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Rapid Solid-State Photopolymerization of Cyclic Acetal-Containing Acrylates

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ABSTRACT: A cyclic acetal-functionalized urethane acrylate monomer is synthesized here and polymerized in a crystalline state without the polymerization kinetics being deleteriously affected by the solid state. Depending on the processing conditions, the cyclic acetal urethane acrylate monomer exists in either a metastable liquid state or a crystalline state at ambient conditions. Because of mobility restrictions, extremely poor polymerization kinetics and functional group conversions are typically achieved in solid-state polymerizations. However, the solid-state photopolymerization of a cyclic acetal urethane acrylate results in nearly identical polymerization rates and ultimately higher conversion in the crystalline state than in the liquid state under otherwise identical conditions. We conclude that the crystallization process occurs in such a manner as to template the acrylic double bonds in a structure that facilitates rapid, minimally activated propagation.

Introduction

Radical-mediated photopolymerization reactions are ubiquitous with applications in dental materials, coatings, and lithographic processes.[1−3] These reactions proceed by photoinitiation of the radicals followed by bimolecular propagation and termination reactions[4,5] where the bimolecular events, particularly propagation, require sufficient monomer and/or radical mobility to facilitate the reaction. Because of this limitation, to our knowledge, no rapid, radical-mediated photopolymerization has previously been demonstrated when the monomer(s) are in a crystalline state.[6] The ability to polymerize in the crystalline state necessitates templating of the monomer structure such that the propagation reaction is facilitated by the crystalline structure that exists in the solid state. In fact, previous work in templated polymerization systems, particularly of liquid crystalline monomers and polymer stabilized liquid crystalline mixtures, has demonstrated that such templating leads to dramatic acceleration of the polymerization kinetics.[7−14] The ability to polymerize in the solid state has limited practical benefits associated with tacticity though one could envision the ability to form polymeric materials with enhanced shape control,[15] including coatings and lithographically patterned materials, when low-viscosity monomers could first be solidified followed by rapid photopolymerization.

In this work, a cyclic acetal functionalized urethane acrylate monomer is reported wherein polymerization kinetics are not deleteriously affected by the solid state. The cyclic acetal urethane acrylate monomer falls into a class of highly reactive monovinyl monomers that has recently been the focus of significant investigation. It has been found that certain secondary and tertiary functionalities, such as carbonates, urethanes (carbamates), urea, cyclic carbonates, oxazolidone, cyclic acetals, and aromatic rings can drastically enhance the reactivity of monovinyl monomers.[16−27] Such monomers have exhibited cure rates approaching and in many cases exceeding that of higher functionality (meth)acrylates. The mechanistic factors leading to this enhanced reactivity vary depending on the chemical nature of the monomer. In certain cases, hydrogen abstraction has been shown as a means for leading to cross-linking and increased polymerization rates.[28] Hydrogen bonding and conjugation of aromatic rings lead to increased viscosity and subsequently an increase in polymerization rate through suppressed termination.[29,30] In general, a combination of different intermolecular and intramolecular factors such as molecular conformation,[30] reactive intermediates,[19,32] polarity, conjugation, and hydrogen bonding all contribute to monomer reactivity as has traditionally been measured in the liquid state.[18]

Finally, these functional groups have also been postulated to lead to templating of the monomer structures in the liquid state.[33,34] This templating, resulting from intermolecular interactions such as hydrogen bonding or $\pi-\pi$ stacking, facilitates more rapid propagation and limited termination. While the incorporation of these structures results in significant enhancements of desirable polymer properties and liquid-state polymerization kinetics, they also commonly result in the formation of monomers with higher melting points that are crystalline at the desired ambient polymerization temperature. In general, because of the mobility restrictions in the solid state, extremely poor polymerization kinetics and functional group conversions are achieved when polymerizations are attempted in the solid state. Thus, many of these monomers are not practical for ambient temperature polymerizations, and they must be copolymerized in solution or at elevated temperature in the melt state to achieve rapid, or even reasonable, photopolymerization kinetics.

