

Synthesis, Characterization and Cleavage of Linear Polymers Attached to Silica Nanoparticles Formed Using Thiol-Acrylate Conjugate Addition Reactions

VAIBHAV S. KHIRE,¹ APRIL M. KLOXIN,¹ CHARLES L. COUCH,¹ KRISTI S. ANSETH,^{1,2}
CHRISTOPHER N. BOWMAN^{1,3}

¹Department of Chemical and Biological Engineering, University of Colorado, Boulder, Colorado 80309-0424

²Howard Hughes Medical Institute, University of Colorado, Boulder, Colorado 80309-0424

³Department of Restorative Dentistry, University of Colorado Health Sciences Center, Denver, Colorado 80045-0508

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ABSTRACT: This study investigates the formation of linear polymer grafts using thiol-acrylate conjugate addition reactions on nanoparticle surfaces. Silica nanoparticles were first modified with an amine functionality, followed by the attachment of a photocleavable acrylate. Dithiol-diacrylate films were attached to the particles through the surface acrylate groups at various stoichiometric ratios of thiol to acrylate by conducting amine-catalyzed conjugate addition polymerizations. The particles were then exposed to UV light to release the grafted polymer by photocleavage. The cleaved, grafted polymers were analyzed using infrared spectroscopy and gel permeation chromatography and compared to polymers formed in the bulk, which remained unattached to the particles. The measured number and weight average molecular weights were similar for both polymer types within experimental error and increased from 2000 to 5000 g/mol and 4000 to 10,000 g/mol, respectively, as the ratio of limiting to excess functionality increased from 0.8 to 1. Both number and weight average molecular weights followed the trend of step growth polymers with the highest molecular weight achieved for stoichiometric monomeric mixtures. Surface coverage of the nanoparticles was estimated using the molecular weight and thermogravimetric data and was found to be uniform (~ 0.15 chains/nm²) irrespective of the stoichiometry of the reacting monomers. © 2008 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 46: 6896–6906, 2008

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INTRODUCTION

Various polymerization mechanisms such as free radical polymerization, living/controlled radical

polymerizations and ionic polymerizations, are routinely used for modifying surfaces with thin polymer films to alter a variety of surface properties.^{1–5} Grafted polymer film properties including thickness, chemistry, chain density, chain length, uniformity, and the nature of the attachment determine the final effectiveness of a coating. These properties are controlled by tuning the polymerization mechanism, molecular weight and polydispersity of the grafted polymer, careful

Additional Supporting Information may be found in the online version of this article.

Correspondence to: C. N. Bowman (E-mail: christopher.bowman@colorado.edu)

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selection of monomer chemistry and functionality, and the polymerization conditions.

Surface-attached polymers are generally investigated with techniques such as scanning probe microscopy and various spectroscopic and optical techniques including ellipsometry and X-ray spectroscopy.^{5,6} Although information such as film thickness, composition and arrangement of the polymer chains is readily obtained using these methods, polymer-specific properties such as molecular weight, molecular weight distribution and polydispersity cannot be readily obtained using these techniques. As a result, separation of the attached polymers from the surface is desired to facilitate further characterization of polymerizations at surfaces. Typically, chemical cleavage of the polymer chains or the destruction of the substrates is carried out for this purpose.^{7–9} One popular technique consists of growing polymer brushes on silica nanoparticle surfaces and dissolving the particles in hydrofluoric acid (HF), thereby separating the polymer chains from the surfaces.^{7,10–13} Another popular technique is the incorporation of a chemically cleavable group, such as an ester group, in the anchoring molecule or the initiation of polymer chains from the surface, followed by its cleavage using acid or base hydrolysis.^{14–16}

In this work, polymer films grafted using thiol-acrylate conjugate addition reactions were investigated. Traditionally, thiol-ene step growth polymerizations are conducted using a radical-mediated, photoinitiated mechanism. When exposed to UV light in the presence of a UV photoinitiator, a radical is formed on a thiol molecule, which propagates through the ene carbon-carbon double bond to form a carbon-sulfur bond and a carbon radical. The carbon radical chain transfers to another thiol molecule, thereby forming a thiol-ene product and regenerating the thiyl radical.^{17–23} When the polymerization is carried out on a thiol-terminated surface, it results in the participation of surface thiols in the reaction, and a thiol-ene film is covalently coupled to the surface.^{24–28}

The primary difference between the thiol-acrylate conjugate addition reaction and the traditional thiol-ene photopolymerization reaction is that the addition reaction proceeds via a base catalyst, without any exposure to light. Recently, we reported the investigation of thiol-acrylate conjugate addition reactions for modifying surfaces with ultrathin polymer films with control over the thickness in the range of 0–7 nm by altering the

stoichiometry of the reacting thiol and acrylate monomers to control the polymer properties.²⁹ The thiol-acrylate conjugate addition reactions are particularly attractive since they lead to rapid polymerization in the presence of only catalytic amounts of base.^{30,31} In addition, this method also incorporates the use of acrylate functionalities in a step growth polymerization reaction, which increases the range of available monomers, since a wide variety of acrylates are commercially available. Also, as no photoinitiation is required, thick films are easily formed. Since the reactions take place under mild conditions, such as no exposure to light or heat, they are well-suited for applications involving biological entities such as cells, proteins, or nucleic acids.

