Synthesis, Characterization and Cleavage of Surface-Bound Linear Polymers Formed Using Thiol−Ene Photopolymerizations

Vaibhav S. Khire,[†] **Tai Yeon Lee,**[†] **and Christopher N. Bowman***[,†,‡]

Department of Chemical and Biological Engineering, University of Colorado,
Boulder, Colorado 80309-0424, and Department of Restorative Dentistry, University of Colorado
Health Sciences Center, Denver, Colorado 80045-0508

Received April 22, 2008; Revised Manuscript Received August 4, 2008

ABSTRACT: The formation of linear polymer films using thiol−ene photopolymerizations was investigated by grafting thiol−ene films on the surface with subsequent cleavage and polymer analysis. Silica nanoparticles were first modified with an acrylated silane molecule, and then a dithiol was reacted to this surface using a base catalyzed thiol−acrylate conjugate addition reaction to prepare a uniform surface presenting thiol groups attached to the surface with a cleavable ester linkage. Photopolymerization of difunctional thiol and ene monomers present in various stoichiometric ratios was carried out in the presence of the nanoparticles, and a thiol−ene film was attached to the surface. The polymer film was cleaved from the surface using acid-catalyzed hydrolysis and separated from the particles. It was found that the particle presence does not affect the polymerization of thiol−ene polymers in bulk; however, the presence of surface thiols changes the relative stoichiometry of the thiol and ene monomers at the surface and hence strongly affects the molecular weight of the attached polymer. The number average and the weight average molecular weight of the unattached polymers ranged from 900 to 12,600 g/mol and 1500 to 25,700 g/mol, respectively, as the thiol:ene ratio in the bulk increased from 0.6 to 1. The highest molecular weight of the grafted polymers (M_n = 1600 g/mol, M_w = 2700 g/mol) was achieved when the thiol:ene ratio was close to 0.77:1 in the bulk and decreased monotonically for both higher and lower stoichiometric ratios. When the polymerization rate was decreased and the time scales for reaction increased, the grafted polymer molecular weight increased for stoichiometric thiol−ene monomer mixtures, because the relative effect of surface thiols was decreased.

Introduction

Over the past few decades, a variety of methods have been utilized for modifying planar and curved surfaces with polymer films with controlled properties. The most popular approach for attaching surface-bound polymer films is the reaction or deposition of an initiator molecule onto the surface and subsequently initiating a polymerization from the surface.[1−3] Based on the type of initiator various polymerization mechanisms such as the free radical polymerizations,[4−7] living and controlled radical polymerization,[8−14] ionic polymerizations[15] and atom transfer radical polymerization (ATRP)[16−20] have been used for growing surface-bound polymer films. In this work, a step growth thiol−ene photopolymerization reaction is used to synthesize and cleave polymer films attached to nanoparticle surfaces.

Characterization of surface-bound organic films has generally been performed using a variety of techniques consisting of spectroscopy, mechanical or optical characterization techniques such as ellipsometry and microscopy.[1,2,21] Usually, a combination of these techniques is employed to investigate the structure, composition and spatial variations of surface-bound films. Although significant progress has been achieved in the application of each of these film characterization techniques over the past few years, direct characterization of polymer films attached to surfaces remains a challenge. Investigation of polymer-specific properties such as molecular weight, molecular weight distribution and polydispersity is not a straightforward process for grafted polymers.[3,22−24]

One popular method to overcome these limitations, which has been employed in several studies, is the cleavage of polymer films from the surface after the polymerization reaction.[3,7,25−31] Initial studies in this field relied on using a destructible substrate such as silica particles that could be removed in a hydrogen fluoride solution and the separation of polymer films from the solution.[26,30,32] Another technique used for the same purpose is the introduction of a cleavable functional group on the surface. This group is frequently used to initiate the attachment of the polymer film and is then cleaved from the surface to release the attached polymer films.[7,25,29] Films formed using various polymerization mechanisms, most popularly atom transfer radical polymerization (ATRP), have been characterized using this technique.

Although various researchers have investigated polymer films formed using chain addition mechanisms, the work done in investigating films formed using step growth polymerization mechanism has been quite limited.[33,34] Step growth polymerizations form an attractive method for surface functionalization since, in addition to using polymerization conditions such as initiation, time of polymerization or addition of initiators in the bulk for controlling polymer growth, the stoichiometry and functionality of the monomers can be exploited to control the film properties and graft polymer characteristics. Use of stoichiometry for controlling film thickness is particularly attractive since it is self-limiting, viz., no external stimulus or monitoring is required to control the film growth and film properties.[35,36] Photopolymerizable step growth systems are further attractive since the spatial growth of polymer films is controlled by exposing selective areas of the substrate using photomasks, and these reactions can rapidly be driven to high conversions.[37,38]

In this work, the formation and cleavage of polymer films formed using thiol−ene photopolymerizations are investigated. Thiol−ene polymerizations are step growth, radical-mediated photopolymerization reactions, in which a thiol molecule adds across the carbon−carbon double bond of an ene molecule.[39−43]

---

* Corresponding author. E-mail: christopher.bowman@colorado.edu.

[†] Department of Chemical and Biological Engineering, University of Colorado.

[‡] Department of Restorative Dentistry, University of Colorado Health Sciences Center.

