Differential Scanning Calorimetry and Cantilever Deflection Studies of Polymerization Kinetics and Stress in Ultraviolet Curing of Multifunctional (Meth)acrylate Coatings

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Received February 21, 2001

ABSTRACT: Polymerization kinetics and stress development were measured during the UV curing of multifunctional acrylate and methacrylate coatings by photodifferential scanning calorimetry and a cantilever deflection method. Higher light intensity leads to higher double-bond conversion but unfortunately also to higher stress. Higher monomer functionality unfortunately leads both to lower conversion and to higher stress; substituting methacrylate for acrylate does likewise. Longer monomer chain length and more plasticizer, though, lead both to higher conversion and to lower stress. In all cases, it is shown that significant stress starts to develop only late in reaction—at the vitrification conversion. The vitrification conversion falls as more rigid networks are formed (with higher functionality, shorter monomer chain length, lower plasticizer concentration, or methacrylate rather than acrylate), but it is not affected by the light intensity. After vitrification—in the vitrified state—the stress rises monotonically with conversion. The rate of stress growth with conversion in the vitrified state rises with higher monomer functionality, shorter monomer chain length, or lower plasticizer concentration. It also rises when methacrylate is substituted for acrylate. These trends of stress growth in the vitrified state are consistent with an increase in the elastic modulus as more rigid networks are formed.

Introduction

Ultraviolet (UV) curing of acrylate and methacrylate coatings eliminates the need for solvent and allows ambient temperature solidification. Moreover, curing of multifunctional monomers can produce highly cross-linked polymer networks with enhanced hardness, toughness, and solvent resistance. Therefore, UV curing is widely used in decorative and protective coatings and magnetic and optical disks.[1−4] However, incomplete conversion of functional groups (i.e., double bonds) and defects from excessive stress such as cracking, delamination, and curling impede the growth of applications. The incomplete conversion is caused by severe limitation of the mobilities of functional groups and free radicals. The defect formation is caused by high stress developed during polymerization. As polymerization proceeds, volume shrinks, both because each propagation step exchanges a van der Waals bond and a covalent double bond with two covalent single bonds and because the newly formed linkage causes segments to move to a new configuration. When the volume shrinkage is frustrated by adhesion to a substrate, stress develops. On the other hand, stress also relaxes through thermal motions of molecules, tending toward a thermodynamic stress-free state. The rate of stress relaxation depends on the degree of curing and the current molecular configurations, entanglements, and cross-links. Therefore, it is important to understand the coupling of the extent of polymerization and the stress development.

UV-induced free-radical polymerization of multifunctional monomers can be followed by using photodifferential scanning calorimetry[5−8] and infrared spectroscopy.[9−12] The polymerization of multifunctional monomers often shows features that seem anomalous compared to the typical behavior of monofunctional monomers. These features include exaggerated autoacceleration, autodeceleration,[5,7,13−15] and severe reaction−diffusion,[16,17] each associated with increasingly severe limitations of the mobility of free radicals attached to growing polymer chains or networks. Autoacceleration results from a decreasing rate of termination compared to initiation and propagation as radicals on chains and networks move less and less easily, while monomer and oligomer mobilities remain high. Consequently, the radical concentration accumulates and so propagation accelerates. At some point the apparent mobility of free radicals is controlled mainly by reaction−diffusion, i.e., through propagation reactions along kinetic chains. Autodeceleration appears later in reaction and results from the slowing of propagation as the mobility of double bonds, and their access by free radical sites becomes more restricted. Furthermore, the polymerization rate in multifunctional systems can be affected by significant delays in volume shrinkage. Kloosterboer et al.[5,18] proposed that as the rate of reaction rises, the polymer system cannot shrink to its thermodynamic equilibrium specific volume (at a given conversion), causing the retention of excess free volume. This excess free volume might help preserve the mobility of radicals and functional groups, delaying in particular autodeceleration to higher conversion; thus, a higher final conversion might be reached by using a higher light intensity. (The stress consequences of doing this, though, have not yet been systematically explored.)

Stress develops in a coating when the material is unable to shrink freely because of adhesion to the substrate. Frustrated shrinkage leads to elastic strain, and the elastic strain leads to in-plane elastic stress. The strain is the deformation of current state relative to the current mechanical stress-free state. One must recognize that there are two types of stress-free states:

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10.1021/ma010310h CCC: $22.00 © 2002 American Chemical Society
Published on Web 10/12/2001

mechanical and thermodynamic. The mechanical stress-free state is the state at which the net of all stresses, i.e., the divergence of the stress tensor, is zero (mechanical equilibrium). There could still be internal microscopic stresses, but all the tensile, shear, and compressive microscopic stresses are locally in balance. The thermodynamic stress-free state is the state at which all the internal microscopic stresses are zero, apart from uniform pressure (thermodynamic equilibrium). The in-plane elastic stress depends on the product of modulus and strain.

The stress development generally undergoes different stages during curing depending on the evolution of material mechanical stiffness. Stress may be negligible well before the gelation point because flow of liquid monomers, and oligomers should rapidly accommodate shrinkage. At the gelation point, though, a sample-spanning, loading-bearing network forms, and the system should start to develop stress if it is constrained. However, from the gelation point to the vitrification point (rubbery regime), the modulus may remain low enough to lead only to a low stress. Moreover, the stress might still relax quickly in the gel/rubbery state. If curing is much slower than the stress relaxation, the stress developed may be negligible. In any event, and perhaps more importantly, when the system enters the vitrified state (e.g., when the glass transition temperature of the system reaches the curing temperature), the modulus becomes high and the stress relaxation becomes slow. Stress development certainly becomes significant if reaction proceeds in the vitrified state.

Stress development during curing can be measured by the bending of a beam on which coating is applied[12,19] and by the deformation of a steel ring embedded in the curing materials.[20,21] Stress data reported to date for both epoxy and acrylate materials confirm that vitrification is central. In general, in the rubbery regime stress is negligible in the epoxy-type materials.[19−21] In the acrylate-type materials, stress observed in the room-temperature photopolymerization of trimethylopropane triacrylate (TrMPTrA)[12] and tripropylene glycol diacrylate (TPGDA)[22] starts to develop only at conversions (e.g., more than 30%) far beyond their gel conversions. (Gel conversion is generally less than 10% in this highly cross-linked system.[16,23,24]) In such systems, then, it is clear that significant stresses develop mainly after vitrification. In some cases, though, stress can become significant even before vitrification. During the thermal curing of TPGDA above the ultimate glass transition temperature of the system (in the rubbery regime) stress can also reach as high as 1 MPa.[19] In such a case, the stress developed during curing depends on the volume shrinkage, the modulus developed, the rate of curing, and the stress relaxation.

