A Photochromic Technique To Study Polymer Network Volume Distributions and Microstructure during Photopolymerizations

Kristi S. Anseth, Mark D. Rothenberg, and Christopher N. Bowman*

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309-0424

Received September 8, 1993

Introduction

Homopolymerizations of multifunctional monomers result in highly cross-linked polymer networks whose structure is strongly dependent on the curing conditions and monomer functionality. In this high cross-linking polymerization regime, anomalous behavior is often observed and includes autoacceleration and autodeceleration,[1-4] trapping of free radicals,[5-9] delayed volume shrinkage with respect to equilibrium,[1,11,20] incomplete functional group (i.e., double bond) conversion,[10-12] varying functional group reactivity, and microgel formation. Microgel formation is the primary cause of polymer heterogeneity[13-15] as pendant double bonds near the location of the active radical are extremely reactive to primary cyclization. This behavior directly influences the final polymer structure and properties.

Therefore, it is of great importance that these tendencies be understood and characterized. This work develops a technique based on photochromic probes to quantify the free volume distribution and heterogeneity during photopolymerization reactions. Gardlund[16] first used photochromic probes to study thermal back reactions in polymer glasses. The photoinduced forward reaction, as opposed to the thermally induced back reaction, is a sensitive measure of the local volume and has been used to establish volume distributions by others studying physical aging in linear polymer systems.[17-23] These volume distributions are closely related to the distribution of free volume in the system, and if the mean free volume of the system is known, the free volume distribution can be calculated (assuming symmetric probe volume distributions and free volume distributions).

We propose, for the first time, the use of these photochromic probes in establishing free volume distributions during a photopolymerization reaction. Our preliminary results have shown that these probes provide a sensitive measure of the local volume changes and qualitatively show the trends in heterogeneity during a polymerization.

Experimental Section

The multifunctional monomers studied were trimethylolpropane trimethacrylate (TrMPTrMA; Polysciences Inc., Warrington, PA) and diethylene glycol dimethacrylate (DEGDMA; Polysciences Inc., Warrington, PA). The monomers were used as received and mixed with 1 wt % photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba Geigy, Hawthorn, NY). Samples were prepared by dissolving 0.1 wt % of a photochromic probe in the monomer–initiator solution. The photochromic probes chosen for this study were azobenzene and stilbene (Aldrich; Milwaukee, WI). Torkelson and co-workers[17-19] have previously quantified the critical volume required for isomerization of various probes, and stilbene and azobenzene require at least 224 and 127 Å^3 to isomerize, respectively.

Thin films of monomer, probe, and initiator solutions were cured using a 365-nm 6-W ultraviolet light source (Cole-Parmer; Chicago, IL). The UV light also served to induce the trans to cis conformational change in the probe. The absorbance of the system was simultaneously monitored with an HP8452 UV-vis spectrophotometer (Hewlett Packard; Fort Collins, CO). To characterize the conversion of monomer as a function of time, the monomer was cured under identical reaction conditions (temperature and UV light intensity) in a differential scanning calorimeter equipped with a photocalorimetric accessory (Perkin-Elmer DSC-DPA 7; Norwalk, CT).

Analysis

Four possible states for any given photochromic probe are the trans and mobile (or free) state, the trans and immobile (or bound) state, the cis and mobile state, and the cis and immobile state. A molecule is considered immobile when the local volume is smaller than the critical volume required to isomerize and the probe becomes locked in a single conformation. During polymerization, the probe may undergo the following reactions:

$$t_f \underset{k_2}{\overset{k_1}{\rightleftharpoons}} c_f \tag{1}$$

$$t_f \xrightarrow{k_3} t_b \tag{2}$$

$$c_f \xrightarrow{k_4} c_b \tag{3}$$

where t represents the trans state, c represents the cis state, f refers to the free or mobile state, and b is the bound or immobile state. Assuming the probes are mobile in the liquid monomer, the reactions in eqs 2 and 3 would not exist in the absence of polymerization. The probe reactions are occurring in parallel with the polymerization reaction.

For a monomeric system (monomer and probe only), the absorbance as a function of time was monitored and is related to the trans and cis concentrations by

$$A_m = \epsilon_t l t_f + \epsilon_c l c_f \tag{4}$$

Here, ϵ is the molar absorption coefficient of the respective state, l is the sample thickness, m refers to the monomer system, and A is the absorption.

A similar expression exists for the polymerizing sample, but not all of the probe is mobile and the fraction that is mobile changes as a function of polymerization time. Therefore,

$$A_p = \epsilon_t l(t_f + t_b) + \epsilon_c l(c_f + c_b) + A_i \tag{5}$$

where p refers to the polymer system. For a photopolymerized sample, the absorbance of the polymer sample includes the absorbance of the photoinitiator, A_i, in the sample. A_i was measured during identical reactions without the probe molecules and generally was insignificant above 300 nm. For the polymerizing system, the kinetic constants in eq 1 are assumed to be independent of double-bond conversion in the sample. The kinetic constants for eqs 2 and 3 are the same and represent the rate of conversion of any mobile state to a bound state. Now, we define a variable z which is the fraction of probe molecules that are mobile

$$z \equiv \frac{[P]_f}{[P]} = \frac{c_f + t_f}{[P]} \tag{6}$$

where the total concentration of the probe is [P]. Then,

$$k_3 = k_4 = -\frac{\partial \ln z}{\partial t} \tag{7}$$

This analysis reduces to a system of eight equations and

* Author to whom correspondence should be addressed.