10.1021/ma8008965 CCC: $40.75

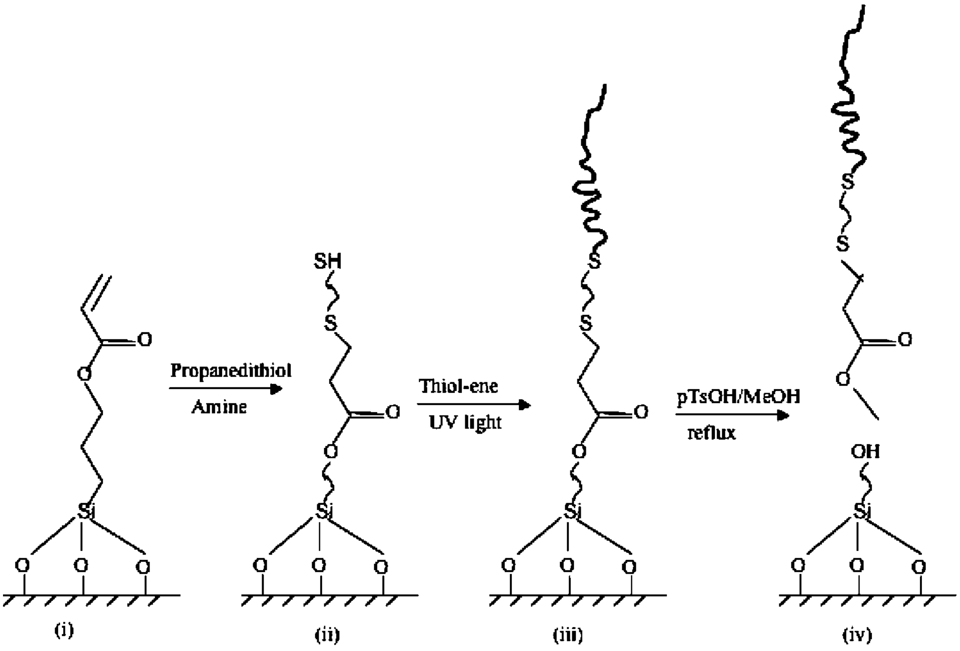

Figure 1. Schematic representation of the formation and cleavage of thiol−ene films on surfaces. (i) Hydroxy-terminated silica surfaces were treated with 3-acryloxypropyl trichlorosilane in the presence of triethylamine as catalyst. (ii) The acrylated surfaces were reacted with 1,3-propanedithiol in the presence of diethylamine as a catalyst to form thiol-terminated surfaces. (iii) 1,6-Hexanedithiol and triethylene glycol divinyl ether were photopolymerized on the thiol-terminated surfaces using 0.1% DMPA as photoinitiator by exposing to UV light (15 mW/cm^2, 365 nm) for 30 s. (iv) Polymer-modified surfaces were treated with *p*-toluenesulfonic acid (50 mg) solution in methanol (10 mL) mixed in chloroform (100 mL) and maintained under reflux conditions for 18 h.

Since these reactions occur in a step growth manner, the monomer stoichiometry and functionality are tuned to control properties such as modulus, cross-linking density and polymer chain characteristics. These reactions are further useful since they polymerize rapidly, with minimal or no initiator present, have low shrinkage and shrinkage stresses and are insensitive to oxygen.[44,45] As a result, several novel applications of thiol−ene polymers have been investigated including dental composites,[46,47] holographic gratings,[48−50] biodegradable materials for tissue engineering,[51−53] formation of nanoimprinted polymers[54−56] and stabilizing and aligning liquid crystals in polymer matrices.[50,57,58]

Recently, Lee and Bowman used thiol−ene photopolymerizations for modifying silica nanoparticles using a variety of thiol−ene monomers and reaction conditions.[59] Using real-time infrared spectroscopy, it was shown that, even in the presence of a significant amount of nanoparticles, near-complete conversion of the monomers was achieved in most cases including the cases where multifunctional monomers forming cross-linked polymer structures were used. Although the reaction rate was not significantly impacted due to the presence of nanoparticles, it was proposed that the presence of surface thiols leads to alteration of thiol−ene stoichiometry at the surface, thereby changing the reaction kinetics. Here, the surface-bound linear polymers are investigated by cleaving the formed films from the surface and characterizing the films using GPC.

We recently investigated the formation and cleavage of films formed using step growth thiol−acrylate conjugate addition reactions using amines as a catalyst.[60] A photocleavable group with an acrylate functionality was synthesized and used as an anchoring molecule to attach films to the surface, which were subsequently cleaved by exposure to UV light. This technique is, however, not appropriate for films formed using the photopolymerization mechanism since the photocleavable group is damaged due to exposure to UV light during polymerization. As a result, ester group hydrolysis was used to cleave grafted films formed by thiol−ene photopolymerizations.

To introduce a cleavable ester group on the surface, an acrylated trichlorosilane was used to functionalize the surface. Silica nanoparticles were used as the surface for functionalization to increase the surface to volume ratio. The acrylate groups were capped with a dithiol molecule, which acts as the anchoring group for the attachment of polymer films formed in the bulk on the surface. Photopolymerization was carried out using dithiol (thiol) and divinyl ether (ene) monomers in various stoichiometric ratios, and polymer films were attached to the surface. The surface-bound linear polymers were cleaved using acid hydrolysis, and the cleaved polymer films were separated from the surface. Both types of polymers—the unattached polymer from the first step and the grafted polymer cleaved as a result of acid hydrolysis—were investigated using GPC and IR and compared to provide information on the different polymerization behavior in the bulk and on the surface. The process of surface modification and cleavage of polymer films is schematically shown in Figure 1.

Experimental Section

Materials. Triethylene glycol divinyl ether (DVE3), 1,6-hexanedithiol (HDT), 1,3-propanedithiol (PDT), diethylamine and triethylamine were purchased from Sigma Aldrich and used as received. The silane 3-acryloxypropyltrichlorosilane was purchased from Gelest. The photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) was purchased from Ciba-Geigy. *p*-Toluenesulfonic acid (*p*-TsOH) was purchased from Mallinckrodt Baker, Inc. (Phillipsburg, NJ). All solvents were purchased from Fisher and used as received. Silica particles (OX-50, primary size = 40 nm)[61] were donated by Degussa.

Immobilization of Acrylated Chlorosilane and Propanedithiol. The detailed procedure for immobilizing acrylated chlorosilane on silica nanoparticles has been described elsewhere.[59] Briefly, the nanoparticles (1 g) were dried in vacuum at 150 °C for 3 h and dispersed in dried toluene (50 mL) by vigorous mixing. 3-Acryloxypropyltrichlorosilane (1 g) was dissolved in dried toluene (10 mL) and added dropwise to the solution followed by addition of 1 mL of triethylamine. The reaction mixture was stirred under nitrogen for 18 h. The particles were washed with toluene, ethanol, ethanol/water mixture (2 times), ethanol and methylene chloride (2 times). The particles were separated from solvent by repeated centrifugation (3000 rpm, 10−15 min). The functionalized particles were dried in vacuum for 24 h. The acrylated particles were dispersed again in toluene by vigorous mixing. Propanedithiol (3 g) was added to the solution, and diethylamine (10 drops) was added as a catalyst. The solution was stirred for 24 h, and the resultant particles were washed 5 times with methylene chloride and dried in vacuum for 24 h.

Polymerization of Thiol−Ene Films. DVE3 and HDT were mixed in various stoichiometric ratios of thiol to ene functionalities, and 0.1% DMPA was added. The monomer solution was mixed with 5 wt % thiol-modified particles, and the solution was stirred for 1−2 h until the particles were uniformly distributed in the monomers. Small aliquots (~1 mL) of the monomer were withdrawn and immediately polymerized under UV light (365 nm, 15 mW/cm^2) for around 1 min, and the formed polymer was dissolved in methylene chloride. The polymerization reaction was complete within a few seconds as monitored using IR. The methylene chloride solution was centrifuged to separate the particles from the solvent and the unattached polymer. The particles were washed 5−10 times with methylene chloride until no unattached polymer was extracted from the particles. The methylene chloride solution from the washes was evaporated to separate the unattached polymer.

