc., Milwaukee, WI) and divinylbenzene (DVB, Aldrich Chemical Co. Inc., Milwaukee, WI) with different mass ratios. The following initiators were used in the study: photopolymerizations, *p*-xylylene bis(*N*,*N*-diethyl dithiocarbamate) (XDT, 3M Corp., Minneapolis, MN, 1 wt %), and thermal polymerizations, 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich Chemical Co. Inc., Milwaukee, WI, 1 wt %). Styrene was purifed with DE-HIBIT 100 ion-exchange resin (Polysciences Inc., Warrington, PA). Divinylbenzene was purified with 10 wt % aqueous sodium hydroxide solution and then washed with distilled water to remove the excess sodium hydroxide. TEGDMA, DEGDMA, and the initiators were used as received.

Near-IR. Near-IR spectroscopy was used to monitor the cure of the relatively thick (1 mm) monomer samples. The use of this spectroscopic technique to monitor the cure behavior of dimethacrylates has been published elsewhere[15,18] and will not be in discussed in detail here. To investigate the effect of the cure temperature, samples were cured inside the FTIR chamber (Magna 750, series II, Nicolet Instrument Corp., Madison, WI) with a 365 nm UV-light source (Ultracure 100SS, EFOS, Mississaugua, Ontario, Canada). A horizontal-mounting unit, which redirects the near-IR white light beam vertically, was used in combination with a temperature cell (0−120 °C) to allow for real-time kinetic characterization.[19] Specially designed for use in the temperature cell, the sample mold was made from transparent glass slides with a silicon rubber O-ring in the middle. The O-ring was used to prevent the evaporation of the monomer during the polymerization. The solution was injected inside the O-ring using a syringe.

Prior to irradiation, the samples were kept inside the temperature cell for 15 min to allow the temperature to stabilize. A near-IR spectrum (5000−7000 cm^{-1}) of the uncured sample was collected (KBr beam splitter and DTGS detector), and the area of the =C−H peak (6102−6233 cm^{-1} for TEGDMA and 6095−6192 cm^{-1} for St/DVB) was recorded with 64 scans per spectrum and 4 wavenumber resolution. The photopolymerization reaction was monitored by real-time near-infrared spectroscopy (8 scans per spectrum and 4 wavenumber resolution) using a series run. Finally, the spectrum of the cured sample was collected (64 scans per spectrum and 4 wavenumber resolution) immediately after the series collection to determine the conversion immediately after cure. Several samples were checked after DMA testing to ensure that no additional cure or evaporation had occurred during the mechanical analysis.

To investigate the exothermic heat release and the subsequent temperature rise in free radical polymerizations initiated by XDT, the sample temperature during the polymerization was measured by implanting a thin thermocouple (J-type Precision Fine Wire Thermocouple, OMEGA Engineering Inc., Stanford, CT) into the monomer solution before irradiation, and the temperature was recorded periodically throughout the polymerization. The diameter of this thermocouple is only 0.005 in.; therefore, high sensitivity is possible.

DMA. Dynamic mechanical analysis was performed on a DMA7e dynamic mechanical analyzer (Perkin-Elmer, Norwalk, CT). The samples were of uniform size (15 mm × 4 mm × 1 mm). Dynamic mechanical analysis was conducted over a temperature range of 0−200 °C with a ramping rate of 5 °C/min using extension mode (sinusoidal stress of 1 Hz frequency).

By combining the near-IR and DMA techniques, one can obtain significant information about the polymer material being studied. In particular, the curing behavior (polymerization rate) and network status (double-bond conversion) of the exact sample used for mechanical testing can be easily monitored.