Theoretical analysis of stress development during the whole curing process would require a complex constitutive equation to incorporate both stress formation and stress relaxation. Martin and Adolf[25,26] put forward a constitutive equation for viscoelastic stress by appealing to the Boltzmann superposition procedure, adopting a "memory function" of modulus. Similarly, Lang and Manson[27] developed an equation for viscoelastic stress by incorporating a Maxwell model of stress relaxation. Both equations require relaxation times and must be solved simultaneously with kinetic equations. For qualitative analysis, when stress starts to develop in the solidified state without relaxation, it can be calculated through the biaxial plane stress ($\sigma = \sigma_x = \sigma_y$, $\sigma_z = 0$, where x, y directions are on the plane of the substrate, z-direction is perpendicular to that plane)

$$\sigma = \frac{E}{1-\nu}\epsilon \qquad (1)$$

where E is Young's modulus of the coating, ϵ is the linear elastic strain ($\epsilon = \epsilon_x = \epsilon_y$, $\epsilon_z = 0$) calculated from the solidification point, and ν is its Poisson's ratio.[12] This formula was originally developed by Croll,[28] who took the solidification point to be the vitrification point.

In the stress development of UV curing of coatings, Payne et al.[12] studied the polymerization of tri- and tetraacrylate monomers. They found that the rate and magnitude of stress development rose with photoinitiator concentration (until too high a concentration led to severe attenuation of light intensity through the film). The rate and magnitude of stress development also rose with the light intensity. Monomers with higher functionality had a higher rate and magnitude of stress development, even though they reached a lower final conversion.

Though there are several experimental studies of either polymerization kinetics or stress development in UV curing of multifunctional acrylates and methacrylates;[5,7,12,14−17,19,22] few works systematically investigate the relation between stress and conversion. For example, in Payne et al.'s work,[12] it is still unclear why the rate and magnitude of stress development rose with monomer functionality while the final conversion fell.

In this work, systematic studies of polymerization kinetics and stress development in UV curing of multifunctional acrylates and methacrylates are reported. The effects of light intensity, monomer functionality, monomer chain length, plasticizer concentration, and monomer type (acrylate vs methacrylate monomers) are studied. Stress development as a function of conversion is analyzed in light of Croll's model to find out ways to optimize the coating process, i.e., to achieve high conversion of double bonds and low stress.

Experimental Section

Materials. Commercially available monomers used in this work included diethylene glycol diacrylate (DEGDA, MW 214, Sartomer, West Chester, PA); trimethylopropane triacrylate (TrMPTrA, MW 296, Aldrich Chemical Co., Milwaukee, WI); pentaerythritol tetraacrylate (PETeA, MW 353, Aldrich Chemical Co., Milwaukee, WI); triethylene glycol diacrylate (TrEGDA, MW 258, Sartomer, West Chester, PA); tetraethylene glycol diacrylate (TeEGDA, MW 302, Sartomer, West Chester, PA); poly(ethylene glycol) (400) diacrylate (PEG(400)DA, MW 508, Sartomer, West Chester, PA); and trimethylopropane trimethacrylate (TrMPTrMA, MW 338, Aldrich Chemical Co., Milwaukee, WI). These monomers were used without further purification. The plasticizer used was poly(ethylene glycol) (400) (PEG, MW 400, Aldrich Chemical Co., Milwaukee, WI). The photoinitiator used was 2,2-dimethoxy-2-phenylacetophenone (DMPA, MW 256, Aldrich Chemical Co., Milwaukee, WI). The monomers were mixed with 1 wt % photoinitiator. Plasticizer concentration was varied from 0 to 25 wt %.

Conversion Measurements. The propagation rate during UV curing of the mixture of monomer and photoinitiator was monitored with a differential scanning calorimeter fitted with a photocalorimetric accessory (Perkin-Elmer, DSC-DPA 7, Norwalk, CT). Ultraviolet light (365 nm) was selected by using a monochromator. The light intensity was controlled by neutral density filters (Melles Griot, Irvine, CA). Approximately 1 mg of sample was placed in an uncovered aluminum DSC pan. The DSC cell was continuously flushed with nitrogen. To

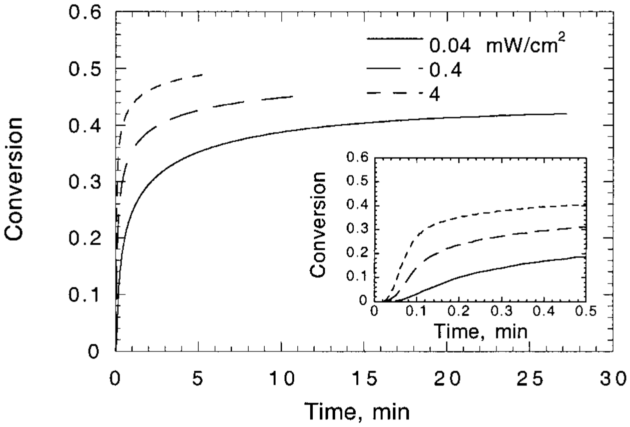

Figure 1. Conversion of double bonds in the polymerization of TrMPTrA at three different light intensities. Accurate measurements by DSC are difficult beyond the "final" conversion shown.

completely purge the DSC cell, nitrogen flushing was started 10 min before exposing the sample to UV light. Curing took place at 25 °C under continuous UV irradiation.

The propagation rate was determined from the heat flux monitored by DSC, using the theoretical reaction heat for double bonds in ref 7. A standard definition of the "final" conversion was adopted (to allow comparison among different systems) as the point when the rate dropped to 0.1% of its maximum value.[1,6] Here, 0.1% was chosen because in the slowest reaction studied here (i.e., the polymerization of TrMPTrA at the lowest light intensity 0.04 mW/cm^2), the rate of heat production fell below the limit of detection shortly after 0.1% of its maximum value. Reaction was still going on slowly. For example, in the polymerization of TrMPTrA at 4 mW/cm^2, the conversion of double bonds rose to 0.013 when doubling the irradiation time.

Stress Measurement. An apparatus for measuring stress in coatings by means of cantilever deflection in a controlled environment was used to study stress development. The details of this device were described in refs 12 and 29. A blade coater was used to coat liquid layers with thickness of about 60 μm on 0.3 mm thick steel substrates. The substrate was clamped so that the cantilever was 30 mm long. The resolution of stress detection was around 0.1 MPa according to the minimum deflection that could be detected.