In this work, the properties of the thiol-acrylate films were further investigated by photochemically cleaving the films from the substrate following grafting, enabling the polymers to be characterized with gel permeation chromatography (GPC) and infrared spectroscopy (IR). Unfortunately, the chemical cleavage and isolation techniques described earlier are inapplicable in this case as the acrylate groups in the grafted polymer also contain ester groups, which would be cleaved during the separation of the polymer from the surface resulting in the degradation of the grafted polymer. Hence, a photocleavable acrylate (PDA), based on a nitrobenzyl ether moiety, was attached to the amine groups on the surface and was used as an anchoring group for the thiol-acrylate polymers and was subsequently used for removal of the grafted polymers from the surface.³² To increase the amount of surface-attached polymer, the polymerization was performed on nanoparticle surfaces, which possess a high surface area to volume ratio. After polymerization, the polymers were cleaved by exposing the modified particles to UV light and separating the particles from the cleaved polymer. The schematic of the entire process is shown in Figure 1. The particles were characterized using TGA and IR, whereas the polymer films were investigated using GPC and IR.

EXPERIMENTAL

Materials

1,6, hexanedithiol (HDT) and triethylamine were purchased from Aldrich. 1,6 hexanediol diacrylate (HDDA) was obtained from Polysciences. The

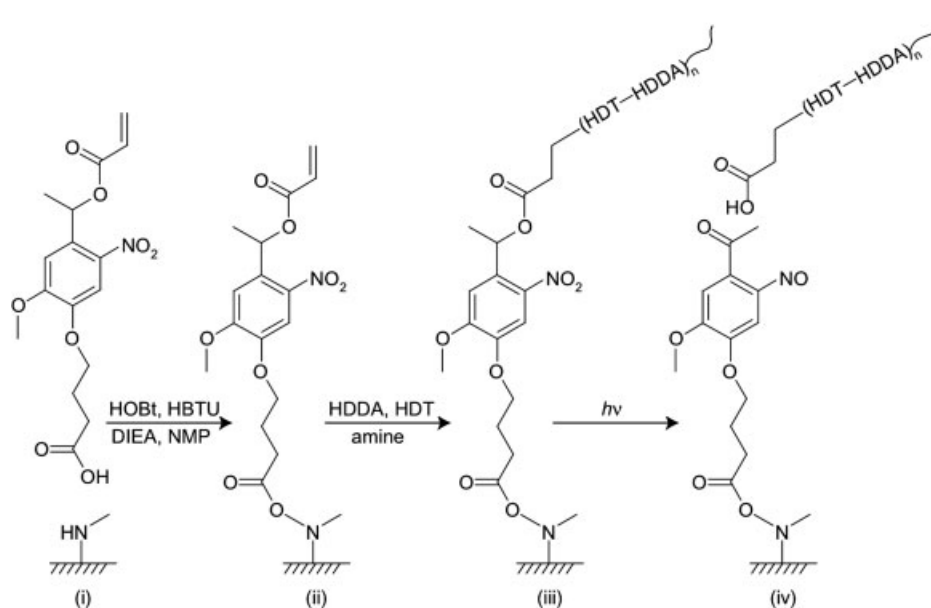


Figure 1. Schematic of the formation and cleavage of thiol-acrylate films on surfaces. (a) An amine-functionalized surface was functionalized with a photodegradable acrylate in the presence of coupling agent HBTU, HOBt, and DIEA in an NMP solution (see details in experimental section). (b) The acrylate-terminated surface was reacted with a thiol-acrylate mixture using a conjugate addition reaction between 1,6-hexanediol diacrylate and 1,6-hexanedithiol with triethylamine as catalyst. (c) Grafted polymer was cleaved from the surface by exposing to UV light (15 mW/cm², 365 nm) for 10 h. (d) Cleaved surface and the separated polymer.

silane, *N*-methyl aminopropyl trimethoxysilane, was purchased from Gelest. All solvents were obtained from Fisher. Silica nanoparticles (OX-50, primary particle size 40 nm) were donated by Degussa. All materials were used as received unless otherwise specified. Diisopropylethylamine (DIEA), 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU), and 1-hydroxybenzotriazole (HOBt) were purchased from Anaspec (San Jose, CA). *N*-Methylpyrrolidone (NMP) was purchased from Applied Biosystems (Foster City, CA).