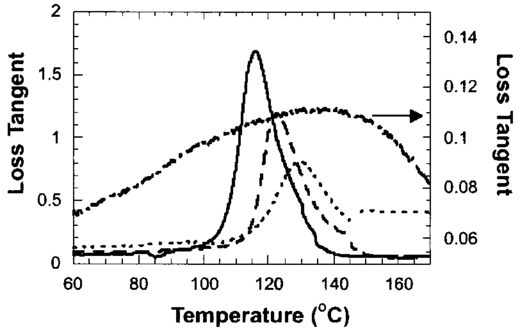


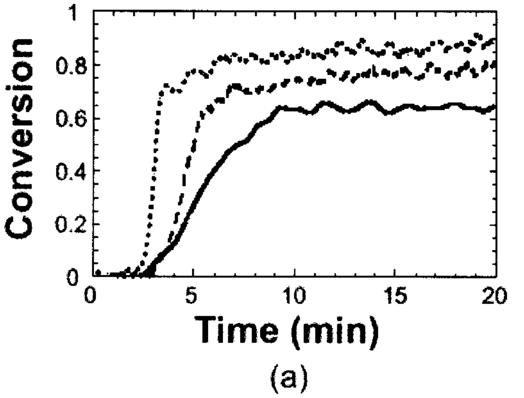
Figure 1. Loss tangent vs temperature for St polymers with 5 wt % (—), 8 wt % (– –), and 12 wt % (· · ·) DVB, and pure TEGDMA (— · —). All polymers are fully cured at 95 °C with 1 wt % AIBN.

Results and Discussion

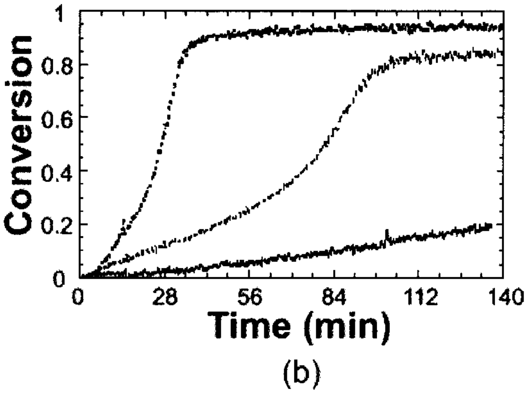
Effect of DVB Concentration on the Mechanical Properties of St-*co*-DVB Network. To investigate the differences in the cross-linking TEGDMA and St-*co*-DVB networks, styrene with different concentrations of DVB as the cross-linking agent was thermally polymerized (1 wt % AIBN) and compared with fully cured TEGDMA. Figure 1 shows the loss tangent (tan δ, ratio of loss to storage modulus) curves of TEGDMA and St-*co*-DVB networks as a function of temperature. As the polymers go from a glassy to a rubbery state, the tan δ goes through a maximum, which is recorded as the T_g for that sample. The loss tangent peak clearly illustrates that the T_g of completely cured TEGDMA is quite high (135 °C) and that the glass transition range is very broad, as reflected by the rather wide loss tangent peak (spanning more than 100 °C). This behavior is due to the heterogeneous nature plus the broad distribution of relaxation times and mobilities in the TEGDMA network.[14,15,20]

The network formation of multifunctional monomers occurs with extensive cyclization and multiple cross-linking reactions.[21] These reactions of the pendant double bonds with radical centers located on the same macromolecule do not contribute to the overall cross-linking density; however, they do facilitate microgel formation.[22] Intermolecular cross-linking reactions, which are responsible for the aggregation of the microgels, lead to the formation of the macrogel and contribute to the overall strength of the network. Microgels, which are typically formed near initiation sites, quickly become regions of very low radical mobility. However, other portions of the formed network, which have experienced less polymerization, possess far more mobile microenvironments. This nonideal network development causes an inhomogeneous distribution of chain mobilities and local free volume that leads to a broad distribution of relaxation times as evidenced in Figure 1 for TEGDMA.[23]

Furthermore, Figure 1 illustrates that, as the DVB concentration increases from 5 to 12 wt %, the T_g rises from 115 to 130 °C and the loss tangent peak broadens. As the concentration of DVB is increased, more intermolecular cross-linking reactions occur, and the mobility of the chain segments becomes more restricted. Thus, the gradual broadening of the loss tangent peak with increasing amount of cross-linking agent (DVB) is attributed to an increase in the heterogeneity of the network and has been reported by others.[24] By varying the amount of DVB, the network properties of the St-*co*-DVB network were adjusted to obtain a similar T_g to that of fully cured TEGDMA. The St + 12% DVB system was chosen for further study since its T_g is nearly identical to the T_g of fully cured TEGDMA; however, the heterogeneity and distribution of relaxation times of these two systems are dramatically different.