Liquid coatings were illuminated continuously for 2 h by an ultraviolet light source (Ultracure 100, EFOS, Mississauga, Ontario, Canada) with a 365 nm selection filter. The light intensity was adjusted by neutral density filters (the same as used in the DSC experiments). The light intensity was monitored with a radiometer (Spectronics Corp., Westbury, NY). The chamber of the apparatus was completely purged of oxygen by flushing it with room temperature nitrogen for 15 min before exposing the sample to UV light. Curing took place under continuous nitrogen purge at about 25 °C. No cracks were observed in the coatings discussed in the Results section, but cracks could be seen when stronger light intensities were applied to thicker liquid layers (e.g., a 200 μm layer with 2 min of exposure time, at 60 mW/cm^2 light intensity.

Results

Effect of Light Intensity. Figure 1 shows the conversion of double bonds vs time in the polymerization of TrMPTrA at three light intensities: 0.04, 0.4, and 4 mW/cm^2. At very short times (shown in the inset), the reaction rate is zero because of the presence of some inhibitor in the monomer—this induction time is always negligibly short in the experiments described here. After reaction begins, the conversion rate autoaccelerates until the maximum rate time is apparent as an inflection point (e.g., 0.053 min at 4 mW/cm^2; see Table 1). During the autoacceleration period, reaction–diffusion generally starts to dominate termination.[16,17] After the inflection point, the conversion rate begins to drop. Thereafter, cross-linking lowers the rate of propagation as the mobility of monomers becomes restricted.[30] Finally, when radicals and double bonds become almost trapped, the polymerization rate becomes extremely slow and difficult to measure by DSC. The "final" conversion in this context is defined as the conversion where the reaction rate drops to 0.1% of its maximum,[1,6] shown as the end of conversion profiles in Figure 1.

When the light intensity is raised, both the conversion of double bonds at the maximum reaction rate and the "final" conversion rise as shown in Table 1. Other researchers have found similar trends.[1,5,18,31] This trend might be explained by the presence of excess free volume caused by the delay in volume shrinkage upon reaction. The greater the light intensity, the faster the reaction and with it the more rapid the decrease of the specific volume at the thermodynamic equilibrium state (which is also the specific volume at the thermodynamic stress-free state). The current actual specific volume, though, may not be able to shrink rapidly enough, and so more excess free volume is produced. At any given conversion, the excess free volume enhances the mobilities of free radicals and double bonds. Consequently, the conversion at the maximum reaction rate and the "final" conversion grow.

Figure 2 shows the stress development over 2 h of irradiation. (The stress increase is much easier to measure late in reaction than the conversion increase, so the stress is shown well beyond the "final" conversion, which is marked.) The stress remains negligible for a short time (shown in the inset), but then it develops quickly once the coating solidifies, and finally its growth slows. Stress starts to develop only after a certain conversion is achieved. At the time of the maximum reaction rate (Table 1), the stress is still negligible. However, the stress continues to develop over a much longer period of time than does conversion. When the "final" conversion is achieved (shown in Figure 2), the stress is still developing. This behavior has been noted previously by Payne et al.[12] As the intensity is raised, the rate and magnitude of stress development rise. At 2 h, the stresses are 4.32 MPa at 4 mW/cm^2, 2.36 MPa at 0.4 mW/cm^2, and 1.19 MPa at 0.04 mW/cm^2 (Table 1). (Stress still keeps rising slowly with continued irradiation after 2 h, but it is not followed further in this paper.)

The conversion and stress profiles together show that increasing the light intensity has a moderate effect on improving conversion, but it has a large effect on raising stress. Therefore, using stronger light may not be the best way to increase conversion, since the ensuing stress may cause coating defects.

Effect of Functionality. Figure 3 shows the conversion of double bonds in the polymerization of monomers with different functionalities: DEGDA (diacrylate), TrMPTrA (triacrylate), and PETeA (tetraacrylate). When the monomer functionality is raised, the reaction rate in the autoacceleration period drops. This is probably caused both by the increased monomer viscosity and by the formation of more highly cross-linked networks. In addition, propagation may become diffusion-limited at a lower conversion, evidenced by the lower conversion at the maximum reaction rate (0.193 in DEGDA, 0.101 in TrMPTrA, and 0.066 in PETeA, as shown in Table

Table 1. Photopolymerization Kinetics and Stress

monomer mixture	intensity, mW/cm^2	$R_{p,max}$, 1/s[a]	t at $R_{p,max}$, min	x at $R_{p,max}$	x_{final}[b]	t_{final}, min	x_v[c]	stress at 2 h, MPa
TrMPTrA	4	0.0812	0.053	0.101	0.488	5.2	0.34	4.32
TrMPTrA	0.4	0.0418	0.07	0.073	0.45	10.9	0.33	2.36
TrMPTrA	0.04	0.0129	0.116	0.045	0.42	27.2	0.35	1.19
DEGDA	4	0.155	0.057	0.193	0.566	2.0	0.49[d]	1.57
PETeA	4	0.0543	0.05	0.066	0.386	10.1	0.25	7.56
TrEGDA	4	0.174	0.063	0.237	0.636	1.3	0.61[d]	0.5
TeEGDA	4	0.177	0.073	0.268	0.685	0.8	0.68[d]	0.29
PEG(400)DA	4	0.182	0.063	0.282	0.736	0.9		0.03
TrMPTrA 15% PEG	4	0.079	0.05	0.120	0.53	4.4	0.41	3.29
TrMPTrA 25% PEG	4	0.078	0.05	0.121	0.56	5.0	0.43[d]	1.91
TrMPTrMA	4	0.0324	0.083	0.07	0.44	7.2	0.3	4.62

[a] Normalized maximum propagation rate of double bonds by dividing the actual maximum propagation rate by the initial double-bond concentration. [b] Conversion where 0.1% of maximum propagation rate of double bonds is reached. [c] Conversion estimated where 0.1 MPa of stress is reached. [d] Conversion estimated where the stress is greater than 0.1 MPa above a linear extrapolation of the stress growth at low conversions.

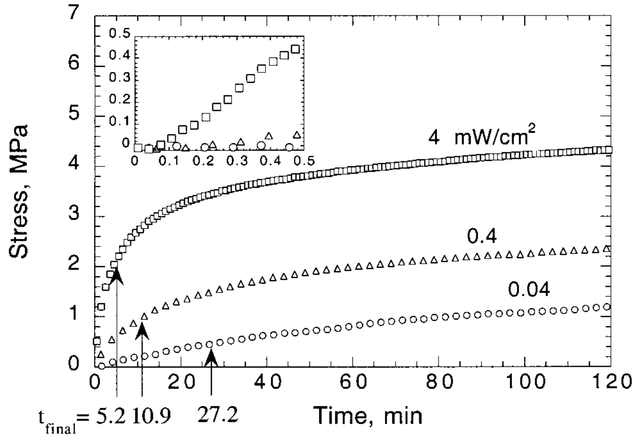

Figure 2. Stress development at continuous irradiation in the polymerization of TrMPTrA at three light intensities. Points where the “final” conversions are reached are identified.