Immobilization of Aminosilane on Silica Nanoparticles

The silica nanoparticles (40 nm, 1 g) were dried at 150 °C for 3 h under high vacuum to remove moisture and then dispersed in dried toluene for 1 h by vigorous agitation. The mixture was brought to reflux and *N*-methyl aminopropyl trimethoxysilane (1 g, dissolved in dry toluene) was added to the mixture. The system was refluxed for 6 h, and the particles were separated from the toluene by centrifugation. The particles were washed with toluene (5×) and methylene chloride (2×) to

remove the adsorbed, unreacted silane and dried under vacuum at room temperature for 24 h.

Immobilization of Photodegradable Acrylate on the Silica Nanoparticles

The amine-functionalized particles (1 g) were dispersed for 30 min in *N*-methyl pyrrolidone (NMP) by vigorous mixing. A mixture of 2-(1H-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium hexafluorophosphate (HBTU) (1 g, 2.5 mol:mol PDA), hydroxybenzotriazole (HOBt) (0.4 g, 2.5 mol:mol PDA) and *N,N*-diisopropylethylamine (DIEA, 0.8 g, 4 mol:mol PDA) was dissolved in 2 mL NMP and stirred for 5 min. The photolabile nitrobenzyl ether moiety, ethyl 4-(4-(1-hydroxyethyl)-2-methoxy-5-nitrophenoxy)butanoic acid, whose synthesis is based on a procedure described elsewhere,³² was acrylated to form the photodegradable acrylate (PDA). PDA (0.4 g) was dissolved in 1 mL NMP and mixed with the above mixture. The activated PDA mixture was then added to the particles, purged with argon, and allowed to react for 72 h. The particles were separated from NMP by repeated centrifugation and washed with methylene chloride (5×). The particles turn red in

color and were stored in vacuum at room temperature for 24 h. The particles are stored in the dark until further use.

Polymerization of Thiol-acrylate Films

HDDA and HDT monomers were mixed in various stoichiometric ratios and amine-PDA functionalized silica nanoparticles (5 wt %) were added to the monomer solution. The mixture was stirred vigorously for 2–3 h until uniform dispersion of the particles in the liquid monomer was achieved. Triethylamine (2.5 mol % of the total thiol-acrylate functionality) was added to the mixture and the mixture was stirred overnight. The polymer was then dissolved in methylene chloride and the unattached polymer in the solution was separated from the particles by repeated centrifugation. Normally, 5–10 washes were sufficient to remove the entire unattached polymer, which was confirmed by the absence of any peaks related to the polymer in the IR spectrum of the concentrated methylene chloride obtained from the last wash. The particles were dried under vacuum and stored in the dark until further use.

Cleavage of Polymer Films

Polymer-modified particles (1 g) were dispersed in methylene chloride (50 g) by vigorous mixing for 2 h and exposed to UV light (365 nm, 15 mW/cm²) for 10 h. The particles were separated from the cleaved polymer by repeated centrifugation (5–10 times) and dried under vacuum at room temperature.

Characterization of the Polymer and the Nanoparticles

A Nicolet 750 Magna FTIR spectrometer with KBr beam splitter and an MCT detector was used to record the spectra of nanoparticles at all stages as well as spectra of the unattached and cleaved polymers. Polymer samples were sandwiched between salt crystals, whereas silica nanoparticles were deposited on salt crystals from a methylene chloride solution.

A Waters GPC with chloroform as a solvent was used to characterize the molecular weight and molecular weight distribution of the cleaved and unattached polymers. Toluene was added as an internal standard.

A Perkin–Elmer TGA was used for thermogravimetric analysis. The particles were stored under

vacuum at 100 °C for 15 h before TGA analysis to remove adsorbed moisture. The particles were then heated in the TGA from 50 to 800 °C at a rate of 10 °C/min, held at 800 °C for 20 min and cooled to room temperature at a rate of 20 °C/min. The percentage weight loss throughout the process was recorded.

The centrifuge used for separating particles was manufactured by the Thermo Electron Corp. (IEC Centra CL2). All washes were 10 min at the speed of 3000 rpm.

RESULTS AND DISCUSSION

Cleavage of polymer chains from a substrate is an effective method to characterize surface-bound polymer films and to measure various properties that are not measurable when the film remains attached to the surface. Usually, a chemically cleavable moiety, which does not affect the polymerization reaction, is introduced in the anchoring group and is cleaved after polymerization for separating the polymer chain from the surface. This cleavage enables the investigation of a polymer film either formed as a result of surface-initiated polymerization, or as a result of attachment of a preformed polymer chain to the surface. The typical method for cleaving polymer films from a surface involves the hydrolysis of an ester linkage in the polymer chains. This reaction is, however, unsuitable for a thiol-acrylate polymer chain, since the acrylate monomer itself has a cleavable ester. To circumvent this problem a photocleavage mechanism was applied. An acrylate molecule with a photocleavable group was used as the surface anchoring molecule for the polymer grafts. Nanoparticles were utilized to increase the surface available for polymerization and hence the amount of cleaved polymer.