Cleavage of the Thiol−Ene Polymer Films. Polymer modified particles (0.5 g) were dispersed in chloroform (100 mL) by vigorous mixing, and a solution of 50 mg of *p*-TsOH in 10 mL of methanol was added to the solution. The solution was mixed and refluxed for 18 h, and the cleaved polymer was separated from the solvent by repeated washing with methylene chloride. The particles were dried in vacuum, and the cleaved polymer was concentrated by evaporating methylene chloride.

Functionalization of Silicon Wafers. The surface-attachment and cleavage of the polymer films was performed on silicon wafers before replicating it on silica nanoparticles. Silica wafers were cleaned using “piranha” solution (1:3 vol:vol ratio of hydrogen peroxide:sulfuric acid) and washed with water and acetone. The silicon wafer was immersed in a 1 mM solution of acrylated trichlorosilane in toluene for 10 min and washed with acetone for functionalizing the surface with acrylate. Propanedithiol (100 μL) was mixed with 10 mL of toluene, and a few drops of diethylamine were added to the solution. The acrylated silicon wafer was immersed in the solution for 2 h, and the wafer was washed with acetone and dried with nitrogen. Polymerization of thiol−ene films was carried out as described in earlier sections. The cleavage of the films was carried out in the exact same manner as described for the nanoparticles in the previous section.

Characterization. The nanoparticles were characterized using IR and TGA, while the polymer samples were characterized using IR and GPC. A Nicolet 750 Magna FIR spectrometer with a KBr beam splitter and fitted with an MCT detector was used to record the IR spectra of all samples. A small sample of nanoparticles was dissolved in $MeCl_2$ and deposited on a NaCl salt crystal, and the solvent was evaporated. Polymer samples were sandwiched between two salt crystals, and spectra were recorded. For real-time measurement of the monomer conversion, a series of spectra were recorded while the samples were irradiated with UV light. The double bond concentration was monitored using the ene absorption peak at 1636 cm^{-1}, and the thiol peak was monitored at 2575 cm^{-1}. All reactions were performed at ambient temperature.

The TGA used for characterizing nanoparticles was a Perkin-Elmer TGA. Particles were stored in vacuum at 100 °C before TGA analysis to remove adsorbed moisture. Particles (5−15 mg) were then heated from 50 to 800 °C at the rate of 10 °C/min, held at 800 °C for 20 min and cooled to room temperature at the rate of 20 °C/min. The percent weight loss of the particles was recorded throughout the process.

A Waters GPC using chloroform as an elution solvent was used to characterize the molecular weight distribution of all polymer samples. Toluene was added as an internal standard. A custom calibration curve for thiol−acrylate polymers was obtained and used to calculate the molecular weights. The detailed procedure used to obtain the calibration curve has been described elsewhere.[60] The accuracy of the thiol−acrylate calibration for predicting thiol−ene molecular weights was tested prior to using it here. It is possible to theoretically predict the molecular weight distribution of a step growth polymer for a specific stoichiometric ratio assuming equal reactivity of all reactive components.[62−64] The molecular weight distribution was predicted for various stoichiometric ratios of thiol−ene monomers and verified with the experimental results obtained form GPC. To obtain accurate values of the stoichiometric ratios, the concentration of thiol and ene functionalities in the monomer samples were measured using NMR and used for the calculations.

Silicon wafers were characterized using ellipsometry using a Multiskop, Optrel GBR ellipsometer. All measurements were performed at an incident angle of 70°.

Results and Discussion

The effectiveness of a polymer film coating on a surface depends on the properties of the polymer film. Depending on properties such as thickness, uniformity, spatial variations and chain density of the attached polymer films, various properties of the surface such as chemistry, wettability, surface roughness and biocompatibilty are suitably modified. Various techniques such as changing polymerization conditions, initiator and monomer concentrations as well as the addition of inhibitor or sacrificial initiator in the bulk are employed to control polymer film properties.[1,2] However, an accurate determination of properties to test the effectiveness of these techniques is difficult. Although spectroscopic and microscopic techniques are used for the determination of properties of the film as a whole, polymer-specific properties such as molecular weight and molecular weight distribution cannot be determined with surface-bound films. Cleavage of films from the surface is a necessary advancement for extending the characterization of polymer films.

Thiol−ene polymer films are attractive because of their ability to form uniform ultrathin films without external control, since the thickness control is achieved using a stoichiometric imbalance.[35,38] A unique feature of thiol−ene polymer films is that functional groups on the surface act as anchors. Thus, the polymerization process is initiated from the surface, and polymer chains formed in the bulk attach to surface thiols or enes to form a polymer film. Thus, the polymer film attachment proceeds via both the “grafting to” and the “grafting from” approaches.

In this work, the attachment and cleavage of polymer films formed using thiol−ene polymerization are investigated. Properties of the polymer films formed using step growth polymerizations depend on the stoichiometry in which the two monomer species are added. Here, polymer films were formed using various stoichiometric ratios and the effects of stoichiometry on both the bulk and the surface polymer properties were investigated.

Silica nanoparticles were used as substrates for the growth and cleavage of the polymer films due to their high surface area to volume ratios. The method for film formation as well as cleavage was first tested on flat silicon wafers. Acrylated trichlorosilane was deposited on a silicon wafer, which has a thin silicon oxide coating, using a solution method. Since the overall surface area is very small, a low concentration of silane is sufficient for a uniform coating on the surface. The deposition of a monolayer was verified by ellipsometry, which shows a thickness increase of ~0.8 nm, corresponding to an acryloxypropyl trichlorosilane monolayer. A thin layer of propanedithiol (~0.5 nm) is reacted on top of the acrylated silane monolayer using the thiol−acrylate amine catalyzed reaction, which corresponds to a near complete coverage of the surface acrylates.

Table 1. Ellipsometric Thicknesses of Attached Films on a Silicon Wafer Measured at Various Steps of Surface Modification[a]

modified surface	acrylate SAM	acrylate SAM + PDT	thiol–ene polymer	after cleavage
thickness (nm)	0.8(0.1)	0.5(0.1)	6.1(0.4)	0.9(0.4)

[a] Silicon wafers were modified subsequently with acrylated trichlorosilane, propanedithiol and thiol–ene polymer with the HDT and DVE3 such that thiol:ene = 1:1 in the monomer by exposing to UV light (365 nm, 15 mW/cm^2). The modified silicon wafers were treated with *p*-TsOH and methanol as described in the Experimental Section to cleave the polymer from the surface and the thickness of the layer remaining after cleavage was measured. The thickness values in the table denote only the thickness of the outermost or last layer. Thickness after cleavage denotes the thickness of the entire residual organic layer on the silicon wafer. Numbers in parentheses denote standard deviations taken over three samples.