(a)



(b)

Figure 2. Conversion vs irradiation time for (a) TEGDMA and (b) St with 12 wt % DVB cured at 25 (—), 50 (– –), and 80 °C (· · ·) with 1 wt % XDT and 8 mW/cm^2 light intensity.

Effect of Cure Temperature on the Polymerization Kinetics. To gain more insight into the effect of cure temperature on the polymerization, both the St-*co*-12 wt %DVB and TEGDMA systems were isothermally cured at a range of temperatures, keeping the XDT concentration and light intensity constant. By irradiating within the near-IR unit, real-time conversion measurements were obtained.

Figure 2a shows the conversion of TEGDMA as a function of irradiation time for different cure temperatures (25, 50, and 80 °C). The figure illustrates that the polymerization of TEGDMA exhibits very pronounced diffusion-controlled kinetics since the autoacceleration effect is observed at the very early stages of the polymerization for all of the cure temperatures studied. After the conversion plateaus, the polymerization continues at a very slow rate. Even though the sample is quite vitrified at this point, increased conversion of the functional groups is still measurable.

Figure 2b shows the polymerization behavior of the St/DVB system as a function of cure temperature (25, 50, and 80 °C). The polymerization rate is much slower than TEGDMA since the reaction kinetic constants for styrene-based systems are lower because of conjugation–stabilization of the styrene free radical.[25] However, as reflected by the dramatic increase in the polymeri-

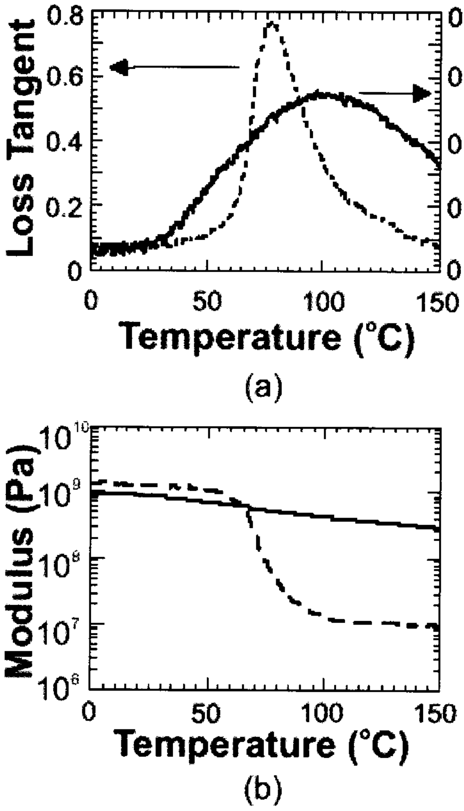


Figure 3. Loss tangent (a) and storage modulus (b) vs temperature for St with 12 wt % DVB (– –) and TEGDMA (—) cured at 50 °C (1 wt % XDT, 8 mW/cm^2 light intensity).

zation rate with cure temperature, the Arrhenius-type behavior is much more pronounced in the St-*co*-DVB system.

In addition, it was found that no significant temperature increase occurred during the XDT-initiated photopolymerizations. For example, when St-*co*-DVB was polymerized at 80 °C, the maximum temperature rise was only 3 °C. This result indicates that the overall sample temperatures remained quite close to the initial temperatures during the polymerization, primarily due to the very low polymerization rates attained in these XDT initiated polymerizations.

Effect of Heterogeneity on the T_{cure} vs T_g Relationship. Figure 3 shows the loss tangent and storage modulus of St-*co*-DVB and TEGDMA networks photocured and mechanically tested under the same experimental conditions. Although the cure temperature for both of these systems was 50 °C, the T_g of the TEGDMA specimen is about 25 °C higher than that of the St-*co*-DVB network specimen. In addition, as illustrated by the loss tangent curves, the width at the half-maximum of tan δ for the TEGDMA network is about 100 °C, while the same width for the St-*co*-DVB network is only 15 °C. This phenomenon is attributed to the difference in the structural heterogeneity of the two systems.

