Polymerizable Living Free Radical Initiators as a Platform To Synthesize Functional Networks

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Photopolymerizations of multifunctional monomers afford spatial and temporal control of cross-linked network formation whereas living radical polymerizations provide a means to synthesize well-defined architectures from monovinyl monomers. By combination of these technologies in a two-stage polymerization process, a novel method is developed to synthesize functional polymer networks, and supporting results are provided for preparing controlled polymer grafts *within* photo-cross-linked networks. To demonstrate the concept of internal grafting, an alkoxyamine living radical initiator (for nitroxide-mediated polymerization, NMP) and a tertiary bromide initiator (for atom-transfer radical polymerization, ATRP) were functionalized with a methacrylate group and either was copolymerized with mono- and divinyl methacrylic monomers during the initial network formation step. Activation of the living radical initiators within styrene-swollen networks resulted in controlled molecular weight polystyrene grafts covalently bound to the photo-cross-linked methacrylic networks. To demonstrate the applicability of this technology for synthesizing functional networks, hydrogels with nitroxide groups were first photopolymerized, and different concentrations of acetoacetoxy, (i.e., ketoester) functionality were subsequently grafted within the loosely cross-linked networks. When the grafted networks were swollen in aqueous solutions containing Fe^{3+}, the cations coordinated with the grafted ketoester moieties. In general, this robust technology could be applied to a wide array of monomers and functional groups to control the chemical, physical, and mechanical properties of the final grafted network for application in sensors, catalysis, separations, and combinatorial chemistry platforms.

Introduction

Cross-linked polymers formed from multifunctional monomers have applicability in current and emerging technologies such as MEMS and microfabricated devices,[1−3] combinatorial chemistry platforms,[4−7] delivery vehicles for drug or genetic therapies,[8,9] tissue engineering scaffolds,[8,10,11] advanced materials in microelectronics and biomaterials,[8,9,12] and a number of other areas. Photoinitiated polymerizations of multifunctional monomers offer a number of advantages in the synthesis of these cross-linked materials. For example, masking and shuttering the initiating light provide spatial and temporal control of the initiation step, respectively, and result in control of the overall polymerization process. However, traditional radical chain copolymerization of monovinyl and divinyl monomers does not facilitate well-controlled macromolecular architecture of the resulting networks.

In contrast, controlled radical initiators have been implemented for synthesis of low-polydispersity linear polymers, controlled di- or multiblock copolymers, and/or graft and brush copolymers, and more complex architectures such as star or dendridic polymers from monovinyl monomers.[13,14] These polymerizations exploit persistent radical species that reversibly deactivate propagating radicals.[15] The general mechanism of this type of polymerization includes equilibrium between active and dormant states of a propagating radical that favors the dormant species. Monomer units are

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added to growing chains during short periods of activity. The low instantaneous concentration of active radical chains facilitates well-defined polymer growth. Three categories of LRPs exist: (1) stable free radical polymerizations, such as nitroxide-mediated polymerization (NMP);[13] (2) metal-catalyzed atom-transfer radical polymerization (ATRP);[16,17] and (3) degenerative transfer processes such as reversible addition−fragmentation chain transfer (RAFT).[18] In each case, propagating radicals are mediated by a less reactive species, and the resulting dormant species can be reactivated readily.

From the perspective of designing advanced polymer networks with controlled chemical functionality, LRP approaches to synthesize cross-linked polymers and modify polymer networks are highly desirable. These systems have not been explored previously because covalent attachment of specific macromolecular functionality and architecture throughout a photopolymerized, three-dimensional network is very difficult or impossible with traditional chain (photo)-polymerizations of cross-linking monomers or living radical polymerizations, independently.