0024-9297/94/2227-2890$04.50/0

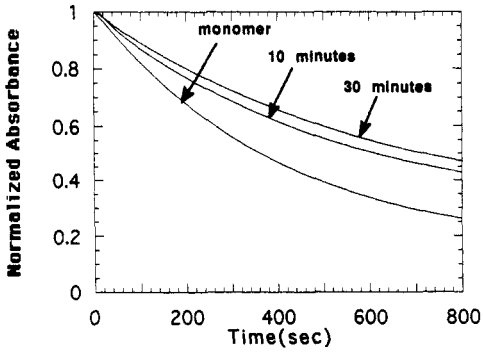

Figure 1. Absorbance as a function of time for a sample thermally polymerized 0 (monomer), 10, and 30 min.

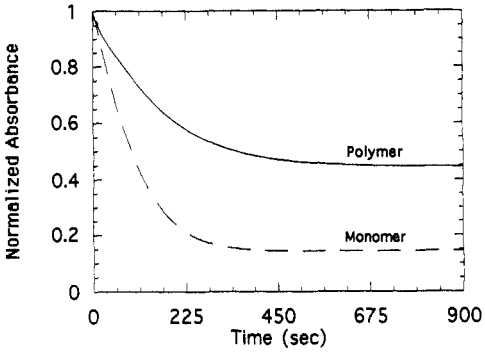

Figure 2. Typical absorbance versus time curves for a monomer system and a polymerizing system.

eight unknowns: t_f, c_f, t_b, c_b, k_1, k_2, k_3, and z. Solving for z,

$$z = \left.\frac{\partial A_p/\partial t}{\partial A_m/\partial t}\right|_{t=\text{constant}} \tag{8}$$

To address the assumption that the free probes in a polymerizing sample will behave as those in a monomer sample (i.e., k_1 and k_2 are not functions of conversion in the sample), a series of experiments was conducted as follows. A monomer sample was doped with 0.1 wt % probe and mixed with 1 wt % thermal initiator. The absorbance versus time was monitored for a monomer sample, and samples that were thermally cured for 10 and 30 min. Thermally curing the sample ensured that the probe remained in the trans state, and the complication of simultaneous reaction and isomerization present in photopolymerizations was eliminated. Figure 1 shows the absorbance versus time curves for each of these systems, and the decay time of the probe in each sample was independent of the polymerization time (k = 0.001 95 ± 0.000 028 4) with only an offset in the final absorbance present. This offset shows the trend of more probe being locked in the trans state for samples polymerized to higher conversions.

Results and Discussion

Figure 2 shows absorbance versus time curves for a monomer and a polymerizing system. At low reaction times, the conversion is nearly zero and all of the probe in the sample is in a mobile state. Therefore, at the initial time, the slopes of both curves are identical and z is 1. As the polymerization continues, some of the probe becomes locked in the trans state, and the absorbance of the polymerizing curve remains higher than the absorbance of the monomer curve. When the polymerization is complete (after 2 min in Figure 2), the slope of the polymer curve reduces to the same exponential decay as the slope of the monomer curve (the monomer system has been

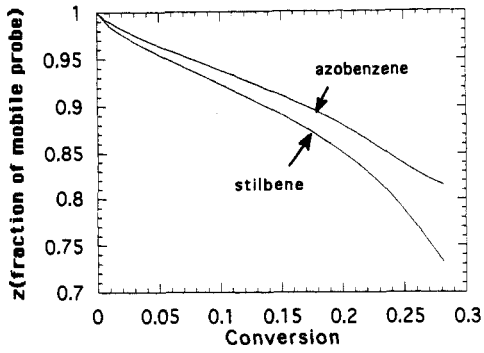

Figure 3. Fraction of probes that are mobile as a function of double-bond conversion of TrMPTrMA polymerized with 1.2 mW/cm² of UV light and 1 wt % DMPA.

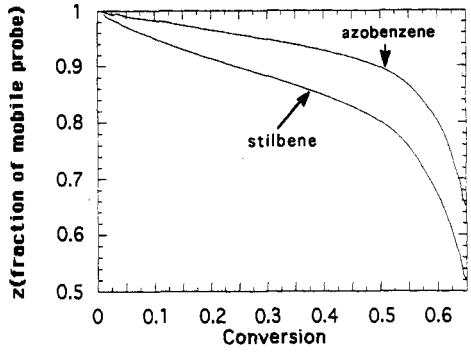

Figure 4. Fraction of probes that are mobile as a function of double-bond conversion of DEGDMA polymerized with 1.2 mW/cm² of UV light and 1 wt % DMPA.

mathematically analyzed, and the slope was found to decay exponentially). The polymer system, however, has a different preexponential factor due to the locked probe molecules. Therefore, when the polymerization is complete, z reduces to a constant value or offset which represents the fraction of probes that are still mobile in the polymer.