It has been previously shown that polymerizations in bulk and at a surface proceed differently and the corresponding polymer chain length distribution in the bulk and on the surface is often significantly different. Several studies have been conducted to investigate these differences by separating the polymer films from the surface.^{1,5,8,9,12,33} Most of these studies have been focused on radical polymerizations, specifically the living/controlled radical polymerizations. In this study, polymer films formed using thiol-acrylate step polymerizations, which proceed by addition of a thiol across an acrylate carbon–carbon double bond in the presence of an amine catalyst,

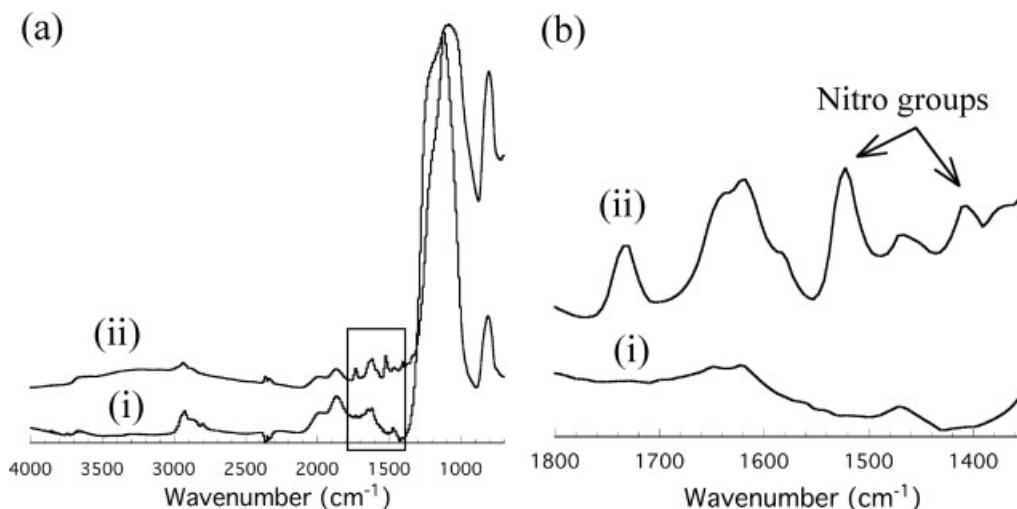


Figure 2. IR spectra of amine-functionalized silica particles before (i) and after (ii) modification with PDA molecules. (a) The entire spectrum of (i) and (ii) and (b) expansion of the selected region shown in (a). Amine-functionalized particles were formed by the deposition of *n*-methyl aminopropyltrimethoxysilane on SiO₂ particles. They were reacted with PDA in the presence of HOBt, HBTU, and DIEA in NMP. A small amount of silica nanoparticles was dispersed in methylene chloride and deposited on a NaCl crystal and the solvent was evaporated to obtain the IR spectra.

are investigated. In step growth polymerizations, the stoichiometry of the reacting species plays a critical role in determining polymer properties.^{24–26,34} As a result, various stoichiometric ratios of thiol and acrylate functionalities, with separate cases in which both acrylate and thiols were in excess, are investigated here. Also, most previously investigated systems are ‘grafting from’ systems, where a surface-bound initiator initiates the polymerization of a monomer in the bulk. In contrast, the thiol-acrylate step growth polymerization occurs as a combination of ‘grafting from’ and ‘grafting to’ approaches, as polymerizations start from the surface and polymer/oligomer chains formed in the bulk diffuse and attach to the surface by the coupling reaction.²⁹ This feature makes the study of thiol-acrylate films at surfaces a unique one.

The nanoparticle surface modification was first studied using IR for each of the steps. Figure 2(a) shows the IR spectrum of the nanoparticles modified with the amine silane and the PDA. An expansion of a small region of the spectrum is shown in Figure 2(b). The peaks at 1475 and ~3000 cm⁻¹, corresponding to secondary amine and alkane chains respectively, from the amine silane, are seen in Figure 2(a). The reaction of the PDA to the surface is confirmed by various peaks as seen in curve (ii). The small ester peak at 1732 cm⁻¹ and the peaks from the nitro group at 1525

and 1400 cm⁻¹ in the PDA molecule are seen in Figure 2(b), both of which are part of the PDA molecule.

The particle modification process was also studied using thermogravimetric analysis. The amine functionalized particles show ~3% weight loss, whereas the weight loss increased to around 4.3% after the deposition of PDA. (See Supp. Info.). Using the known molecular weight of both the amine silane and PDA, the amount of each layer present per unit gram of particles was estimated as shown in Table 1. Further, using the value of surface area per g of particles (50 m²/g), the surface coverage (chains/nm²) of the particles was calculated. A near-complete dispersion of nanoparticles in reaction mixture was assumed due to vigorous stirring and the use of low-viscosity monomers, and hence, an average value of the surface area per volume, as provided by the manufacturer, was used for all calculations. It is seen that around 3.4 amine molecules are present per nm² of the particles. This surface density, although not indicative of a completely packed monolayer, is comparable to the typical value of 5 molecules/nm² for a densely packed monolayer.^{25,35} The PDA coverage is much less, and is around 0.2 molecules per nm². Thus, only about 6% of the amine molecules are functionalized with a PDA molecule. This limitation is due to the large size of the PDA molecule, which sterically