The cyclic acetal urethane acrylate monomer is unusual in that at ambient conditions it exists in either a metastable liquid state or a crystalline state, depending on the processing conditions. This dual nature of the cyclic acetal urethane acrylate offers a unique opportunity to study polymerization kinetics in both crystalline and noncrystalline states without other additional convolutions.

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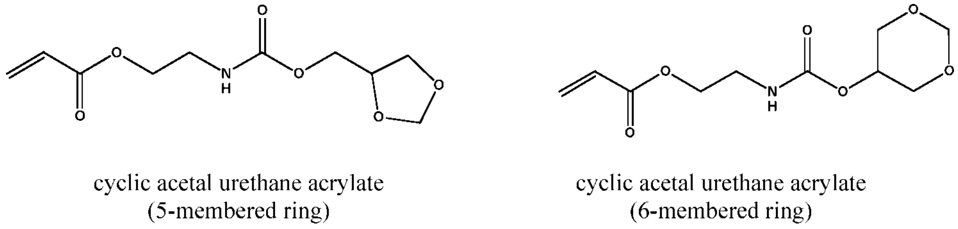
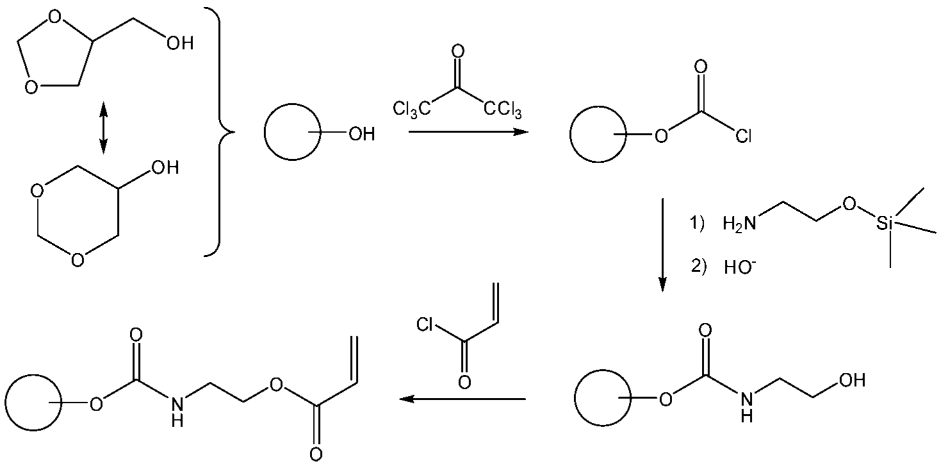


Figure 1. Chemical structures of cyclic acetal urethane acrylate where the monomer polymerized here contains approximately 27% 5-membered ring acetal and 73% 6-membered acetal.

Scheme 1. Synthesis of the Five- and Six-Membered Cyclic Acetal Urethane Acrylate



Experimental Section

Cyclic Acetal Urethane Acrylate Synthesis (Scheme 1). Glycerol formal (20 g) and 30 mL of triethylamine were dissolved in 150 mL of methylene chloride in a three-necked flask, equipped with a magnetic stirrer, reflux condenser, and N_2 gas purge in an ice bath. Bis(1,1,1-trichloromethyl)carbonate (20 g, 98%) in methylene chloride was added dropwise over 5 h. The reaction was continued for 24 h at room temperature. Formation of glycerol chloroformate was confirmed by FTIR spectroscopy. The trimethylsilyl-protected ethanolamine was prepared by the combination of 12.2 g of ethanolamine (99.5+%, redistilled) and 21.5 mL of 1,1,1,3,3,3-hexamethyldisilazane (97%) in 50 mL of toluene at 95−100 °C for 5 h. The TMSi-O-ethyleneamine solution was carefully added to the glycerol chloroformate solution at 5 °C. Following the addition, the reaction was continued at room temperature overnight. Subsequently, the trimethylsilyl-protected glycerol carbamate alcohol was hydrolyzed at room temperature in a methanol/water solution (pH $\geq$ 10) for 24 h to provide the glycerol carbamate alcohol. Glycerol carbamate alcohol (3.5 g) and 3 mL of triethylamine were mixed in 50 mL of chloroform, to which a mixture of 20 mL of chloroform and 3 mL of acryloyl chloride was added dropwise. The temperature of the reaction mixture was gradually increased to room temperature overnight. The reaction mixture was sequentially washed with a 1 wt % aqueous NaOH, a 1 wt % aqueous HCl solution, and three times with a saturated NaCl solution. After drying with Na_2SO_4 overnight, the solvent was removed under vacuum, and the product was purified by column chromatography on silica gel with hexane/ethyl acetate (1/1 by volume) as eluent. Approximately 1 g of the product was obtained as a mixture of the five- and six-membered acetal acrylates in a 27:73 molar ratio.