The polymerization of the thiol–ene polymers on the surface was performed by sandwiching the monomer between the thiol-terminated substrate and a glass slide. The substrate was cleaned using methylene chloride, and the thickness was measured using ellipsometry. The polymer-modified substrate was treated using the cleavage mechanism described for silica particles for 18 h, and the thickness of the residual polymer film was measured. The thickness results for all the steps are shown in Table 1. It is seen that a polymer film of approximately 6 nm thickness was deposited on the surface, which agrees well with previous results for thiol–ene films formed on thiol SAMs.[35] Following cleavage, approximately 0.9 nm of the film remains on the surface. The small residual film thickness is attributed to the dense packing of the acrylate monolayer, which prevents the acid catalyst from entering the film completely. In addition, there is a possibility of a limited amount of homopolymerization of the unreacted acrylate groups when the surface is exposed to light, which further inhibits the acid hydrolysis by making the cleavable ester groups even less accessible. It was found that further increasing the cleavage time does not result in any significant decrease residual in the film thickness.

The polymerization and cleavage reactions were next replicated on silica nanoparticles. To replicate the initial studies performed using thiol–ene photopolymerizable films, a monolayer thiol surface was desirable, along with an ester group linkage, which can be cleaved for film release and analysis. This outcome was achieved by first depositing an acrylate trichlorosilane and reacting the acrylate functional groups with a large excess of dithiol using an amine-catalyzed conjugate addition reaction. An acrylated trichlorosilane was used due to its high reactivity and the resultant high coverage.[59] As shown previously, it is important to remove moisture from the system to prevent the chlorosilanes from polymerizing during the reaction. As a result, both the silica nanoparticles and toluene used as solvent for reaction were dried. The modified nanoparticles were characterized using IR spectroscopy and thermogravimetric analysis.

An excess of propanedithiol compared to the acrylate functional groups on the particle surface (ratio of added thiols to surface acrylates was maintained at 20:1 or more) was used to prevent cyclization of thiol molecules on the surface, where the dithiol molecules would react with both ends of the surface acrylate groups. Figure 2a shows the IR spectra of acrylated particles and acrylated particles modified with thiol groups, and Figure 2b shows an expansion of one region of the same spectra. The attachment of the ester groups is confirmed by the presence of the ester group peak at 1730 cm^{-1} and the peak at 1406 cm^{-1} from the C=C–H bending. The acrylate groups disappear completely after the reaction with thiols. The ester peak in the acrylated particles shows a small shoulder due to the hydrogen bonding of some of the ester groups in the acrylate with the unreacted hydroxyl groups present on the particle surface. The thiol peak is not visible in the IR spectra due to lower molar absorption coefficient. Both spectra show small peaks of alkane absorption around 3000 cm^{-1}.

The particles were characterized using TGA at each step, and it was found that the acrylated particles show approximately 2% weight loss, while the weight loss increases to 3% after reaction with thiol. (See Supporting Information.) This value corresponds approximately to 2.3 molecules/nm^2 of acrylate groups and 1.4 molecules/nm^2 of thiol groups on the surface. The TGA results are summarized in Table 2.

The thiol-functionalized silica nanoparticles were used as substrates for attaching linear thiol–ene polymers. To minimize particle aggregation, they were added to the monomer solution in small quantities (5 wt %) and stirred vigorously for 1–2 h. Aggregation of nanoparticles is a significant issue in using nanoparticles as fillers or as a component in polymerization resins. However, it is possible to disperse them by mixing vigorously and having the particle surface chemistry compatible with the monomer solution.

To verify that the particles do not have a significant effect on the polymerization, polymerizations were performed with and without particles for a 1:1 mixture of thiol and ene monomers and real-time IR kinetic measurements were performed to monitor the conversion of each of the monomer species. The thiol functional group was monitored using the peak at 2575 cm^{-1}, and the ene functional group was monitored using the peak at 1650 cm^{-1} with 0.1% of the photoinitiator DMPA added to initiate the reaction. The results of both series runs are shown in Figure 3, where it is seen that there is no significant effect of the particles on the bulk polymerization kinetics. The polymerization is complete within 10–15 s, and the step growth nature of the reaction was confirmed by the equal consumption of the thiol and ene functional groups. For all future runs, only small quantities of monomer samples were polymerized (~1 mL) and care was taken to ensure that the sample thickness is never more than 1 cm since the nanoparticles will scatter UV light and affect the polymerization kinetics in that manner.

After verifying that the polymerization kinetics remain largely unchanged with the addition of 5 wt % thiolated particles, the same process was performed on a larger scale using ~1 g of particles and using ~20 g of the monomer mixture. Various stoichiometric ratios of thiol and ene were used to deposit polymer films on the surface. Upon polymerization, the particle–polymer mixture was dissolved in methylene chloride, which acts as a good solvent for the formed polymers. The polymer-modified particles were separated from the unattached polymers by centrifugation. The particles were washed repeatedly with fresh methylene chloride and were separated using centrifugation each time. The process was continued until the IR spectra of the concentrated solvent from the last wash did not show a trace of the polymer. This required between 5 and 10 washes. The modified particles were dried under vacuum and used for IR and TGA experiments.

To cleave the polymer attached to the surface, the modified particles were again dispersed in chloroform solution by vigorous mixing for 1–2 h. A solution of 50 mg of *p*-TsOH in 10 mL of methanol was added to the solution, and the solvent was refluxed for 18 h. The particles were separated from the cleaved polymer using the same procedure and dried in vacuum after separation. Both the unattached and the cleaved polymers were concentrated by evaporating the solvent and characterized using GPC.

The particles as well as all the polymer samples were analyzed using IR. The polymer-modified particles showed an increase in peak area corresponding to the alkane chains. This peak area then decreased significantly upon cleavage. The ester group

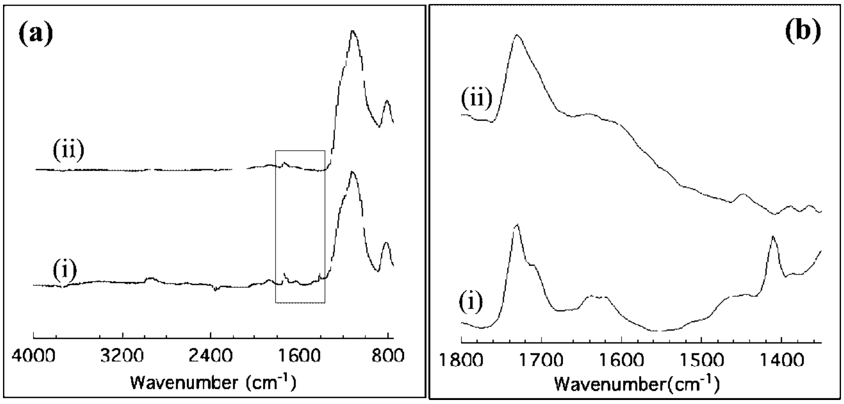

Figure 2. (a) IR spectra of silica nanoparticles modified with (i) acrylated trichlorosilane and subsequently modified with (ii) propanedithiol. Nanoparticles were dispersed in methylene chloride, the solution was placed dropwise on a NaCl crystal and the solvent was evaporated to deposit nanoparticles on the crystal. (b) Expansion of the region from 1800−1350 cm^{-1} from (a).