Preliminary studies have been conducted with two commercially available probes, azobenzene and stilbene. The critical free volumes for isomerization of azobenzene and stilbene are 127 and 224 Å³, respectively. Figure 3 presents the fraction of mobile sites for the azobenzene and stilbene probes as a function of conversion for trimethylolpropane trimethacrylate, TrMPTrMA, cured with 1.2 mW/cm² of 365-nm ultraviolet light and 1 wt % DMPA.

At the beginning of the reaction, the fraction of azobenzene and stilbene probes that are mobile is slowly decreasing. This slow decrease can be explained by the formation of microgel regions. The microgels form at the beginning of the reactions and are highly cross-linked regions with an average local volume that is much smaller than the overall free volume of the system. As conversion is further increased, the average free volume of the entire system is decreasing and the fraction of the probes that are mobile dramatically decreases. In comparing the fraction of mobile stilbene probes to the azobenzene probes, stilbene begins to sharply decrease earlier than the smaller azobenzene probes, and the final fraction of mobile stilbene probes is much smaller than the final fraction of mobile azobenzene probes (0.73 vs 0.81). The fraction of mobile probes observed here is on the same order as others have observed[17-20] but lower because of the high degree of cross-linking.

A similar trend is seen in Figure 4 during the polymerization of diethylene glycol dimethacrylate, DEGDMA, under identical reaction conditions. In the case of poly-

(ethylene glycol dimethacrylate), the final fraction of mobile stilbene and azobenzene in the network is smaller than that in poly(trimethylolpropane trimethacrylate), 0.52 for stilbene and 0.64 for azobenzene. This difference in the final fraction of mobile probes is attributed mainly to the higher conversions reached during the polymerization of DEGDMA. Comparing the TrMPTrMA and DEGDMA curves at lower conversions, the probes are less mobile in the more highly cross-linked poly(TrMPTrMA) network where the reaction stops around 28% double-bond conversion. The mobility of the probes in the poly(DEGDMA) network does not drop below that of the probes in the poly(TrMPTrMA) network until the double-bond conversion exceeds 0.50.

Acknowledgment. The authors thank the National Science Foundation for their support of this research in the form of a grant (CTS-9209899) and a fellowship to K.S.A. We also thank the University of Colorado's Office of the Dean of the Graduate School for a Dean's Small Grant Award.

References and Notes

(1) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(2) Kloosterboer, J. G.; Lijten, G. F. C. M. In *Cross-Linked Polymer Chemistry*; Dickie, R., Labana, S., Bauer, R., Eds.; ACS Symposium Series 367; American CHemical Society: Washington, D. C., 1988; p 409.
(3) Miyazaki, K.; Horibe, T. *J. Biomed. Mater. Res.* **1988**, *22*, 1011.
(4) Allen, P.; Simon, G.; Williams, D.; Williams, E. *Macromolecules* **1989**, *22*, 809.
(5) Klosterboer, J. G.; Van de Hei, G. M. M.; Gosslink, R. G.; Dortant, G. C. M. *Polym. Commun.* **1984**, *25*, 322.
(6) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Macromolecules* **1990**, *23*, 1144.
(7) Best, M. E.; Kasai, P. H. *Macromolecules* **1989**, *22*, 2622.
(8) Bowman, C. N.; Peppas, N. A. *Macromolecules* **1991**, *24*, 1914.
(9) Greiner, R.; Schwarzl, F. R. *Rheol. Acta* **1984**, *23*, 378.
(10) Simon, G.; Allen, P.; Bennett, D.; Williams, D.; Williams, E. *Macromolecules* **1989**, *22*, 3555.
(11) Cook, W. D. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 1053.
(12) Kloosterboer, J.; Lijten, G.; Boots, H. *Makromol. Chem., Macromol. Symp.* **1989**, *24*, 223.
(13) Funke, W. *Br. Polym. J.* **1989**, *21*, 107.
(14) Bastide, J.; *Leibler*, L. *Macromolecules* **1988**, *21*, 2649.
(15) Matsumoto, A.; Hatsuo, H.; Ando, H.; Oiwa, M. *Eur. Polym. J.* **1989**, *25*, 237.
(16) Gardlund, Z. G. *J. Polym. Sci., Polym. Lett. Ed.* **1968**, *B6*, 57.
(17) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1987**, *20*, 2241.
(18) Victor, J. G.; Torkelson, J. M. *Macromolecules* **1988**, *21*, 3490.
(19) Royal, J. S.; Victor, J. G.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 729.
(20) Royal, J. S.; Torkelson, J. M. *Macromolecules* **1992**, *25*, 4792.
(21) Yu, W.-C.; Sung, C. S. P. *Macromolecules* **1988**, *21*, 365.
(22) Yu, W.-C.; Sung, C. S. P.; Robertson, R. E. *Macromolecules* **1988**, *21*, 355.
(23) Lamarre, L.; Sung, C. S. P. *Macromolecules* **1983**, *16*, 1729.