NMR ($CDCl_3$) cyclic acetal urethane Acr): δ 6.4 (d, 1H) δ 6.05 (q, 1H), δ 5.8 (d, 1H), δ 5.2 (s, 1H), δ 5.05 (s, 1H), δ 4.6−5.01 (m, 2.5H), δ 3.9−4.3 (m, 6H), δ 3.4−3.7 (m, 2.5H).

Fourier Transform Infrared (FTIR) Spectroscopy. FTIR was performed with a Nicolet 760 Magna Series II spectrometer with MCT/B detector and XT KBr beamsplitter. Samples were prepared by sandwiching a 5 μL drop of monomer containing 0.1 wt % dimethoxyphenylacetophenone (DMPA) between two NaCl windows. Samples were placed in a horizontal transmission accessory and irradiated with an EXFO Ultracure 100SS light source (Mississaugua, Ontario, Canada) with a 320−390 nm filter. The polymerization rate and conversion were determined from the high-frequency half of the absorbance associated with the carbon−carbon double bond peak at ca. 1637 cm^{-1} to accommodate the presence of an overlapping peak at ca. 1612 cm^{-1}.

Results and Discussion

The physical state and polymerization characteristics of the cyclic acetal urethane acrylate monomer were observed with infrared spectroscopy. For crystallization evaluation, a thin film monomer sample was prepared between two salt windows. The sample was heated above its melting point prior to sample preparation to facilitate creation of a thin liquid film. Shearing the sample was identified as a facile means to induce crystallization. The sample, at ~20 °C, was sheared by moving the top salt crystal slightly and then back to its original position. The transition from the liquid to the semicrystalline solid state is indicated by the formation of an opaque waxy solid with a melting point of ~50 °C. In this case, a metastable amorphous state below the monomer's melting point was fortuitously achieved with this particular isomeric mixture. We speculate that the predominant six-membered acetal structure is prone to crystallization but that the presence of the five-member acetal isomer disrupts order until a shear force is applied to overcome the entropic barrier to extended organization based on intermolecular urethane ordering. The degree of crystallinity attained in this process was not determined. Figure 2 illustrates the evolution of the infrared vibrational spectrum changes during crystallization at ambient conditions. The changes that evolve as the sample crystallizes are quite dramatic.

The NH (~3200−3500 cm^{-1}) and aliphatic CH stretching modes (~2800−3000 cm^{-1}) are presented in Figure 2a. The infrared response to an increase in strength or extent of hydrogen