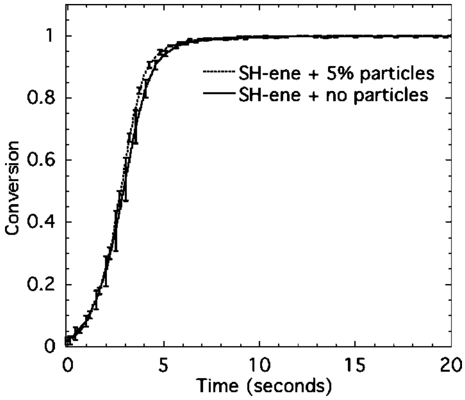

Figure 3. Conversion of thiol−ene monomers with and without silica nanoparticles. 1,6-Hexanedithiol and triethylene glycol divinyl ether were polymerized in the presence of 0.1% DMPA by exposing to UV light (365 nm, 15 mW/cm^2) with and without 5 wt % thiol-modified silica nanoparticles. The monomer solution was sandwiched between two salt crystals and exposed to UV light, while the thiol and ene peaks were monitored using real-time FTIR. The conversion of the ene peak at 1650 cm^{-1} is shown.

peak, corresponding to the thiol−acrylate ester linkage, also reduced to nearly zero upon cleavage using acid hydrolysis. Both the unattached and cleaved polymers showed peaks corresponding to thiol−ene chains in the IR spectra (Supporting Information).

Molecular Weight Determination of the Polymers. A unique characteristic of step growth polymers is the control of the molecular weight of the resultant polymer using the stoichiometric ratio of reacting monomers. To investigate the effect of stoichiometry on both the unattached and the attached polymer molecular weights, polymerizations were carried out in the presence of particles for various stoichiometric ratios of thiol to enes.

The number average molecular weight, weight average molecular weight and the polydispersity obtained using GPC measurements for unattached and cleaved polymers obtained using four different ratios of thiol:ene are shown in Figure 4. The theoretical molecular weight predicted for a step growth polymer sample is also shown in the figure. It is seen that the molecular weights of the unattached polymer samples are similar to the theoretical values for all cases except when the monomer ratio is close to 1. This result is expected as it was seen earlier that the presence of the small amount of nanoparticles does not affect the polymerization kinetics. The theoretical molecular weight for the case when the two monomer functionalities are present in equal amounts is infinity. The calculated molecular weight for this case, taking into consideration the impurities in the monomer species, is still significantly higher than the observed molecular weight. This outcome occurs because high oligomer viscosities and diffusion limitations prevent the complete reaction of the monomer species when the molecular weight of the samples becomes very high, and the observed molecular weight falls short of theoretical predictions.

The molecular weights of the cleaved polymer samples show significantly different trends from the unattached polymer samples. It is seen that the molecular weight maximum for the grafted polymer occurs at the intermittent stoichiometric ratio (0.77:1). This trend is seen in both the number average and weight average molecular weights. A closer scrutiny of the polymerization process taking place near the surface is required to explain this trend. At the surface, both the surface thiols and the bulk monomer functionalities participate in the reaction. As a result, the stoichiometric ratio present at the surface is different from the one present in the bulk. This situation is depicted in Figure 5.

For the case when thiol and ene monomers are present in a stoichiometric ratio in the bulk, although the monomer solution present in the vicinity of the surface has an equal number of thiol and ene endgroups, the surface provides additional thiol groups, which changes the stoichiometry of the overall solution. If a small region of ~5 nm around the particle is taken into consideration, the surface contributes 10−20% of the overall thiol groups, thereby changing the thiol:ene ratio of 1:1 in the bulk to around 1.15:1 near the surface. It was found that the contribution of surface thiols did not change significantly for various meaningful values of the particle diameter, R. When a polymer chain with an ene endgroup reacts with a surface thiol and attaches to the surface, the 1:1 stoichiometry in the bulk is not maintained in the vicinity of the surface and it shifts toward the thiol groups (i.e., bulk thiol:ene ratio becomes slightly greater than 1). As a result of diffusion of bulk thiol and ene terminated chains into and out of the region near the particle surface, there exists a concentration gradient of chains with thiol endgroups. The concentration of the chains with thiol endgroups is highest at the surface and decreases from there to the level of the bulk concentration.

The concentration gradient is highly dependent on the diffusion rate and the time available for diffusion. For slower polymerizations, more time for oligomer diffusion exists which reduces the importance of the surface thiol concentration. Thus, the surface thiol effect decreases as the reaction rate decreases. In contrast, for rapid reactions, there is less time available for the bulk chains to diffuse and the effect of surface thiols on the length of the attached chains is more pronounced. Hence, the molecular weight of the grafted polymer, as seen in Figure 4,