To date, controlled radical polymerization methods have been implemented in modifying polymeric and inorganic surfaces with well-defined linear polymers to impart specific chemical and nanoscale physical properties.[19−21] Pyun and Matyjaszewski[22] reviewed investigations of controlled radical polymerization methods for synthesizing hybrid materials (i.e., polymeric modification of inorganic materials). Sellergren and co-workers demonstrated living polymerization of multiple cross-linked layers from iniferter groups attached to the surface of porous silica. Subsequent layers were templated with D- or L-phenylanaline anilide, and enantioselectivity was shown in each layer.[23,24] However, in this case, the living radical initiator was used only to provide covalent attachment of the cross-linked network to the previous (polymeric or inorganic) surface due to the reinitiatable character of the iniferter: in fact, the architecture of the cross-linked network was not enhanced significantly by the living radical initiator. Matsuda and co-workers[25] have grown low-polydispersity linear chains from various monomers at polymeric surfaces functionalized with dithiocarbamate-containing (photoiniferter), attached by irradiation techniques. Finally, macroporous polymer monoliths have been fabricated by 2,2,6,6-tetramethyl-1-piperidyloxy (TEMPO) mediated polymerization. Subsequently, pore surfaces, containing TEMPO-terminated polymer chains, were functionalized with 2-hydroxyethyl methacrylate or vinylbenzyl chloride to demonstrate the potential for grafting specific chemistries to enhance separation or reactivity characteristics of the monoliths.[7,26]

Copolymerization of a controlled radical initiator containing a vinyl group with other cross-linking monomers is another method for covalently attaching initiator molecules within a polymer network. In fact, by this method, the initiator is incorporated as pendant functionality throughout the substrate bulk, and surface modification is possible due to a fraction of the total amount of initiator species that is accessible at the surface. For example, in our previous work, monomer-photoiniferter molecules were incorporated in cross-linked networks, and the networks were further modified by swelling or coating with additional monomer and UV exposure.[27−29] However, the UV absorbance of the iniferter attenuates the initiating light source; therefore, film thickness and/or iniferter concentration are limited in these systems. Furthermore, the instability of the iniferter during photopolymerization of the original network reduces the potential for creating controlled architectures during subsequent modification steps. Although the *photo*activity of the iniferter for living radical polymerizations of selected monomers is highly desirable, iniferter-mediated polymerizations impart only limited molecular weight and architectural control to polymerizations of many types of monomers.[30] Similarly, utilizing the same ATRP and NMP initiators containing (meth)acrylate groups, which are described in this contribution, other authors have patterned highly cross-linked films and subsequently grown linear polymer chains from the living radical initiators present at the film surface. The controlled polymerization of the grafted chains enabled the authors to tune nanoscale feature dimensions and vary the surface chemistry of the film.[31]

Primarily, living radical polymerization strategies have been developed for *surface* modification. However, when compared to surface-functionalized films, loosely cross-linked three-dimensional networks, containing well-defined chemical functionality distributed throughout the bulk, would provide a significant increase in the total number of active moieties for signal amplification in chemical and biological sensors, catalysis, and combinatorial chemistry platforms and many other applications. In this work, methacrylic NMP and ATRP initiators were conceptualized, synthesized, and copolymerized with commercially available mono- and divinyl monomers to facilitate modification of cross-linked networks throughout the bulk. In this manner, advantages of photoinitiating a copolymerization of mono- and divinyl monomers (i.e., spatial and temporal control) are retained

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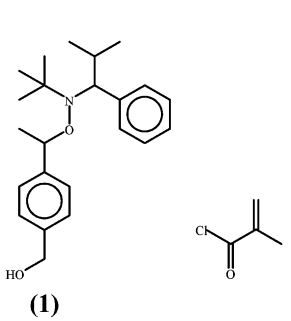
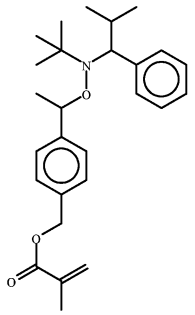
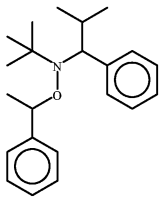
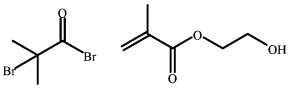
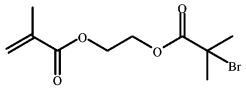
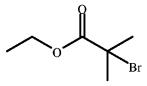
Table 1. Chemical Structures of Living Radical Initiators and Starting Materials