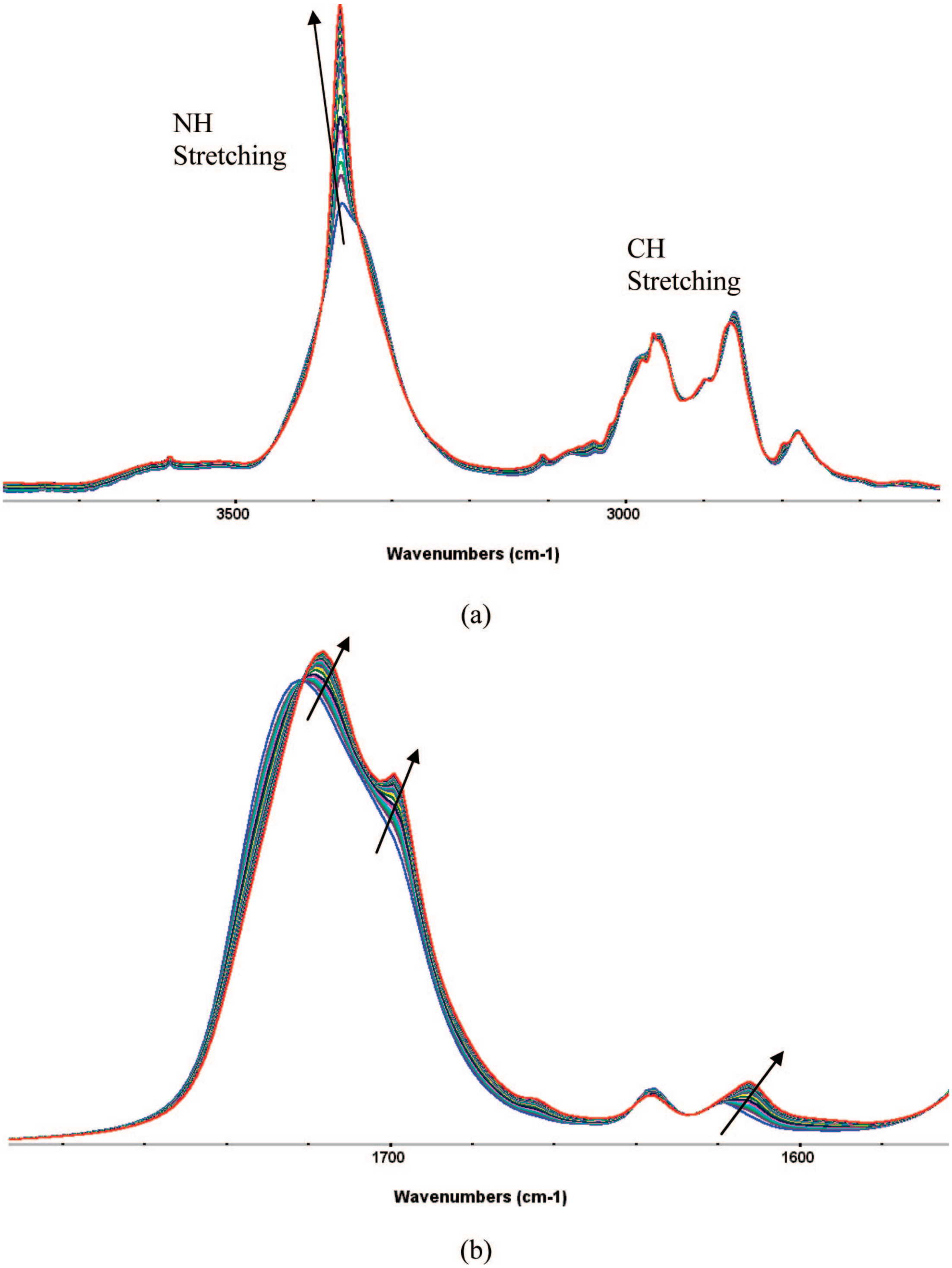


Figure 2. Evolution of cyclic acetal (5/6: 27/73) OCN acrylate infrared spectrum during crystallization at ambient conditions: (a) NH and CH stretching modes and (b) C═O and C═C stretching modes. The NH stretching mode increases in intensity, and a second distinctive carbonyl (C═O stretch) peak develops as crystallization time progresses (blue → red spectrum; arrow indicates increasing time and crystallinity).

bonding typically involves a shift to lower frequency and an increase in intensity.[35] The NH stretching peak contains multiple overlapping peaks corresponding to different hydrogen-bonding conformations with little if any contribution from "free" NH.[36] During crystallization, a significant selective enhancement in intensity is apparent for one of the underlying NH absorption bands. This result is consistent with the expectation that one specific hydrogen-bonding orientation would be dominant in the crystalline state.

Spectral changes in the carbonyl and alkene stretching regions during crystallization (Figure 2b) are also clearly evident. An apparent growth of the hydrogen-bonded carbonyl absorbance at ca. 1697 cm^{-1} and the development of an absorbance at ca. 1612 cm^{-1} that partially overlaps the lower frequency alkene peak are additional changes associated with monomer crystallization. The assignment of this 1612 cm^{-1} band is not straightforward. Urea systems contain a similar absorbance when a high degree of ordering is present. The absorbance at ∼1612 cm^{-1} in ureas is assigned to the highly organized hydrogen-bonded state of the urea hydrogens and carbonyl groups.[37,38] However, a similar absorbance has not been reported in the infrared literature involving urethane organization.