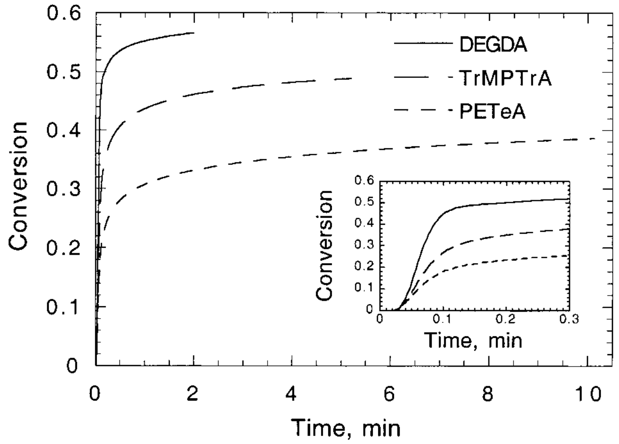

Figure 3. Conversion of double bonds in the polymerization of different functionality monomers at 4 mW/cm^2 light intensity.

1). The “final” conversion also drops. The lowered conversion at the maximum reaction rate and the lowered “final” conversion are likely caused by the formation of more highly cross-linked networks.

Figure 4 shows the stress development over 2 h of irradiation. As in the polymerization of TrMPTrA, the stress development during the polymerization of DEGDA and PETeA continues over a longer period of time than does conversion; when the “final” conversion has been reached (identified in Figure 4), the stress is still developing at a high rate. However, the rate and magnitude of stress development rise with the monomer functionality, even though the conversion is lower. At 2 h, the stresses are 1.57 MPa in DEGDA, 4.32 MPa in TrMPTrA, and 7.56 MPa in PETeA (Table 1). This trend is consistent with the observation by Payne et al.[12]

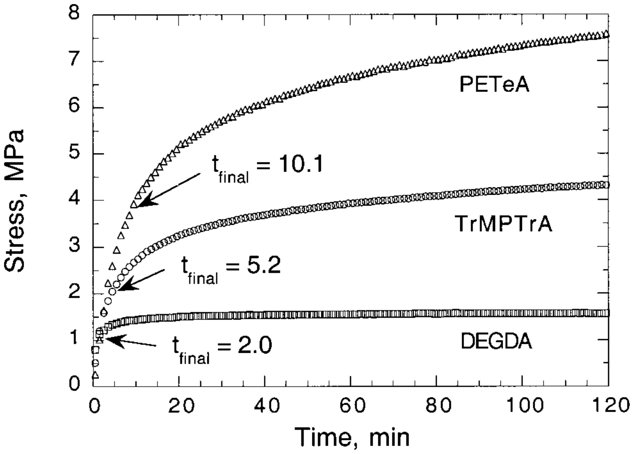

Figure 4. Stress development at continuous irradiation at 4 mW/cm^2 light intensity in the polymerization of different functionality monomers. Points where the “final” conversions are reached are identified.

The conversion and stress profiles together show that increasing monomer functionality seriously lowers conversion, and unfortunately it even more seriously raises stress.

Effect of Monomer Chain Length. Figure 5 shows the conversion of double bonds in the polymerization of diacrylate monomers with different chain lengths (the segment lengths between double bonds in monomers): DEGDA, TrEGDA, TeEGDA, and PEG(400)DA. As the monomer chain length is made longer, the reaction rates during the autoacceleration period are about the same. Even though the monomer viscosity increases (i.e., 12 cps in DEGDA, 15 cps in TrEGDA, 20 cps in TeEGDA, and 57 cps in PEG(400)DA), apparently pendant double bonds are more flexible, and the networks formed are less highly cross-linked. The conversion at the maximum reaction rate rises somewhat with the monomer chain length: from 0.193 in DEGDA, 0.237 in TrEGDA, 0.268 in TeEGDA, to 0.282 in PEG(400)DA as shown in Table 1. The reaction rate in the autodeceleration

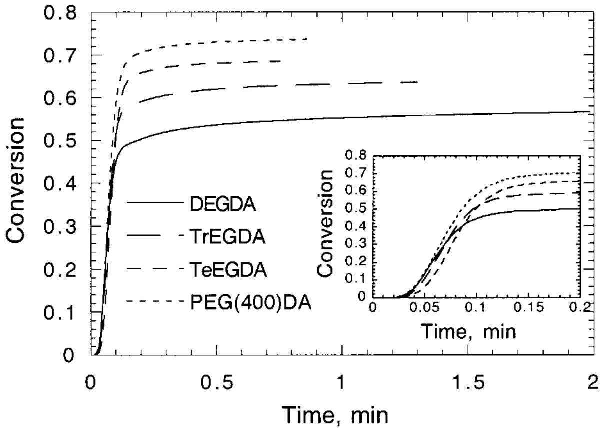

Figure 5. Conversion of double bonds in the polymerization of diacrylate monomers with different chain lengths at 4 mW/cm^2.

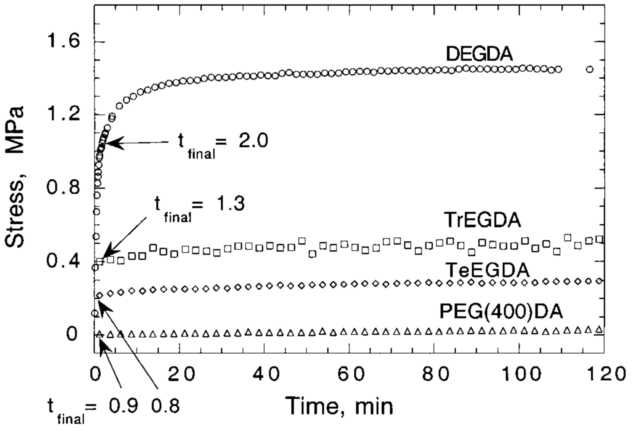

Figure 6. Stress development at continuous irradiation at 4 mW/cm^2 light intensity in the polymerization of diacrylate monomers with different chain lengths. Points where the “final” conversions are reached are identified.