	Starting materials	Methacrylate-functionalized LRIs	Analogous non-methacrylic LRIs
NMP	 (1)	 (2)	 (4)
ATRP		 (3)	 (5)

while subsequent grafting reactions by the covalently tethered NMP and ATRP initiators allows introduction of well-controlled macromolecular architecture and/or chemistry within the network. This contribution provides methodology and supporting results for (1) synthesis of methacrylic controlled radical initiators, (2) photopolymerization of comonomer formulations to form networks containing pendant living radical initiators, and (3) subsequent modification of the photo-cross-linked methacrylic networks with polystyrene grafts of controlled molecular weight. Finally, to illustrate the utility of this technology for creating functional materials, a hydrogel network was grafted internally with a metal-coordinating monomer via NMP. The resulting network could be implemented for a number of applications including hydrogel or other solvent-swellable catalyst supports,[32−34] gels for scavenging specific organic or inorganic species,[35] or precursors for combinatorial chemistry platforms,[6,7] among many others.

Experimental Section

Materials. 2-Methoxyethyl methacrylate (MEMA) was obtained from Polysciences. All other reagents were purchased from Aldrich Chemical Co. Styrene and *N*,*N*-dimethylacrylamide (DMAA) were purified by vacuum distillation prior to use. All other chemicals were used as received without further purification.

Instrumentation. Gel permeation chromatography (GPC) was performed on a Waters chromatograph connected to a Waters 410 differential refractometer or a Waters 996 photodiode array detector. Samples for GPC were prepared at ca. 20 mg/mL in chloroform and filtered with a 0.2-μm Teflon syringe filter prior to injection. The GPC eluted at 1 mL/min. ^{1}H NMR spectra were recorded with a Bruker AM 250 (250 MHz) spectrometer and a Varian Inova-500 (500 MHz) spectrometer. UV−Vis measurements were made with a HP 8453 UV−Vis spectrometer. Near-infrared monitoring (FT-NIR) of substrate polymerizations was carried out on a Nicolet Instruments Magna-IR 750 Series II. Disappearance of the methacrylic double-bond stretch at ca. 6165 cm^{-1} was captured by real-time spectroscopy of the monomer mixture contained in a 1-mm thick glass mold exposed to 365-nm radiation from a Novacure spot curing system (EFOS, Mississauga, Ontario) through a horizontal transmission accessory.

Synthesis of the Methacrylic Alkoxyamine Initiator (2). Table 1 contains the structures corresponding to the methacrylic alkoxyamine initiator (**2**) and the nonmethacrylic analogue (**4**). Synthesis of a hydroxymethyl-containing alkoxyamine initiator (**1**) has been reported previously.[45] **1** (0.6 g, 1.7 mmol) and dry triethylamine (1.1 equiv) were dissolved in 5 mL of anhydrous THF in a 25-mL round-bottom flask with a magnetic stir bar. The solution was cooled to 0 °C, and methacryloyl chloride (1.5 equiv) was added dropwise. The reaction proceeded at 0 °C for 2 h, and then the flask was stirred continuously at 25 °C overnight. The final reaction solution containing methacrylic alkoxyamine product was diluted in methylene chloride and washed with 10% (w/v) $NaOH_{(aq)}$ and 10% (w/v) $HCl_{(aq)}$ solutions. The product (**2**) was purified by flash chromatography with a 19:1 mixture of hexanes and ethyl acetate as the eluent. A white solid (>90% yield) was formed after evaporation of the chromatography eluent. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55−7.15 (m, 9H), 6.19 (m, 1H), 5.61 (m, 1H), 5.24 and 5.21 (s, 2H total, unequal shifts due to diastereomerism), 4.95 (q, 1H, both diastereomers), 3.45 and 3.33 (d, J = 10.5 and 11.1 Hz, 1H total, unequal shifts due to diastereomerism), 2.35 and 1.40 (m, 1H total, unequal shifts due to diastereomerism), 2.00 (m, 3H), 1.65 and 1.57 (d, J = 6.8 and 6.6 Hz, 3H total, unequal shifts due to diastereomerism), 1.33, 0.94, 0.57, and 0.25 (d, J = 6.4 and 6.4 Hz, 6H total, unequal shifts due to diastereomerism), and 1.07 and 0.82 (s, 9H total, unequal shifts due to diastereomerism).