Table 1. Final Residual Weight Percent after TGA Analysis, Amount of Grafted Polymer per Gram of Particles and Surface Coverage of Attached Molecules at Various Stages of Nanoparticle Surface Modification

Modified SiO ₂ Particles	Final Residual Weight after TGA Measurement (%)	Amount of Attached Material per Gram of Nanoparticles ($\mu\text{mol/g}$)	Surface Coverage (chains/nm ²)
Particles + Amine	96.4 (0.6)	282.5 (47.1)	3.40 (0.57)
Particles + PDA	95.7 (0.1)	20.0 (1.9)	0.24 (0.02)
0.8:1 ^a	91.2 (0.2)	22.1 (4.8)	0.17 (0.01)
0.9:1 ^a	90.8 (0.5)	16.9 (1.4)	0.15 (0.01)
1:1 ^a	88.8 (0.5)	20.0 (3.1)	0.15 (0.01)
1:0.9 ^a	91.3 (0.2)	17.4 (0.9)	0.12 (0.02)
1:0.8 ^a	91.7 (0.1)	19.3 (2)	0.14 (0.01)

The particles were consecutively modified with amine SAM, PDA, and thiol-acrylate polymer grafts formed from varying stoichiometric ratios of thiol to acrylate in bulk. The amount of material attached per gram of particles and surface coverage were calculated only for the outermost graft layer, i.e. for amine SAM, PDA, and polymer grafts, respectively, without taking into account the contribution of the previously attached layers. Numbers in parentheses indicate the standard deviations.

^a Numbers indicate the ratio of thiol to acrylate functionalities present in the initial monomer solution.

limits the amount of PDA that can be present on the surface.

The PDA-modified particles were grafted with thiol-acrylate brushes by polymerizing in the presence of varying stoichiometric ratios of thiol and acrylate. PDA-modified particle (5 wt %) suspensions were mixed with thiol-acrylate monomers and allowed to mix completely by vigorous stirring. Aggregation of nanoparticles in resin solutions is generally a significant concern. However, it is overcome by vigorous mixing of particles with the monomers, by using nonviscous monomers, as well as by selecting chemically compatible particle surfaces and monomer functionalities. The weight of the monomer solution used was 20 times more than the weight of the particles to minimize particle-particle interactions and to achieve maximum surface coverage. The triethylamine catalyst was added after completely dispersing the particles in the monomer, and the reaction mixture was stirred overnight. The particle-polymer mixture was then dissolved in methylene chloride and repeatedly centrifuged with fresh solvent to separate the polymer-modified particles from the unattached polymer. The repeated washing from the particles was continued until no further polymer was extracted from them. The particles were dried in vacuum and the unattached polymer, dissolved in methylene chloride, was concentrated by evaporating the excess solvent.

The polymer-modified particles were dispersed again in methylene chloride and exposed to UV light for 10 h to cleave the polymer from the surface of the particles. The cleavage reaction mecha-

nism for nitrobenzyl ether moieties has been well studied in the literature for solution and surface-based applications.^{32,36} The result of the cleavage process is the separation of the polymer from the PDA molecule at the acrylate group, and the conversion of the nitro group on the benzene ring in the PDA molecule into the nitroso group. The particles were separated from the cleaved polymer by repeated washing in methylene chloride.

The particles, as well as the grafted and bulk polymer, were characterized using IR at all stages. The particles showed an increase in the alkane chain peak upon modification with polymer chains, which decreased upon the cleavage of the grafted films. The nitro group corresponding to the PDA disappeared completely upon cleavage, demonstrating near-complete cleavage of the attached polymer chains. A small amount of polymer is attached through the unreacted amine groups on the particle surface, by the slow acrylate addition across amine and remains attached to the particle surface. It was assumed in the further analysis that the amount of polymer attached to amine groups on the surface is negligible. To verify this, control experiments were done by carrying out the polymerization on amine-functionalized particles without depositing PDA. The resultant polymer attachment was found to be very small as observed by the comparison of IR data with the particles modified with polymer using the PDA linkage. The IR spectra of the unattached and the grafted, cleaved polymer are similar, showing peaks corresponding to thiol-acrylate chains. (See Supp. Info.).