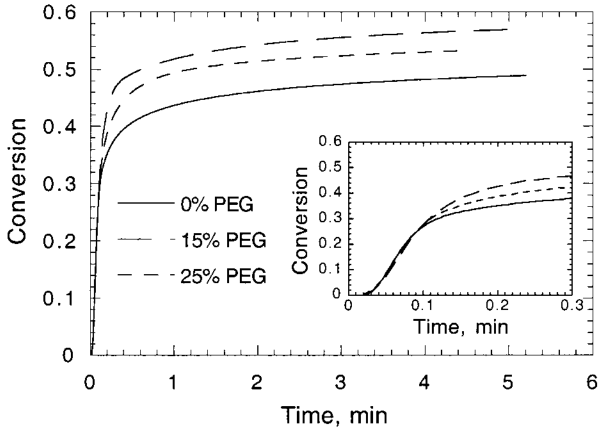

Figure 7. Conversion of double bonds in the polymerization of TrMPTrA at different plasticizer PEG concentrations (wt %) at 4 mW/cm^2 light intensity.

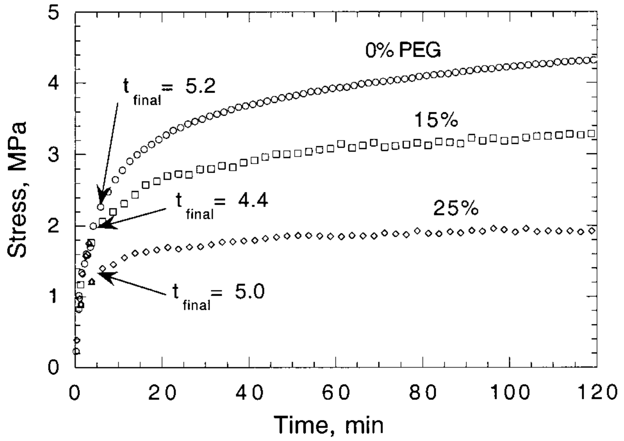

Figure 8. Stress development at continuous irradiation at 4 mW/cm^2 light intensity in the polymerization of TrMPTrA at different plasticizer PEG concentrations (wt %). Points where the “final” conversions are reached are identified.

period and the “final” conversion also rise, indicating that propagation is less diffusion-limited. Apparently, the segmental diffusivity of pendent double bonds rises; less highly cross-linked networks formed allow higher mobilities of free radicals and monomeric and pendant double bonds.

Figure 6 shows the stress development over 2 h of irradiation. Generally, the stress developed drops significantly as the monomer chain length increases. (In the polymerization of PEG(400)DA, stress remains nearly zero, indicating that a low-modulus polymer is formed even at the end of the reaction.)

The conversion and stress profiles together show that increasing the monomer chain length moderately increases conversion while significantly lowering stress. Increasing the monomer chain length is an attractive way to increase conversion, if other material properties meet application requirements.

Effect of Plasticizer. Figure 7 shows the conversion of double bonds in the polymerization of TrMPTrA at different plasticizer (PEG) concentrations: 0, 15, and 25 wt %. The reaction rate in the autoacceleration period barely changes as the plasticizer concentration is increased. Moreover, the conversion at the maximum reaction rate remains almost unchanged (Table 1). However, the reaction rate in the autodeceleration period rises when the plasticizer concentration is raised. This is caused by the enhanced mobilities of double bonds and free radicals with more spacerlike, small plasticizer molecules. As a result, a higher “final” conversion is achieved.

Figure 8 shows the stress development over 2 h of irradiation. As the plasticizer concentration is raised, stress drops. Moreover, it takes a shorter time for the stress to level off because the reaction rate late in reaction increases with the plasticizer concentration.

The conversion and stress profiles together show that the addition of plasticizer has a moderate effect on enhancing conversion but a big effect on lowering stress. Adding plasticizer is an attractive way to increase conversion, if other material properties meet application requirements.

Methacrylate vs Acrylate. To compare UV curing of multifunctional methacrylates with acrylates, the polymerization of trimethacrylate, TrMPTrMA, is examined. Figure 9 compares the conversion profiles in the polymerization of TrMPTrMA and TrMPTrA. The reaction in the autoacceleration period is slower with trimethacrylate than with triacrylate. This is caused by a lower reactivity of double bonds in the methacrylate monomer. The final double-bond conversion is also lower in the polymerization of TrMPTrMA (i.e., 0.44) than TrMPTrA (i.e., 0.488). This can be attributed to the enhanced stiffness of methacrylate networks, which lowers the mobilities of free radicals and double bonds.

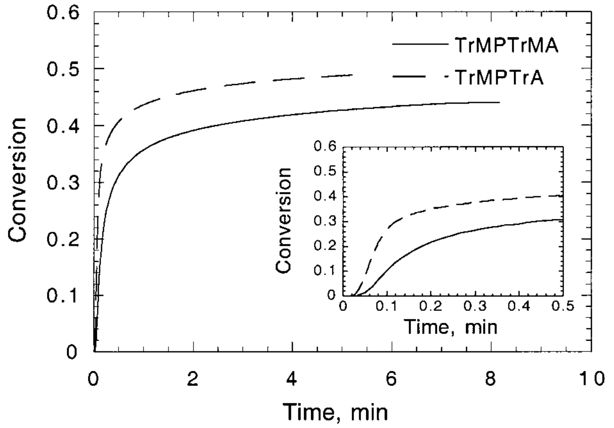

Figure 9. Conversion of double bonds in the polymerization of TrMPTrA and TrMPTrMA at 4 mW/cm^2 light intensity.

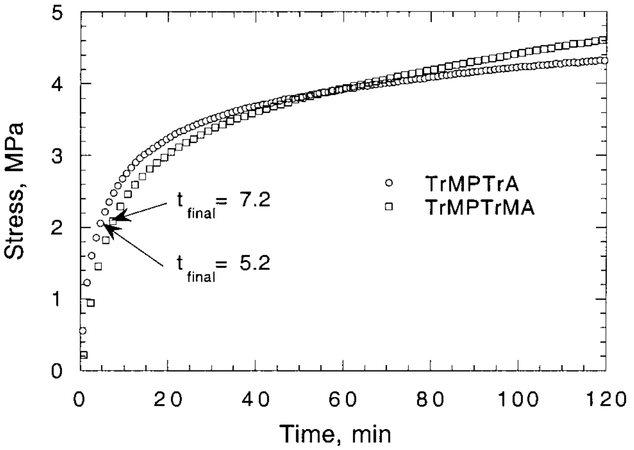

Figure 10. Stress development at continuous irradiation at 4 mW/cm^2 light intensity in the polymerization of TrMPTrA and TrMPTrMA. Points where the "final" conversions are reached are identified.