Synthesis of the Methacrylic Tertiary Bromide (ATRP) Initiator (3). Table 1 contains the structures corresponding to the methacrylic tertiary bromide initiator (**3**) and the commercially available nonmethacrylic analogue (**5**). 2-Hydroxyethyl methacrylate (HEMA, 4.2 g, 33 mmol) and dry triethylamine (1.0 equiv) were added to 60 mL of anhydrous THF in a round-bottom flask. 2-Bromoisobutyryl bromide (BIB) (1.2 equiv) was mixed with 20 mL of anhydrous THF. BIB solution was added dropwise at 0 °C. Upon complete addition, the reaction was mixture warmed to 25 °C and stirred overnight. The final reaction solution containing methacrylic tertiary bromide product was diluted in methylene

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chloride and washed with 10% (w/v) NaOH(aq) and 10% (w/v) HCl(aq) solutions. The final product (**3**) was isolated as a yellow oil by vacuum distillation (with >90% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.15 (m, 1H), 5.61 (m,1H), 4.43 (m, 4H), 1.96 (m, 3H), 1.95 (m, 6H).

Synthesis of the Degradable Substrate Network. Methacrylic anhydride (MA, 2.0% (mol/mol)), **2** or **3** (2.0−4.0%), and the photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone (DMPA, 0.1%), were mixed with 2-methoxyethyl methacrylate (MEMA, 93.9−95.9%). The monomer mixture was cast into glass molds (ca. 2 cm × 4 cm × 1 mm) and exposed to 365 nm radiation (20−50 mW/cm^2, 30 min). Unreacted monomers and initiator were removed from the polymerized substrates with THF in a Soxhlet extractor (>18 h).

NMP Grafting Procedure. Typically, 200 mg of ca. 1 mm^3 sections of substrate containing 2−4% (mol/mol) **2** (0.025−0.05 mmol of 2), **4** (0.15−0.95 mmol), styrene (ca. 20 mmol), and DMF (ca. 10−15% (v/v)) were purged with argon and sealed in a 10 mL ampule (or a 25 mL Schlenk flask) containing a small stir bar. Additional "free" alkoxyamine initiator (**4**) was added to the reaction solution so the grafted chain length could be controlled without changing the concentration of monomer in the reaction solution, the concentration of tethered initiator (**2**), or the conversion of grafted monomer. Vials were stored overnight at −4 °C to allow swelling of the substrate in the grafting solution. Finally, the vials were placed in a 125 °C oil bath for 18 h. The polymerization was quenched by cooling and exposure to atmospheric oxygen. Polymer not bound to the network and unreacted components of the graft solution were removed from the modified networks with THF in a Soxhlet extractor (>18 h).