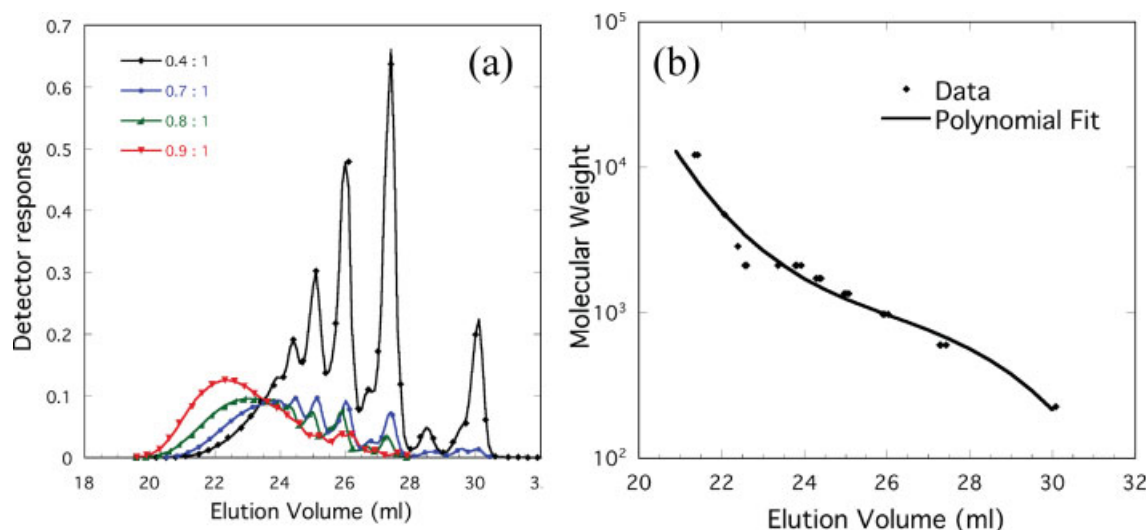


Figure 3. (a) Raw GPC data for four sets of polymer standards used for the generation of the standard calibration curve. HDT and HDDA monomers were polymerized in four different ratios of thiol:acrylate groups (0.4:1, 0.7:1, 0.8:1, and 0.9:1) and the GPC data is shown for each of the polymer samples. Molecular weights corresponding to the individual peaks seen in each curve were theoretically calculated and the elution volume for the peak was matched with the molecular weight. (b) Calibration curve used for calculating molecular weights. The theoretical molecular weights corresponding to individual peaks in (a) were calculated and plotted against the elution volume corresponding to the peak. The data was fit with a third order polynomial to generate the calibration curve.

Molecular Weight Determination of Polymer Samples

Both the unattached and the cleaved polymer samples for various stoichiometric ratios were analyzed using GPC. The thiol-acrylate reactions investigated here proceed via a step growth mechanism and hence the molecular weight is directly dependent on the ratio in which the two monomer species are mixed prior to the reaction. To study the effect of stoichiometry on the molecular weights of the polymers, five different stoichiometric ratios were evaluated. These included the ratio of thiol to acrylate monomers where the functionalities of thiol to acrylate were 0.8:1, 0.9:1, 1:1, 1:0.9, and 1:0.8.

The accurate determination of molecular weights using GPC requires a precise calibration curve. Although several commercial standards are available, differences in monomer chemistries, molecular geometries, and optical properties of the polymer result in severe distortions in the measured molecular weights using GPC. A calibration curve using the standards obtained from the same type of polymer species as those under investigation is hence desirable. To accomplish

this objective, thiol-acrylate polymers using the same monomers in various stoichiometric ratios (thiol:acrylate = 0.4:1, 0.7:1, 0.8:1, and 0.9:1) without any added particles were synthesized. Since one of the monomer species is present in excess in these polymer samples, the final polymer sample contains high concentrations of polymer molecules with “odd molecules” (i.e., the polymer molecules containing an odd number of monomeric repeat units), where both ends of the polymer molecules are capped with the excess reagent and there is an equal amount of either reacting species in the center. Assuming equal reactivity of all reacting functional groups throughout the polymerization reaction, the molecular weight and the relative concentrations of each of these individual molecular species are predictable theoretically.^{37–39} This calculation was done for the aforementioned monomer samples and a standard calibration curve for the polymer species under investigation was generated.

The raw data from the GPC (detector intensity versus elution volume) for the molecular weight species used as standards is shown in Figure 3(a). Each of the individual peaks in Figure 3(a)

corresponds to polymer species containing an odd number of monomeric repeat units. The peak corresponding to 30 mL elution volume is a result of monomer species (diacrylate) as was found by analyzing the unreacted monomer species using the GPC, which eluted at the same elution volume. This is followed by trimers, pentamers, and molecules corresponding to odd number of monomers of dithiol-diacrylate molecules for earlier elution volumes. The molecular weight of each of the individual peaks was theoretically calculated and plotted against the elution volume for that particular peak from the GPC data. The molecular weights versus the elution volumes of the peaks for each of the four curves were recorded and a calibration curve, shown in Figure 3(b), was generated. The ability of the curve to generate molecular weights above the highest data point was verified by predicting the molecular weights of the standard curves in Figure 3(a) beyond the last data point and comparing it with the expected molecular weights. This curve was used for all subsequent molecular weight analyses.