Figure 10 compares the stress development during the polymerization of TrMPTrMA and TrMPTrA over 2 h of irradiation. Initially, the stress develops more slowly in the polymerization of the trimethacrylate because of its slower reaction rate. Then the stress surpasses that of the triacrylate. Though the "final" conversion is less in the polymerization of TrMPTrMA, the stress at 2 h is higher, i.e., 4.62 MPa in the polymerization of TrMPTrMA vs 4.32 MPa in the polymerization of TrMPTrA.

The conversion and stress profiles together show that though changing from acrylate to methacrylate groups severely decreases the maximum reaction rate, moderately decreases the "final" conversion, and moderately increases the stress at a given conversion. To increase conversion with low stress, the acrylate monomer is favored over the methacrylate monomer.

Discussion

To understand the development of stress caused by the polymerization, stress vs conversion of all the systems studied is plotted in Figure 11. (Here all the curves end at "final" conversion, so not all stress data appear.) In all cases it is clear that significant stress develops only at fairly high conversion—in fact, at conversions much higher than might be expected for gelation. For example, stress appears strongly at 0.33−0.35 conversion in the polymerization of TrMPTrA at different light intensities, whereas the gelation conversion is generally lower than 10%.[16,23,24]

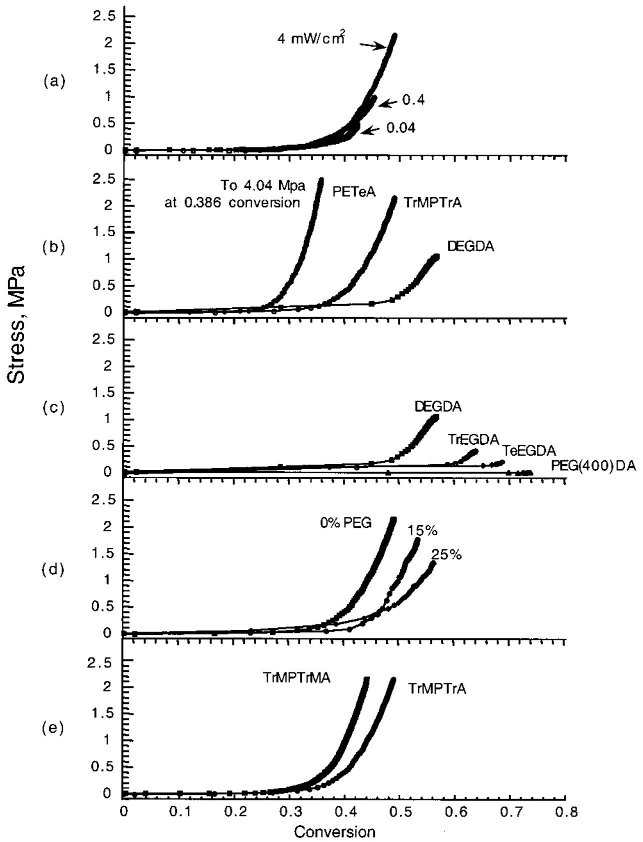

Figure 11. Stress development as a function of conversion in the polymerization of different systems: (a) TrMPTrA at different light intensities, (b) acrylate monomers of different functionalities, (c) diacrylate monomers with different chain lengths, (d) TrMPTrA at different plasticizer concentrations, (e) TrMPTrA vs TrMPTrMA. Light intensities in (b)−(e) systems are all 4 mW/cm^2.

Moreover, the conversions at which significant stress appears are much higher than the conversions at the maximum reaction rates (Table 1). These observations support the view that, generally, stress developed in the gelled state (rubbery regime) is relatively small because of the low modulus and fast relaxation. Most of the stress measured here is developed only in the vitrified state.

Vitrification might be best measured (see Table 1) by monitoring when significant stress appears. In most cases, this can be defined simply, such as when the material has grown strong enough to support a stress greater than 0.1 MPa. When reaction rate is very fast (i.e., in the polymerizations of DEGDA, TrEGDA, TeEGDA, and TrMPTrA at 25% PEG concentration), though, the stress at low conversions is measurable (but small) because the fast reaction allows little time for stress relaxation. In those cases, the vitrification conversion is less simple; here, it is estimated as that when the stress is greater than 0.1 MPa above a linear extrapolation of the stress growth at low conversions.

After the vitrification conversion, the stress develops monotonically with conversion. Because the stress relaxation in the vitrified state should be slow compared to the time scale of conversion measurements (less than 30 min), we may neglect any stress relaxation process. Thus, the stress measured is presumed to be almost purely elastic (e.g., eq 1 is valid).

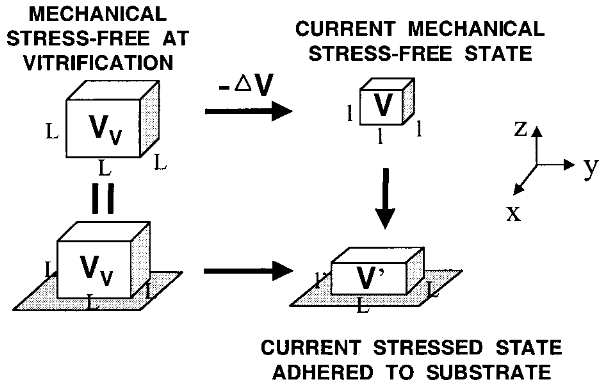

Figure 12. Shrinkage-elastic model for purely elastic materials. The initial mechanical stress-free state at vitrification (volume element V_v (of unit mass), with the dimensions of $L \times L \times L$) is a reference point. It undergoes isotropic shrinkage of volume ΔV to the current mechanical stress-free state (V, with the dimensions of $l \times l \times l$). The current stressed state (V', with the dimensions of $L \times L \times l'$) is obtained by stretching the current mechanical stress-free state to achieve the adhesion to the substrate. Adapted from Scriven,[34] Tam,[35] and Lei.[36]