ATRP Grafting Procedure. Typically, 200 mg of ca. 1 mm^3 sections of substrate containing ca. 4% (mol/ mol) **3** (0.05 mmol of 3), ethyl 2-bromoisobutyrate (**5**, 0.15−0.95 mmol, depending on desired degree of polymerization), copper(I) bromide (CuBr, 0.5 equiv with respect to total initiator), elemental copper (Cu^0, ca. 2 mg), *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA, 0.5 equiv with respect to total initiator), styrene (ca. 20 mmol), and DMF (ca. 10−15% (v/v)) were purged with argon and sealed in a 10 mL ampule (or a 25 mL Schlenk flask) containing a small stir bar. Vials were stored overnight at −4 °C to allow swelling of the substrate in the grafting solution. Finally, the vials were placed in a 65 °C oil bath for 18 h. The polymerization was quenched by cooling and exposure to atmospheric oxygen. Polymer not bound to the network and unreacted components of the graft solution were removed from the modified networks with a 1:4 mixture of water and THF in a Soxhlet extractor (>18 h).

Degradation by Transesterification Procedure. Grafted networks were swollen in 50 mL of solution containing THF (85% (v/v)), methanol (10%), and sulfuric acid (5%) at 65 °C. The gel cross-links degraded within 2 days. Degradation products were isolated by evaporating most of the THF and methanol followed by addition of water to precipitate the polymer. Polymeric degradation products (i.e., poly(methyl methacrylate) kinetic chains from the photopolymerized network and polystyrene grafts) were isolated from the aqueous solution by filtration (and reprecipitation into ethanol, in some cases), before characterization with GPC and ^{1}H NMR. A kinetic chain is the polymethacrylate backbone macromolecule that forms from propagation of a radical through methacrylate groups in mono- or multivinyl monomers.

Synthesis of the Metal-Coordinating Hydrogel Networks. To synthesize a metal-coordinating network, a monomer formulation containing DMAA (97.4% (mol/mol)), poly(ethylene glycol) (M_w ~ 200) dimethacrylate (PEG200DMA, 1.3%), **2** (1.2%), ca. 10% (v/v) DMF, and ca. 0.05% (w/w) DMPA was exposed to ca. 50 mW/cm^2 of 365 nm collimated UV light for 5 min in a 200 μm thick glass mold. Two hundred milligrams of the resulting network (0.023 mmol of **2**) was swollen in a solution containing DMAA (15.3 mmol), 2-acetoacetoxyethyl methacrylate (AEMA, 4.37 mmol), **4** (0.735 mmol), and ca. 15% (v/v) DMF. Oxygen was removed from the swollen networks by three freeze−pump−thaw cycles. Linear grafts of poly(DMAA-*co*-AEMA) were initiated from the pendant alkoxyamine initiator (**2**), and soluble linear polymers were initiated due to the presence of **4**. Unbound polymer and unreacted monomer were extracted from the grafted network with a water/THF mixture (1:3) in a Soxhlet extractor for 18 h. Finally, to demonstrate coordination of metals with the grafted ketoester functionality, the network was swollen in a 0.01 M aqueous solution of $Fe(NO_3)_3$.

Various iron-coordinating networks were synthesized in the same manner as described for the network shown in Figure 4. Different concentrations of **2** were used in the initial network photopolymerization step, and different concentrations of AEMA in the graft monomer formulation were used to affect the density of grafted ketoester moieties in the final material. Each of the four networks described in Table 2 was swollen in 0.1 M $Fe(NO_3)_3$ for 24 h. Next, each of the networks was placed in deionized water, which was changed twice daily for 4 days. Aliquots of each water wash were mixed with equal amounts of 0.1 M KSCN and the absorbance at 471 nm was measured with a UV−Vis spectrometer to determine the level of iron present in the wash solution. After 2 days, the iron content in the wash water was less than 10^{-5} M and undetectable with UV−Vis. Each of the iron-containing networks was dried in a vacuum oven for 2 days. The iron content was measured with thermal gravimetric analysis (TA Instruments Hi-Res TGA 2950) under air with a ramp rate of 10 °C/min to 600 °C. The reported iron content was calculated from the weight fraction of Fe_2O_3 remaining at the end of the TGA experiment. Carbon, hydrogen, and nitrogen were quantified with elemental analysis (Desert Analytics, Tucson, AZ).