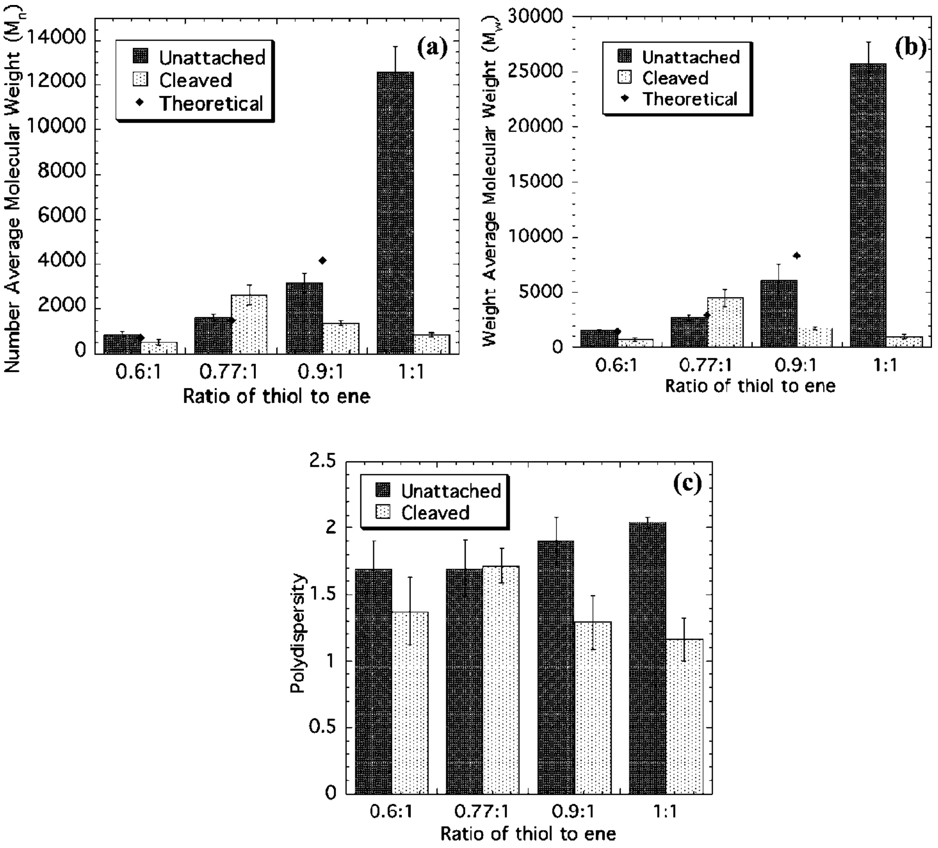

Figure 4. (a) Number average molecular weight, (b) weight average molecular weight and (c) polydispersity obtained using GPC of the unattached and cleaved thiol−ene polymers formed by exposing hexane dithiol and triethylene glycol divinyl ether in various ratios of thiol:ene functional groups. All polymerizations were carried out in the presence of 5 wt % thiolated silica nanoparticles and by exposure to UV light (365 nm, 15 mW/cm^2). The unattached polymer was separated by centrifugation, and the grafted polymer was cleaved from the surface using ester group hydrolysis using *p*-toluenesulfonic acid and methanol.

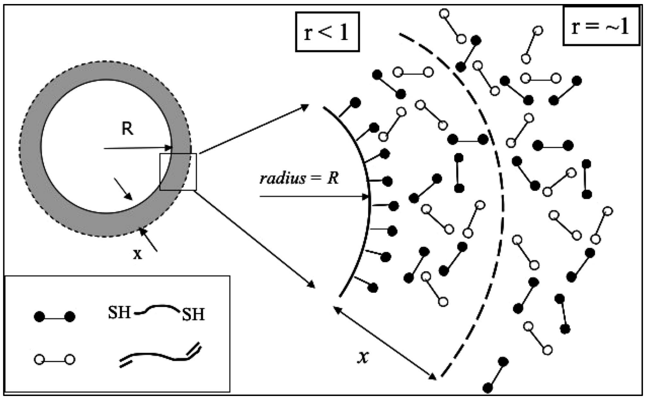

Figure 5. Schematic of the thiol−ene polymerization taking place at the surface of the thiolated nanoparticle. When the thiol−ene ratio in the bulk is close to one, the contribution of surface thiols results in a thiol:ene ratio of more than one near the surface. For well-dispersed nanoparticle solutions, $R = \sim 20$ nm. For a nominal value of $x = 5$ nm, the surface thiols contribute to ~10−20% of the bulk thiols, thereby changing the approximate stoichiometric ratio to 1.15:1 in the region between the particle surface and the dotted line.

is maximum for a bulk stoichiometric ratio that is significantly less than 1:1, since the surface thiols contribute to the stoichiometry to maintain a 1:1 ratio near the surface.

To demonstrate that the reaction rate influences the molecular weight of the attached polymer, the same reaction as that in Figure 4 was carried out at a slower polymerization rate by reducing the initiator concentration and lowering the intensity of the UV light. The initiator concentration was reduced 10-fold to 0.01 wt %, and the intensity was reduced to 1 mW/cm^2. The reaction was complete in around 25 min, in contrast to ~10 s in the case of the results shown in Figure 4. Under these initiation conditions, for a monomer mixture with thiol:ene = 1:1, the number and weight average molecular weights of the grafted polymer were found to be 1940 (±200) g/mol and 2525 (±215) g/mol, respectively. The molecular weights of the unattached polymer were found to be similar to the ones observed for the stoichiometric thiol−ene ratio in Figure 4. Thus, there is a 2-fold increase in the molecular weight of the grafted polymer, for the same thiol:ene stoichiometric ratio, when the polymerization rate was decreased. The increase in the molecular weight of the grafted polymer for the slower reaction rate shows that, compared to the faster reaction investigated in Figure 4, the stoichiometric ratio at the surface is closer to the bulk ratio of 1:1 for the slower reaction, which in turn shows that chain diffusion results in decreasing the effect of surface thiols.

Although the molecular weight of the grafted polymer increases upon decreasing the polymerization rate, as well as by shifting the thiol:ene ratio to 0.77:1 for the faster reaction (as seen in Figure 4), the molecular weight in each of these cases is still an order of magnitude smaller than that of the unattached polymer for the same stoichiometric ratio of thiol:ene monomers. This result is an indication of an incomplete reaction at the surface. In step growth reactions, both stoichiometric ratio and the monomeric conversion need to be close to unity to obtain high molecular weight polymers. It is possible that in these cases the conversion near the surface does not reach unity and hence the attached polymers have significantly lower molecular weights than the bulk polymers. In addition, steric hindrance caused by the attached chains makes the surface thiols inaccessible and prevents further grafting of new polymer,

Table 2. TGA Results for Particles Modified with Acrylated Trichlorosilane (silica + acr), Propanedithiol (silica + acr + PDT) and Thiol−ene Polymers Formed Using Varying Ratios of Thiol:Ene Functionalities[a]

	residual wt (% of original)	μmol/g	chains/nm^2
silica + acr	97.9 (0.03)	193 (4)	2.3 (0.04)
silica + acr + PDT	96.9 (0.2)	113 (19)	1.4 (0.2)
thiol:ene ratio			
0.6:1	93.9 (0.6)	58 (15)	0.7 (0.1)
0.77:1	95.7 (0.2)	4.9 (1.4)	0.06 (0.01)
0.9:1	94 (0.3)	22.4 (4.0)	0.27 (0.05)
1:1	90.7 (0.1)	74 (9)	0.9 (0.1)

[a] Weight loss of silica nanoparticles was measured using TGA by heating the particles from 50 to 800°C. Using the known molecular weights of the acrylated silane and propanedithiol and the measured molecular weights of the thiol−ene polymers from Figure 4, the amount of attached material per gram of particles was calculated at each step. The surface coverage of each layer (no. of chains/nm^2) was calculated by dividing the attached numbers of moles per gram of particle by the particle surface area. Numbers in parentheses denote standard deviations.

thereby reducing the overall molecular weight of the grafted polymer.