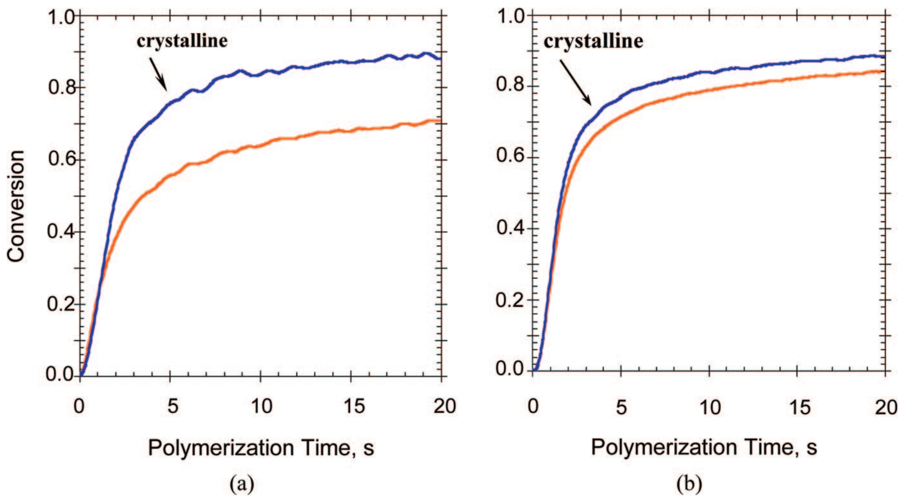


Figure 3. Conversion vs time of cyclic acetal urethane acrylate polymerization of a monomer with ~27% 5-membered acetals at (a) 10 and (b) 25 °C. Crystalline and noncrystalline state polymerizations are compared at both temperatures. Polymerization conditions with the crystalline polymerization reaching the higher conversion in both cases: initiator concentration 0.1 wt % DMPA; light intensity 5 mW/cm^2.

It is also important to address the reversibility of the changes in the infrared spectrum. Upon heating the sample above its melting point, all of the aforementioned changes are reversed. The spectrum then remains in the original liquid-state spectrum upon cooling the sample to ambient conditions until shear is applied to induce crystallization. Though all of the shifts in the spectra are not fully understood, the spectra indicate preferential hydrogen-bonding interactions arise as a result of crystallization as would be expected in a crystalline state.

Polymerization kinetics are examined for the cyclic acetal urethane acrylate in both the liquid and crystalline states. Changes in the polymerization kinetics as a function of physical state provide information regarding the mechanisms and the nature of organization in the crystalline state. The polymerizations were conducted at 10 and 25 °C in both the crystalline and noncrystalline states (Figure 3). Since real-time IR monitoring of the polymerization reaction kinetics provides time-resolved complete mid-IR spectra, the NH stretching data are coupled with the conversion measurement. This complementary spectral data clearly indicate whether the polymerization is occurring in the amorphous liquid state or in the preordered crystalline state. The noncrystalline and crystalline state kinetics are almost indistinguishable at low conversion. The primary difference in the polymerization kinetics between the two states is a higher ultimate conversion attained in the crystalline state. The higher ultimate conversion arises because the traditional mobility limitations associated with vitrification, which stop the “untemplated”, liquid-state polymerization, do not cause the solid-state polymerization to stop. These results potentially alter the way that traditional solid-state polymerizations are viewed, pending verification with X-ray diffraction analyses. Because of lower monomer mobility, solid-state polymerizations are subject to dramatic reductions in both polymerization kinetics and overall conversion. As a specific example of an attempted polymerization of a similar monomer structure, irradiation of a phenylurethane acrylate monomer in its crystalline state does not induce any polymerization. However, noncrystalline state phenylurethane acrylate polymerizations proceed at a polymerization rate similar to the cyclic acetal urethane acrylate.[24] Unlike solid-state polymerizations in highly ordered single crystal monomers, which often require γ-irradiation for initiation, the semicrystalline nature of the isomeric monomer mixture here likely accommodates the photoinitiator in both the amorphous and crystalline states, which is consistent with the observed kinetic results.