With the assumption that no relaxation occurs in the vitrified state, eq 1 can be used to develop a prediction of how stress varies with conversion. According to eq 1, stress is proportional to the linear elastic strain, which is a function of double-bond conversion. The specific volume at the current mechanical stress-free state, V, is assumed as a function of the conversion x by

$$V = V_0(1 - \alpha x) \qquad (2)$$

where V_0 is the monomer specific volume and α is the current shrinkage coefficient (which may be a function of conversion and reaction rate). Equation 2 assumes that the specific volume at the current mechanical stress-free state is always bounded between the specific volume of the monomer and the specific volume at the current thermodynamic stress-free (equilibrium) state. The latter can be calculated by eq 2 with $\alpha = \alpha^e$, where α^e is the shrinkage coefficient at the thermodynamic stress-free state.[31] The current stressed state, with specific volume V', can be obtained by stretching the current mechanical stress-free state to achieve the adhesion to the substrate (as illustrated in Figure 12). The linear elastic strain ϵ (ϵ_x or ϵ_y in the plane of the substrate) can be calculated by $\epsilon = (L - l)/l = (\sqrt[3]{V_v} - \sqrt[3]{V})/\sqrt[3]{V}$, where V_v is the specific volume at the vitrification point. Through a Taylor series expansion (justified because there is only a small volume change after the vitrification point), the linear strain is related to the overall volume strain:

$$3\epsilon \doteq -\frac{\Delta V}{V_v} = \frac{\alpha x - \alpha_v x_v}{1 - \alpha_v x_v} \qquad (3)$$

where $\Delta V = V - V_v$ ($\Delta V/V \ll 1$); x_v and α_v are the conversion and the shrinkage coefficient at the vitrification point. Substituting eq 3 into eq 1 gives the predicted relationship between stress and conversion:

$$\sigma = \frac{E(\alpha x - \alpha_v x_v)}{3(1 - \nu)(1 - \alpha_v x_v)} \qquad (4)$$

Recall that Young's modulus E and shrinkage coefficient α may be functions of conversion and even reaction rate. Nevertheless, eq 4 shows that the in-plane stress should grow monotonically with conversion after vitrification—in agreement with the experiments here. Moreover, eq 4 shows that the in-plane stress should be proportional to Young's modulus.

A more detailed comparison of the measurement with eq 4 can be made. As light intensity (and the radical concentration) is raised, the stress dependence on conversion in the vitrified state (the slope) (Figure 11a) is not just consistent with eq 4, but it also appears that the vitrification conversion x_v (Table 1) does not change at different light intensities. Moreover, because all three curves almost overlay each other, Young's modulus E and the volume strain $(\alpha x - \alpha_v x_v)/(1 - \alpha_v x_v)$ may be similar. This suggests that the glass transition temperature does not depend much on the rate, neither through variation of excess free volume nor through variation of the network structure built at different radical concentrations. This is consistent with the hypothesis that the glass transition temperature is mainly determined by a combination of chain stiffness and cohesive forces in cross-linked polymers as proposed by Bicerano et al.[32] The networks may have already become dense enough that small differences in architecture are not much apparent. Indeed, it has been recently found that the glass transition temperature of a partially cured dimethacrylate copolymer at a given conversion does not depend on light intensity over 4 orders of magnitude change of light intensity.[33] The similar Young's modulus at a given conversion indicates that Young's modulus mainly depends on the rigidity of a network—the rigidity is similar even if the excess free volume and network structures are somewhat different.

However, the fact that the free volume at these three rates is indeed different becomes apparent at the end of the curves. The main difference between the three "final" conversions is simply that a faster rate (higher intensity, higher radical concentration) allows conversion to proceed to higher value beyond where the rate finally becomes imperceptibly slow (by the technique used here). This may occur because of extra trapped free volume, which allows radical to remain active and mobile to a higher dose of light ("final" doses are 1.25, 0.26, and 0.065 J/cm^2 at 4, 0.4, and 0.04 mW/cm^2) and a higher conversion. The higher stress in a higher light intensity appears to be caused only by the extra amount of conversion of double bonds. It is still not clear the contribution of the delayed volume shrinkage caused by a higher reaction rate to the elastic strain in the extra conversion regions.

As a higher functionality monomer is used, monomer chain length is made shorter, plasticizer concentration is lowered, or a methacrylate monomer is used instead of an acrylate monomer, the stress dependence on conversion (Figure 11) remains consistent with eq 4, but it also appears that the vitrification conversion x_v (Table 1) drops. The lower vitrification conversion is consistent with the formation of more highly cross-linked, rigid networks at a given conversion. Moreover, the rate of stress growth with respect to conversion rises. Whereas it is not clear presently how the volume strain $(\alpha x - \alpha_v x_v)/(1 - \alpha_v x_v)$ might change as those conditions are changed—owing to the complicity of delayed volume shrinkage—the observation is consistent with a higher Young's modulus at a given conversion, again no doubt because of the formation of more highly cross-link, rigid networks.

The experiments, considered in light of eq 4, show that a higher "final" conversion alone does not necessarily induce higher stress. Instead, the stress is raised by a combination of these factors—lower vitrification conversion, higher Young's modulus in the vitrified state, and a higher "final" conversion. This explains why the rate and magnitude of stress development can rise even though the conversion falls, for example, when a higher functionality monomer is used. The higher the cross-link density and the stiffer the networks generated, the lower the vitrification conversion and the higher the elastic modulus. Consequently, the higher modulus leads to a higher rate of stress growth at a given conversion. Also, the higher modulus and the lower vitrification conversion lead to higher magnitude of stress even though conversion falls. It is the reaction and elastic strain in the vitrified state that contribute to the bulk of the stress development.

The current shrinkage coefficient at a given conversion depends on the competition of the polymerization rate and the shrinkage rate. When the shrinkage rate becomes comparable to or slower than the polymerization rate, the mechanical stress-free state is not at the thermodynamic stress-free state, so α is hard to predict. A prediction of α would require computer simulations coupling volume relaxation and polymerization through the free volume of the system.[31] Further study should be pursued to reveal the effect of delayed volume shrinkage on volume strain and on stress development in different cases studied above.

It is worth pointing out that only when the shrinkage rate is much faster than the polymerization rate, the mechanical stress-free state is always at the thermodynamic stress-free state and the shrinkage coefficient always equals α^e. Then eq 4 can be simplified as

$$\sigma = \frac{E\alpha^{e}(x - x_{v})}{3(1-\nu)(1-\alpha^{e}x_{v})} \tag{5}$$

Equation 5 is similar to Croll's model of stress development during drying of polymer solutions, where elastic strain is caused by solvent loss rather than reaction and no excess free volume is considered.

Conclusions

The polymerization kinetics of multifunctional (meth)acrylate monomers is mainly determined by diffusion limitations on reactions among double bonds and free radicals. Higher "final" double-bond conversion (at which the reaction rate drops to 0.1% of its maximum value) can be achieved by (1) raising the light intensity to maintain more excess free volume, (2) lowering the monomer functionality to lower the cross-link density, (3) raising the monomer chain length to enhance the mobility of pendent double bonds and to lower the cross-link density, (4) adding plasticizer to create more free volume, and (5) using acrylate monomers instead of methacrylate to form flexible networks.