For the specimens shown in Figure 3, the TEGDMA polymerizations were not halted until high conversions. Therefore, as the polymerization progressed, the isolated microgel regions interconnected through intermolecular cross-linking of pendant double bonds and a highly cross-linked, inhomogeneous polymer formed.[21] Because of the presence of microgel clusters, the microenvironments of highly cross-linked polymers are quite heterogeneous. This phenomenon leads to a wide distribution in the local free volume of the polymer segments. Since regions of high mobility still exist in the heterogeneous polymer, the free radicals, pendant double bonds, and unreacted monomer units can still diffuse and react. Consequently, the more heterogeneous systems can react further at low cure temperatures and have higher average T_g's when compared to more homogeneous networks.

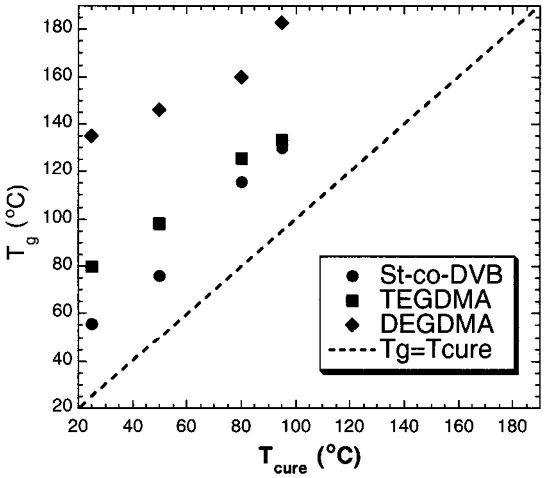


Figure 4. Glass transition temperature (T_g) vs cure temperature (T_{cure}) for the TEGDMA (■), DEGDMA (◆), and St-*co*-DVB (●) polymers. Samples were photocured with 1 wt % XDT and 8 mW/cm^2 intensity.

It should also be noted that the samples shown in Figure 3 are not fully cured (conversion ≈ 85%), but only one loss tangent peak appears. This result coupled with the extensive FTIR experiments indicates that, unlike common initiator systems, no additional polymerization occurred during the DMA test though the polymer was heated well above its glass transition temperature. It can also be observed in Figure 3 that neither system shows an increase in the storage modulus with temperature, which may occur for polymers containing trapped radicals. Also, the TEGDMA system shows less change in the storage modulus during the glass transition, when compared to the St-*co*-DVB system (i.e., the storage modulus decreases by 2 orders of magnitude within 70 °C for St-*co*-DVB network).

In this work, we also investigated the mechanical properties of polymers cured at different temperatures. Figure 4 presents the comparison of the glass transition temperature of TEGDMA and St-*co*-DVB networks as a function of cure temperature. For each cure temperature, the cure conditions for both systems are the same except for St-*co*-DVB network cured at 25 °C. (The curing time is twice as long as the other samples.) Figure 4 illustrates that for the lower cure temperature the TEGDMA system has a larger $T_g - T_{cure}$ than the St-*co*-DVB system. For example, the T_g of the TEGDMA network cured at 25 °C is 80 °C, while the T_g of St-*co*-DVB network cured at 25 °C (and for a much longer time) is only 55 °C. This result indicates that the more heterogeneous system can obtain a T_g much higher than T_{cure}, particularly when a significant number of unreacted functional groups remain in the system.

Furthermore, an even more heterogeneous system DEGDMA with the same amount of XDT has been investigated. Within the range of cure temperatures studied (25, 50, 80, and 95 °C), a significant difference between the cure temperature and glass transition temperature was observed. For the DEGDMA cured at room temperature, the T_g was 135 °C, which is more than 100 °C higher than the ambient cure temperature (25 °C). Our work showed that for an extremely heterogeneous system, a high-T_g polymer can be formed even if it is cured under ambient conditions. This observation is in stark contrast to the rule of thumb that it is not possible to have significant differences between T_g and T_{cure}.