Figure 4c shows the polydispersity values obtained for both unattached and cleaved polymers formed using various thiol:ene ratios. It is seen that, for the unattached polymers, the polydispersity increases with the increasing molecular weight and the values lie between one and two with a maximum at the 1:1 stoichiometric ratio as theoretically predicted. For the grafted polymers, the polydispersity follows the same trend as obtained for the molecular weights, having the maximum value at a thiol:ene ratio of 0.77:1 and decreasing for higher and lower stoichiometric ratios. This result also shows that for the grafted polymers the stoichiometric ratio at the surface is closer to unity for an intermediate bulk thiol:ene ratio, as indicated by the molecular weight results. The different trends in polydispersity for the bulk and grafted polymers further show that the surface thiols have a continuous effect on the stoichiometry at the surface throughout the reaction. This result in turn shows that there is no significant preferential reaction at the growing chain-ends, as compared to the surface thiols, which would have resulted in higher values of polydispersities for the surface-bound polymers, as compared to the unattached polymers.

The modified particles were also investigated using TGA, and the results are shown in Table 2. The particles were heated from 50−800 °C and cooled down, and the weight loss throughout the process was monitored. It is seen that the amount of attached polymer decreases with the increase in the molecular weight. Using the number average molecular weight measures from GPC, the number of moles of attached polymer per gram of nanoparticles as well as the surface coverage of the particles (chains/nm^2) is calculated. The surface coverage is also found to decrease with an increase in the molecular weight. It is seen that the number of chains attached per unit area decreases as the ratio of thiol to ene near the surface reaches unity, which corresponds to a bulk thiol:ene ratio of ~0.8.

A method for the formation and cleavage of step growth thiol−ene photopolymers is thus presented. It has been shown here that the polymerizations at surfaces follow a different mechanism as compared to the polymerizations in bulk. The impact of thiol−ene stoichiometry on the molecular weight has previously been investigated.[35,37] However, in this case, in addition to the thiol−ene stoichiometry, the presence of surface thiols and the reaction rate have been shown to affect the molecular weight of the grafted polymers. Reducing the polymerization reaction rate was found to result in decreasing the effect of surface thiols. Other studies involving chain growth polymerizations have shown that the grafted polymers have higher molecular weights due to the shielding of the radicals and thereby decreasing the termination rate.[25,26] On the other hand, the living radical mechanism results in uniform molecular weight for both surface and bulk polymers.[30−32] In the case of thiol−ene step growth polymers, the molecular weight is affected by both stoichiometry and reaction rate, and a judicious selection of both can potentially be used to tune the grafted polymer molecular weight and hence the surface properties. While very high molecular weight polymers have not been attached in this work, further reducing the polymerization rate or adding small amounts of multifunctional thiol or ene monomers can lead to the grafting of polymer films with an even wider range of molecular weights.

Conclusions

Silica nanoparticles were modified with acrylated trichlorosilane and a thiol group to investigate the formation and cleavage of polymers formed using thiol−ene photopolymerization. Step growth polymers formed from difunctional thiol and ene monomers were produced in the presence of thiolated silica nanoparticles, and the grafted polymers were cleaved from the surface using acid hydrolysis of ester groups. While the unattached polymer followed the theoretical molecular weights for step growth polymerizations, the surface thiols were found to contribute to the stoichiometry of the monomers at the surface and hence the molecular weight of the grafted polymers. Due to the rapid reaction and the contribution of surface thiols, the grafted polymer molecular weight reached a maximum when the thiol:ene ratio in bulk was close to 0.8 in contrast to the theoretical value of 1. However, reducing the polymerization rate was found to decrease the effect of the surface thiols. The surface chain densities of the modified particles were calculated using TGA and were found to be inversely proportional to the molecular weight of the attached polymers.

Acknowledgment. The authors would like to acknowledge the financial support from the NSF MRSEC program (DMR-0213918).

Supporting Information Available: TGA weight loss curves and IR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Zhao, B.; Brittain, W. J. *Prog. Polym. Sci.* **2000**, *25* (5), 677–710.
(2) Advincula, R. C. *Polymer brushes: synthesis, characterization, applications*; Wiley-VCH: Weinheim, 2004; pp xxiii, 483.
(3) Ruhe, J.; Knoll, N. *J. Macromol. Sci., Polym. Rev.* **2002**, *C42* (1), 91–138.
(4) Bialk, M.; Prucker, O.; Ruhe, J. *Colloids Surf., A* **2002**, *198*, 543–549.
(5) Harant, A. W.; Whipple, S. G.; Douglas, K.; Bowman, C. N. *J. Vac. Sci. Technol., B* **2005**, *23* (2), 354–358.
(6) Prucker, O.; Ruhe, J. *Langmuir* **1998**, *14* (24), 6893–6898.
(7) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31* (3), 592–601.
(8) Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. *Macromolecules* **1999**, *32* (5), 1424–1431.
(9) Hutchison, J. B.; Haraldsson, K. T.; Good, B. T.; Sebra, R. P.; Luo, N.; Anseth, K. S.; Bowman, C. N. *Lab Chip* **2004**, *4* (6), 658–662.
(10) Reddy, S. K.; Sebra, R. P.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (10), 2134–2144.
(11) Yang, W. T.; Ranby, B. *Macromolecules* **1996**, *29* (9), 3308–3310.
(12) Luo, N.; Hutchison, J. B.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40* (11), 1885–1891.
(13) Luo, N.; Hutchison, J. B.; Anseth, K. S.; Bowman, C. N. *Macromolecules* **2002**, *35* (7), 2487–2493.
(14) Rahane, S. B.; Kilbey, S. M.; Metters, A. T. *Macromolecules* **2005**, *38* (20), 8202–8210.
(15) Mather, B. D.; Viswanathan, K.; Miller, K. M.; Long, T. E. *Prog. Polym. Sci.* **2006**, *31* (5), 487–531.
(16) Shah, R. R.; Merreceyes, D.; Husemann, M.; Rees, I.; Abbott, N. L.; Hawker, C. J.; Hedrick, J. L. *Macromolecules* **2000**, *33* (2), 597–605.