On the other hand, lower stress can be achieved through (1) lowering light intensity, (2) lowering monomer functionality, (3) raising monomer chain length, (4) raising plasticizer concentration, and (5) using acrylate monomers instead of methacrylate.

Significant stress starts to develop late in reaction, at the vitrification conversion, and then it grows monotonically with conversion. The rate of stress growth with respect to conversion in the glassy regime rises when the monomer functionality is raised, when the monomer chain length is shortened, when the plasticizer concentration is lowered, and when methacrylate monomers are used instead of acrylate monomers. These trends are consistent with the formation of more rigid networks at a given conversion, which raises the modulus. However, raising the light intensity appreciably affects neither the vitrification conversion nor the rate of stress growth with respect to conversion.

The effects of reaction conditions on volume strain are complicated because of the delayed volume shrinkage. Further studies about the volume shrinkage are necessary to understand the elastic strain caused by the delayed volume shrinkage. Moreover, a more detailed analysis can be pursued with a model that incorporates stress relaxation behavior[25,27]—particularly when stress developed in the gelled state is measurable (i.e., in the polymerization of DEGDA, TrEGDA, TeEGDA, and TrMPTrA at 25% PEG concentration).

To optimize UV curing of coatings—particularly to maximize conversion of double bonds for an acceptable level of stress or to minimize stress at a target conversion—ways should be sought to raise the mobilities of double bonds and free radicals and to postpone the vitrification to a conversion as high as possible. Raising monomer chain length or adding plasticizer is the best to achieve both high conversion and low stress if the polymer mechanical properties meet application demands.

Acknowledgment. We acknowledge support from the Center for Interfacial Engineering, a NSF Engineering Research Center at the University of Minnesota, through its Coating Process Fundamentals Program.

References and Notes

(1) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1−66.
(2) Pappas, S. P. *Radiation Curing: Science and Technology*; Plenum: New York, 1992.
(3) Decker, C.; Zahouily, K. *Polym. Mater. Sci. Eng.* **1993**, *68*, 70−71.
(4) Fouassier, J.-P., Rabek, J. F., Eds. *Radiation Curing in Polymer Science and Technology;* Elsevier Applied Science: London, 1993; Vol. 4.
(5) Kloosterboer, J. G.; van de Hei, G. M. M.; Dorant, G. C. M. *Polym. Commun.* **1984**, *25*, 322−325.
(6) Kloosterboer, J. G.; Lijten, G. F. C. *Polymer* **1990**, *31*, 95−101.
(7) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* **1994**, *35*, 3243−3250.
(8) Gunduz, N.; Shultz, A. R.; Shobha, H. K.; Sankarapandian, M.; McGrath, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1998**, *39*, 647−648.
(9) Decker, C.; Moussa, K. *Makromol. Chem.* **1988**, *189*, 2381−2394.
(10) Decker, C.; Moussa, K. *J. Coat. Technol.* **1990**, *62*, 55−61.
(11) Anseth, K. S.; Decker, C.; Bowman, C. N. *Macromolecules* **1995**, *28*, 4040−4043.
(12) Payne, J. A.; Francis, L. F.; McCormick, A. V. *J. Appl. Polym. Sci.* **1997**, *66*, 1267−1277.
(13) Cook, W. D. *Polymer* **1992**, *33*, 2152−2161.
(14) Kurdikar, D. L.; Peppas, N. A. *Polymer* **1994**, *35*, 1004−1011.
(15) Goodner, M. D.; Lee, H. R.; Bowman, C. N. *Ind. Eng. Chem. Res.* **1997**, *36*, 1247−1252.
(16) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650−655.
(17) Anseth, K. S.; Bowman, C. N. *Polym. React. Eng.* **1993**, *1*, 499−520.
(18) Kloosterboer, J. G.; Lijten, G. F. C. M. In *Chemistry, Properties, and Applications of Crosslinking Systems*; Dickie, R. A., Labana, S. S., S., B. R., Eds.; American Chemical Society: Washington, DC, 1988; Chapter 28, pp 409−438.
(19) Lange, J.; Toll, S.; Manson, J.-A. E. *Polymer* **1995**, *36*, 3135−3141.

(20) Ochi, M.; Yamashita, K.; Shimbo, M. *J. Appl. Polym. Sci.* **1991**, *43*, 2013−2019.
(21) Shimbo, M.; Ochi, M.; Shigeta, Y. *J. Appl. Polym. Sci.* **1981**, *26*, 2265−2277.
(22) Stolov, A. A.; Xie, T.; Penelle, J.; L.; H. S. *ACS Polym. Mater.: Sci. Eng.* **2000**, *82*, 371−372.
(23) Kloosterboer, J. G.; Lijten, G. F. C. M. *Polym. Commun.* **1987**, *28*, 2−5.
(24) Sun, X.; Chiu, Y.; Lee, L. J. *Ind. Eng. Chem. Res.* **1997**, *36*, 1343−1351.
(25) Martin, J. E.; Adolf, D. *Macromolecules* **1990**, *23*, 5014−5019.
(26) Martin, J. E.; Adolf, D. *J. Composite Mater.* **1996**, *1*, 13−34.
(27) Lange, J.; Toll, S.; Manson, J.-A. E. *Polymer* **1997**, *38*, 809−815.
(28) Croll, S. G. *J. Appl. Polym. Sci.* **1979**, *23*, 847−858.
(29) Payne, J. A. Stress Evolution in Solidifying Coatings. Ph.D. Thesis, University of Minnesota, 1998.
(30) Anseth, K. S.; Bowman, C. N. *Chem. Eng. Sci.* **1994**, *49*, 2207−2217.
(31) Bowman, C. N.; Peppas, N. A. *Macromolecules* **1991**, *24*, 1914−1920.
(32) Bicerano, J.; Sammler, R. L.; Carriere, C. J.; Seitz, J. T. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 2247−2259.
(33) Lovell, L. G.; Lu, H.; Stansbury, J. W.; Bowman, C. N. Los Angeles, 2000. AIChE Fall Annual Conference: Poster Session.
(34) Scriven, L. E. *Short Course: Coating Process Fundamentals;* University of Minnesota: Minneapolis, MN, 1996.
(35) Tam, S. Y. Stress Effects in Drying Coatings. Ph.D. Thesis, University of Minnesota, 1997.
(36) Lei, H. Flow, Deformation, Stress and Failure in Solidifying Coatings. Ph.D. Thesis, University of Minnesota, 1999.

MA010310H