Both sets of polymer samples, the unattached polymer formed during the surface modification reaction, as well as the polymer originally attached to the surface of the nanoparticles were analyzed using GPC. The number and weight average molecular weights for all the polymer samples (unattached and cleaved polymers of various stoichiometric ratios) are shown in Figure 4. The theoretically predicted molecular weights of the different polymer species for the specific molar ratios used were calculated and are also shown. As the molecular weight is sensitive to the stoichiometric ratios of the monomer species, the actual concentration of the reacting functional groups was determined using NMR and used for the calculation of the stoichiometric ratios. It is seen that the molecular weight increases as the stoichiometric ratio approaches unity. Also, for all the cases except for the case when the stoichiometric ratio is one, the cleaved and the unattached polymer samples have similar molecular weights within experimental errors.

The similarity in the molecular weights of the two parts is a distinct outcome resulting from the reaction rate being slow as well as the step growth nature of the thiol-acrylate polymerization. Since the reaction proceeds via a step growth mechanism, molecular weight buildup is very slow and most molecules have facile access to the surface throughout the polymerization. Even at

very high conversions ($\sim 90\%$), the average chain length is relatively small (~ 20 repeat units), and hence the overall viscosity of the polymer is very low. This attribute results in high mobility of chains in the bulk and their uniform attachment to the surface. The slow reaction rate further increases the probability of chain attachment at the surface. This process, however, is hindered when the stoichiometric ratio is close to one, when the viscosity is high, and the attached polymer molecular weight is significantly lower than the unattached polymer. The deviations of the measured molecular weight from the theoretical predictions increase as the molecular weights increase because of diffusional limitations.

Table 1 shows the final weight loss during TGA experiments of polymer-modified particles for particles modified with all stoichiometric ratios. The highest weight loss is for the nanoparticles with the highest molecular weight films attached. Combining the weight loss from the TGA with the molecular weights obtained using GPC; the surface coverage of the polymer films per gram of particles is estimated. Assuming that the dispersion is complete (i.e., with minimal aggregates formed), the surface area of the particles is calculated, and the surface coverage per gram of particles is converted to surface coverage per unit area. This result is shown in Table 1. It is seen that for all stoichiometric ratios, the number of polymer chains attached to the surface per unit area is the same within error. This outcome is expected since the chain attachment is not affected by molecular weights until very high molecular weight chains are formed during the polymerization, which happens only at very high conversions in stoichiometric step growth polymerizations. Since the polymerization time is very long (~ 10 h) for the catalyst concentrations used, there is sufficient time for the reaction of polymer chains with the surface. The rate of surface reaction is typically slower than the bulk reaction because of inaccessibility of molecules or steric factors, which is countered here by using a slow bulk polymerization rate and by utilizing a step growth reaction.

This work thus shows the applicability of thiol-acrylate polymerizations for attaching polymer films on surfaces with control over the molecular weight. It should be noted that the molecular weights of the unattached and the cleaved polymers were similar for most of the cases, especially when the value of the molecular weights is not very high. Experimental studies comparing the