In summary, by controlling the cure temperature and eliminating trapped radicals from the cured network, this work definitively demonstrates that using a monomer that forms a heterogeneous polymer (i.e., DEGDMA) allows one to obtain a high-T_g material even if it has been cured at ambient conditions. The polymer network heterogeneity plays a key role in dictating the maximum difference between the polymer T_g and T_{cure} as the more heterogeneous sample contains regions of high mobility where polymerization can readily proceed. By contrasting the multi(EG)DMA polymerization to a more homogeneous system (St-*co*-DVB), this study illustrated that, at high cure temperatures, the effect of thermal activation is more important to the evolution of mechanical properties; whereas at low cure temperature, the effect of heterogeneity dominates the network formation.

Acknowledgment. The authors thank the National Institutes of Health for its support through research grant DE10959-01A2, the Industry/University Cooperative Research Center on Fundamentals and Applications of Photopolymers for financial support, the National Science Foundation for its support through a Presidential Faculty Fellowship to C.N.B. and by granting a fellowship to L.G.L., and the 3M company for donation of the XDT iniferter.

References and Notes

(1) Hill, L. W. *J. Coat. Technol.* **1992**, *64*, 28−42.
(2) Davy, K.; Kalachandra, S.; Pandian, M. S.; Braden, M. *Biomaterials* **1998**, *19*, 2007−2014.
(3) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650.
(4) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* **1994**, *35*, 3243.
(5) Wang, X.; Gillham, J. K. *J. Appl. Polym. Sci.* **1993**, *47*, 425−446.
(6) Venditti, R. A.; Gillham, J. K. *J. Appl. Polym. Sci.* **1997**, *64*, 3−14.
(7) Simon, S. L.; Gillham, J. K. *J. Appl. Polym. Sci.* **1994**, *51*, 1741−1752.
(8) Wang, X.; Gillham, J. K. *J. Appl. Polym. Sci.* **1992**, *45*, 2127−2143.
(9) Rozenburg, B. A. *Adv. Polym. Sci.* **1986**, *75*, 113−166.
(10) Wise, C. W.; Cook, W. D.; Goodwin, A. A. *Polymer* **1997**, *38*, 3251−3261.
(11) Cook, W. D.; Simon, G. P.; Burchill, P. J.; Lau, M.; Fitch, T. J. *J. Appl. Polym. Sci.* **1997**, *64*, 769−781.
(12) Kloosterboer, J. G.; Lijten, G. F. *Polymer* **1990**, *31*, 95−101.
(13) Kannurpatti, A. R.; Liu, S.; Bunker, G. M.; Bowman, C. N. *Macromolecules* **1996**, *29*, 7310−7315.
(14) Kannurpatti, A. R.; Anderson, K. J.; Anseth, J. W.; Bowman, C. N. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2297−2307.
(15) Lovell, L. G.; Lu, H.; Elliott, J. E.; Stansbury, J. W.; Bowman, C. N. *Dental Mater.*, in press.
(16) Matsuda, T.; Funae, Y.; Yoshida, M.; Yamamoto, T.; Takaya, T. *J. Appl. Polym. Sci.* **1997**, *65*, 2247−2255.
(17) Bland, M. H.; Peppas, N. A. *Biomaterials* **1996**, *17*, 1109−1114.
(18) Stansbury, J. W.; Dickens, S. H. *Dental Mater.* **2001**, *17*, 71−79.
(19) Lovell, L. G.; Berchtold, K. A.; Elliott, J. E.; Lu, H.; Bowman, C. N. *Polym. Adv. Technol.* **2001**, *12*, 1−11.
(20) Kloosterboer, J. G.; Lijten, G. F. C. M. *Polymer* **1987**, *28*, 1149−1155.
(21) Funke, W.; Okay, O.; Joos-Muller, B. *Adv. Polym. Sci.* **1998**, *139*, 139−234.
(22) Chiu, Y. Y.; Lee, L. J. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 257−267.
(23) Dusek, K.; MacKnight, W. In *Cross-Linked Polymers: Chemistry, Properties, and Applications*; Dickie, R. A., Labana, S. S., Bauer, R. S., Eds.; American Chemical Society: Washington, DC, 1988; pp 3−27
(24) Glatz-Reichenbach, J. K. W.; Sorriero, L. J.; Fitzgerald, J. J. *Macromolecules* **1994**, *27*, 1338−1343.
(25) Odian, G. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons: New York, 1991; Chapter 6, pp 481−484.

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