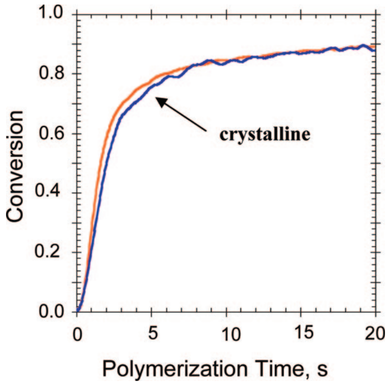


Figure 4. Effect of temperature on the crystalline state cyclic acetal urethane acrylate polymerization of a monomer with ~27% 5-membered acetal at 10 and 25 °C. Polymerization conditions: initiator concentration 0.1 wt % DMPA; light intensity 5 mW/cm^2.

The observed kinetic results indicate a degree of ordering or templating in the crystalline state, similar to that in liquid crystalline systems, that significantly enhances the propagation reaction while also leading to reduced termination, higher effective active center concentrations, and ultimately higher overall conversion as compared to other solid-state polymerizations.

Interestingly, the polymerization rate and final conversion are both essentially temperature independent in the crystalline state (Figure 4) and temperature dependent in the noncrystalline state. This behavior in the solid state, in which the hydrogen-bonding interactions are largely unaffected by temperature rise below the melting point, is consistent with minimally activated propagation and termination processes associated with the templating of the monomer.[39]

Interestingly, the characteristics of the infrared spectrum attributed to crystallinity are minimally affected during polymerization, suggesting that the organization due to crystallization is not disrupted during polymerization. Similarly, polymerization in the liquid state does not induce the infrared spectral changes associated with the crystalline transition. Samples polymerized in the crystalline state were heated after polymerization to determine whether polymerization had “locked in” the organized structure. The postpolymerization spectra (not shown) illustrate the loss of infrared characteristics associated with the crystalline state after heating the sample to 75 °C. This result is interesting, as many organized liquid crystalline systems exhibit disruption of organization upon polymerization[40] while here the crystalline structure is preserved following polymerization but can still be thermally reversed.

Conclusions

In summary, here we report the solid-state photopolymerization of a cyclic acetal urethane acrylate which achieves higher conversion in the crystalline state than in the liquid state while completing the polymerization in 3−5 s under very mild initiation conditions. This behavior is unique among (meth)-acrylic photopolymerizations and is uniquely verifiable because the cyclic acetal urethane acrylate can be supercooled and polymerized in either the liquid or solid state at ambient conditions. Infrared spectroscopy was used to monitor both the crystallization and polymerization processes with distinct increases in hydrogen bonding observed during the shear-induced crystallization process. The temperature dependence of the solid-state polymerization was also measured with minimal changes observed in either the polymerization rate or final conversion as a function of temperature. Here, we conclude that the crystallization process occurs in such a manner as to template the acrylic double bonds in a structure that facilitates rapid, nonactivated propagation. This propagation reaction does not require significant mobility that is not available in the solid state.