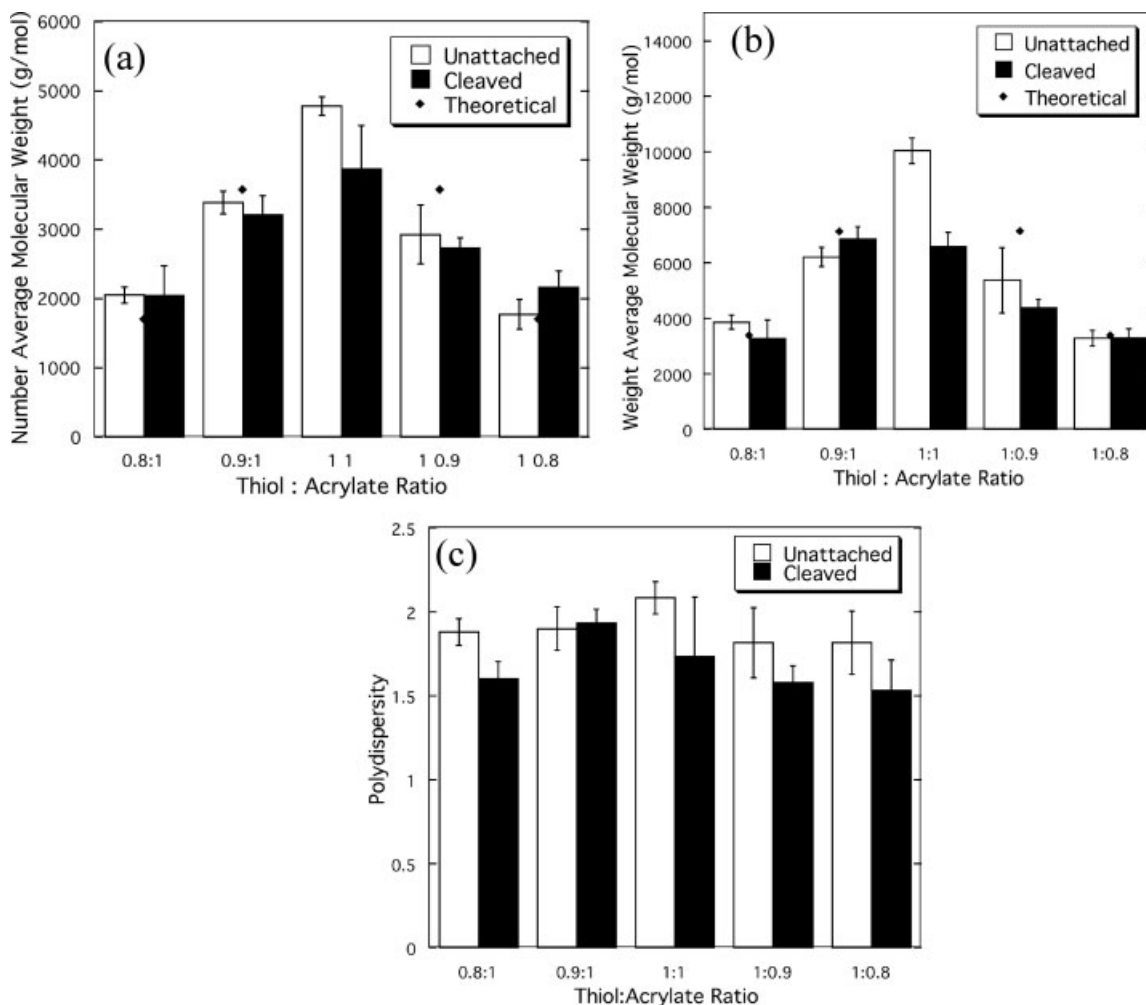


Figure 4. Theoretical and measured molecular weights of unattached and cleaved polymers formed by polymerizing HDDA and HDT in various ratios of thiol to acrylate functionalities. (a) Number average molecular weight, (b) Weight average molecular weight and (c) Polydispersity of the unattached and cleaved polymers for various thiol:acrylate ratios. HDDA and HDT were polymerized in the presence of PDA-modified particles where the ratio of thiol:acrylate was 0.8:1, 0.9:1, 1:1, 1:0.9, and 1:0.8 in bulk. The unattached polymer during polymerization and the attached polymer after cleavage from the particle surface were analyzed using GPC and the calibration curve from Figure 3(b) was used to determine the molecular weights.

molecular weights of grafted and unattached polymers show that the polymer molecular weight in each of these phases is strongly dependent on the polymerization mechanism. For example, it was shown that in the case of free radical polymerizations, termination plays an important role in determining the grafted polymer molecular weight, and at high molecular weights, a two-dimensional “gel effect” results in the increase in the molecular weight of the grafted polymer.^{7,9} On the other hand, in living radical polymerizations such as ATRP,^{11,12,40} as well as in RAFT

polymerizations with a living characteristic,⁴¹ the living nature is maintained in both the bulk and surface phases, and as a result the grafted and free polymers have similar molecular weights. In our work, since the molecular weights are typically much lower than those observed using either free or living radical polymerizations, there is sufficient mobility and time for the bulk chains to attach to the surface throughout the polymerization. In addition, since the conjugate addition reactions are slow, the surface reactive groups contribute minimally to altering the reactive

stoichiometry near the surface, which is similar to the stoichiometry in the bulk. This results in similar molecular weights of the grafted and unattached polymer weights. This outcome is in contrast with the step growth thiol-ene photopolymerization systems, which are extremely rapid, where the surface thiols result in decreasing the grafted polymer molecular weight compared to the bulk polymer.⁴² Also, since the polymerization proceeds via a catalyzed conjugate addition reaction, the concentration of the catalyst molecule, which is not deactivated or consumed similar to an initiator molecule, remains predominantly constant throughout the reaction, and hence near-complete conversion is achieved in most cases.

The use of a PDA for the cleavage of polymer chains is another interesting application, as this procedure of exposing to light for separation of polymer is more straightforward as compared to chemical cleavage or dissolution of the silica particles in an HF solution. This technique is useful for the investigation of the formation and cleavage of polymer grafts formed via a variety of grafting polymerization reactions since it does not possess the limitations associated with chemical cleavage. Finally, the use of distinct peaks in step growth polymers for generating standards for GPC can be potentially used for accurate molecular weight determination of other polymer species and provides a novel method for generating calibration curves for polymers formed via a step growth mechanism.

CONCLUSIONS

The modification and cleavage of linear polymer formed using base-catalyzed thiol-acrylate polymerizations was investigated. A PDA was used for anchoring thiol-acrylate chains and subsequently cleaved to separate the chains from the surface. The distinct molecular weight species present in a polymer sample formed using step growth polymerization were utilized to form a calibration curve specific to the thiol-acrylate polymer samples for GPC and used for molecular weight determination. The molecular weight of the attached and unattached parts of the polymer found to be similar except for the case when the monomer species were present in stoichiometric ratios, which resulted in high molecular weights. TGA analysis of the modified nanoparticles shows that the surface coverage of various polymer species is uniform across all the investigated ratios.

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