(17) Pyun, J.; Kowalewski, T.; Matyjaszewski, K. *Macromol. Rapid Commun.* **2003**, *24* (18), 1043–1059.
(18) Feng, W.; Brash, J.; Zhu, S. P. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (12), 2931–2942.
(19) Kurosawa, S.; Aizawa, H.; Talib, Z. A.; Atthoff, B.; Hilborn, J. *Biosens. Bioelectron.* **2004**, *20* (6), 1165–1176.
(20) Ramakrishnan, A.; Dhamodharan, R.; Ruhe, J. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (5), 1758–1769.
(21) Ulman, A. *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly*; Academic Press Inc.: New York, 1991.
(22) Goodman, D.; Kizhakkedathu, J. N.; Brooks, D. E. *Langmuir* **2004**, *20* (15), 6238–6245.
(23) Goodman, D.; Kizhakkedathu, J. N.; Brooks, D. E. *Langmuir* **2004**, *20* (8), 3297–3303.
(24) Yamamoto, S.; Tsujii, Y.; Fukuda, T. *Macromolecules* **2000**, *33* (16), 5995–5998.
(25) Prucker, O.; Ruhe, J. *Macromolecules* **1998**, *31* (3), 602–613.
(26) Boven, G.; Oosterling, M. L. C. M.; Challa, G.; Schouten, A. J. *Polymer* **1990**, *31* (12), 2377–2383.
(27) Coad, B. R.; Steels, B. M.; Kizhakkedathu, J. N.; Brooks, D. E.; Haynes, C. A. *Biotechnol. Bioeng.* **2007**, *97* (3), 574–587.
(28) Rakhmatullina, E.; Braun, T.; Kaufmann, T.; Spillmann, H.; Malinova, V.; Meier, W. *Macromol. Chem. Phys.* **2007**, *208* (12), 1283–1293.
(29) Jayachandran, K. N.; Takacs-Cox, A.; Brooks, D. E. *Macromolecules* **2002**, *35* (11), 4247–4257.
(30) Ejaz, M.; Tsujii, Y.; Fukuda, T. *Polymer* **2001**, *42* (16), 6811–6815.
(31) Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. *Macromolecules* **1998**, *31* (17), 5934–5936.
(32) Marutani, E.; Yamamoto, S.; Ninjbadgar, T.; Tsujii, Y.; Fukuda, T.; Takano, M. *Polymer* **2004**, *45* (7), 2231–2235.
(33) Beinhoff, M.; Appapillai, A. T.; Underwood, L. D.; Frommer, J. E.; Carter, K. R. *Langmuir* **2006**, *22* (6), 2411–2414.
(34) Iacono, S. T.; Budy, S. M.; Mabry, J. M.; Smith, D. W. *Polymer* **2007**, *48* (16), 4637–4645.
(35) Harant, A. W.; Khire, V. S.; Thibodaux, M.; Bowman, C. N. *Macromolecules* **2006**, *39* (4), 1461–1466.
(36) Khire, V. S.; Lee, T. Y.; Bowman, C. N. *Macromolecules* **2007**, *40* (16), 5669–5677.
(37) Khire, V. S.; Harant, A. W.; W., W. A.; Anseth, K. S.; Bowman, C. N. *Macromolecules* **2006**, *39*, 5081–5086.
(38) Khire, V. S.; Benoit, D. S. W.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (24), 7027–7039.
(39) Cramer, N. B.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39* (19), 3311–3319.
(40) Cramer, N. B.; Davies, T.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2003**, *36* (12), 4631–4636.
(41) Cramer, N. B.; Reddy, S. K.; O'Brien, A. K.; Bowman, C. N. *Macromolecules* **2003***36* (21), 7964–7969.
(42) Reddy, S. K.; Cramer, N. B.; O'Brien, A. K.; Cross, T.; Raj, R.; Bowman, C. N. *Macromol. Symp.* **2004**, *206*, 361–374.
(43) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42* (21), 5301–5338.
(44) Good, B. T.; Reddy, S.; Davis, R. H.; Bowman, C. N. *Sens. Actuators. B* **2007**, *120* (2), 473–480.
(45) O'Brien, A. K.; Cramer, N. B.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44* (6), 2007–2014.
(46) Carioscia, J. A.; Lu, H.; Stanbury, J. W.; Bowman, C. N. *Dent. Mater.* **2005**, *21* (12), 1137–1143.
(47) Lu, H.; Carioscia, J. A.; Stansbury, J. W.; Bowman, C. N. *Dent. Mater.* **2005**, *21* (12), 1129–1136.
(48) Natarajan, L. V.; Brown, D. P.; Wofford, J. M.; Tondiglia, V. P.; Sutherland, R. L.; Lloyd, P. F.; Bunning, T. J. *Polymer* **2006**, *47* (12), 4411–4420.
(49) Natarajan, L. V.; Shepherd, C. K.; Brandelik, D. M.; Sutherland, R. L.; Chandra, S.; Tondiglia, V. P.; Tomlin, D.; Bunning, T. J. *Chem. Mater.* **2003**, *15* (12), 2477–2484.
(50) Senyurt, A. F.; Warren, G.; Whitehead, J. B.; Hoyle, C. E. *Polymer* **2006**, *47* (8), 2741–2749.
(51) Rydholm, A. E.; Held, N. L.; Bowman, C. N.; Anseth, K. S. *Macromolecules* **2006**, *39* (23), 7882–7888.
(52) Rydholm, A. E.; Anseth, K. S.; Bowman, C. N. *Acta Biomater.* **2007**, *3* (4), 449–455.
(53) Rydholm, A. E.; Reddy, S. K.; Anseth, K. S.; Bowman, C. N. *Polymer* **2007**, *48* (15), 4589–4600.
(54) Hagberg, E. C.; Malkoch, M.; Ling, Y. B.; Hawker, C. J.; Carter, K. R. *Nano Lett.* **2007**, *7* (2), 233–237.
(55) Yi, Y.; Khire, V. S.; Bowman, C. N.; Maclennan, J.; Clark, N. A. *J. Appl. Phys.* **2008**, *103*, 093518.
(56) Khire, V. S.; Yi, Y.; Clark, N. A.; Bowman, C. N. *Adv. Mater.* **2008**, 10.1002/adma.200800672.
(57) Beckel, E. R.; Cramer, N. B.; Harant, A. W.; Bowman, C. N. *Liq. Cryst.* **2003**, *30* (11), 1343–1350.
(58) Cramer, N. B.; Beckel, E. R.; Harant, A. W.; Davies, T.; Williamson, D. L.; Bowman, C. N. *Liq. Cryst.* **2002**, *29* (10), 1291–1296.
(59) Lee, T. Y.; Bowman, C. N. *Polymer* **2006**, *47* (17), 6057–6065.
(60) Khire, V. S.; Kloxin, A.; Clouch, C. L. C.; Anseth, K. S.; Bowman, C. N. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, *46* (20), 6896–6906.
(61) http://www.aerosil.com.
(62) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877–1885.
(63) Flory, P. J. *Principles of polymer chemistry*; Cornell University Press: Ithaca, 1953; p 672.
(64) Odian. *Principles of Polymerization*, 3rd ed.; John Wiley & Sons, Inc.: New York, 1991.

MA8008965