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References and Notes

(1) Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Biopolymers II* **1995**, *122*, 177.
(2) Kloosterboer, J. G. *Adv. Polym. Sci.* **1988**, *84*, 1.
(3) Decker, C. *Chimia* **1993**, *47*, 378.
(4) Decker, C.; Moussa, K. *J. Coat. Technol.* **1993**, *65*, 49.
(5) Decker, C. *Acta Polym.* **1994**, *45*, 333.
(6) Hohn, W.; Tieke, B. *Macromol. Chem. Phys.* **1996**, *197*, 2753.
(7) Guymon, C. A.; Hoggan, E. N.; Clark, N. A.; Rieker, T. P.; Walber, D. M.; Bowman, C. N. *Science* **1997**, *275*, 5296.
(8) Guymon, C. A.; Bowman, C. N. *Macromolecules* **1997**, *30*, 5271.
(9) Hoyle, C. E.; Chawla, C. P.; Kang, D.; Griffin, A. C. *Macromolecules* **1993**, *26*, 758.
(10) Hoyle, C. E.; Kang, D. *Macromolecules* **1993**, *26*, 844.
(11) Hoyle, C. E.; Watanabe, T. *Macromolecules* **1994**, *27*, 3790.
(12) Broer, D. J.; Mol, B. N. *Makromol. Chem.* **1989**, *190*, 19.
(13) Broer, D. J.; Boven, J.; Mol, G. N.; Challa, G. *Makromol. Chem.* **1989**, *190*, 2255.
(14) Broer, D. J.; Hikmet, R. A. M.; Challa, G. *Makromol. Chem.* **1989**, *190*, 3201.
(15) Matsumoto, A. *Polym. J.* **2003**, *35*, 93.
(16) Jansen, J.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2002**, *35*, 7529.
(17) Jansen, J.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861.
(18) Kilambi, H.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2007**, *40*, 47.
(19) Beckel, E. R.; Stansbury, J. W.; Bowman, C. N. *Macromolecules* **2005**, *38*, 9474.
(20) Decker, C.; Moussa, K. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 159.
(21) Decker, C.; Moussa, K. *Makromol. Chem., Macromol. Chem. Phys.* **1991**, *192*, 507.
(22) Moussa, K.; Decker, C. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2197.
(23) Brosse, J. C.; Chevalier, S.; Couvret, D.; Decker, C.; Moussa, K. Fr. Patent 89.08651, **1989**.
(24) Berchtold, K. A.; Nie, J.; Stansbury, J. W.; Hacioglu, B.; Beckel, E. R.; Bowman, C. N. *Macromolecules* **2004**, *37*, 3165.
(25) Kilambi, H.; Beckel, E. R.; Berchtold, K. A.; Stansbury, J. W.; Bowman, C. N. *Polymer* **2005**, *46*, 4735.
(26) Zhou, H.; Li, Q.; Lee, T. Y.; Guymon, C. A.; Jonsson, E. S.; Hoyle, C. E. *Macromolecules* **2006**, *39*, 8269.
(27) Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Guymon, C. A.; Hoyle, C. E. *Macromolecules* **2004**, *37*, 3659.
(28) Decker, C.; Elzaouk, B. *Eur. Polym. J.* **1990**, *26*, 393.
(29) Jansen, J.; Dias, A. A.; Dorschu, M.; Coussens, B. *Photoinitiated Polym.* **2003**, *847*, 127.
(30) Kilambi, H.; Reddy, S. K.; Beckel, E. R.; Stansbury, J. W.; Bowman, C. N. *Chem. Mater.* **2007**, *4*, 641.
(31) Kilambi, H.; Reddy, S. K.; Schneidewind, L.; Stansbury, J. W.; Bowman, C. N. *Polymer* **2007**, *48*, 2014.
(32) Decker, C.; Jenkins, A. D. *Macromolecules* **1985**, *18*, 1241.
(33) Lee, T. Y.; Roper, T. M.; Jonsson, E. S.; Guymon, C. A.; Hoyle, C. E. *Macromolecules* **2004**, *37*, 3659.
(34) Jansen, J. F. G. A.; Dias, A. A.; Dorschu, M.; Coussens, B. *Macromolecules* **2003**, *36*, 3861.
(35) Irusta, L.; Iruin, J. J.; Fernandez-Berridi, M. J.; Sobkowiak, M.; Painter, P. C.; Coleman, M. M. *Vib. Spectrosc.* **2000**, *23*, 187.
(36) Lemon, M. T.; Jones, M. S.; Stansbury, J. W. *J. Biomed. Mater. Res., Part A* **2007**, *83A*, 734.
(37) Luo, N.; Wang, D. N.; Ying, S. K. *Macromolecules* **1997**, *30*, 4405.
(38) Luo, N.; Wang, D. N.; Ying, S. K. *Polymer* **1997**, *37*, 3577.
(39) Shibasaki, Y.; Fukuda, K. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2947.
(40) Sievens-Figueroa, L.; Guymon, C. A. *Polymer* **2008**, *49*, 2260.

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