Results and Discussion

Synthesis of Living Radical Initiator-Containing Substrates. The methacrylic alkoxyamine initiator (**2**) and a methacrylic tertiary bromide initiator (**3**) are shown in Table 1. Additionally, the nonpolymerizable analogues of both initiators are shown (**4** and **5**, respectively).

Photopolymerization of a substrate containing intact, pendant living radical initiators is a critical aspect of the technology described in this contribution. The molar absorptivity at 365 nm was measured by UV−VIS spectroscopy, and the stability of the living radical initiators was explored by ^{1}H NMR analysis of the initiators after exposure to reaction conditions similar to the photopolymerization step. First, the molar extinction coefficient at 365 nm was measured with UV−Vis spectroscopy for the alkoxyamine initiator by measuring the absorbance of **1** in acetone at 365 nm for four samples ranging in concentration from 0.01 to 0.2 M (0.5−9 wt %). The molar extinction coefficient measured for **1**, which is ca. 1 L/mol·cm, is 2 orders of magnitude lower than the corresponding value for DMPA (ca. 150 L/mol·cm at 365 nm). Thus, absorption of UV light by a nitroxide initiator is much less likely than absorption by the photoinitiator. Furthermore, **2** and **3** were exposed to high doses of UV light (>50 mW/cm^2; >15 min), and ^{1}H NMR revealed no differences in the chemical structures, which suggests that absorption of UV light does not cleave

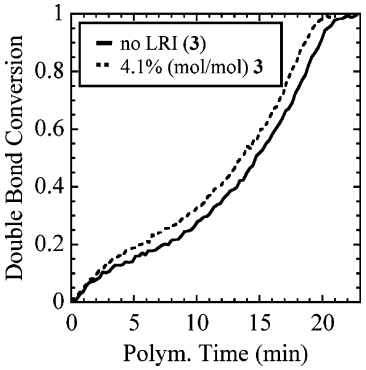


Figure 1. Photopolymerization behavior of comonomer formulations containing methacrylic tertiary bromide initiator. Double-bond conversion was monitored as a function of 365 nm UV exposure time (ca. 5−10 mW/cm^2). The comonomer formulation was either 0 (solid line) or 4.1% (dashed line) methacrylic tertiary bromide initiator (**3**); 2.0% methacrylic anhydride (for cross-linking); 0.1% photoinitiator; and 93.8 or 97.9% (mol/mol) 2-methoxyethyl methacrylate (dashed or solid line, respectively). Double-bond conversion is nearly quantitative for both samples after 20 min of exposure. The addition of the methacrylic living radical initiator does not produce a significant effect on the photopolymerization behavior of the loosely cross-linked network.

the initiator or cause any molecular rearrangement. Finally, **4** and **5** were exposed to UV light in the presence of DMPA. Once again, changes in the chemical structures, from reaction with the radicals generated from the photoinitiator, were not evident by ^{1}H NMR. Therefore, in addition to being stable during exposure to typical photoinitiation conditions (i.e., 365 nm light and radicals), the living radical initiators do not attenuate the photoinitiating light to any appreciable degree; thick samples with relatively high concentrations of living radical initiators can be photopolymerized readily and the density of living radical initiators within the network is easy to control.

Investigation of the polymerization behavior of the comonomer mixture used to synthesize the substrate provides further evidence that the living radical initiators do not impact the photopolymerization step. Figure 1 contains a plot of the conversion of methacrylic double bonds, captured by FT-NIR spectroscopy, as a function of exposure time during the photopolymerization of comonomer mixtures containing or excluding **3**. Although the rate of polymerization of the sample containing 4.1% (mol/mol) of **3** is slightly higher at low conversion, both samples reach complete double-bond conversion within 20 min. In summary, methacrylic living radical initiators are incorporated within photopolymerized networks without significantly changing the photopolymerization step or affecting the structure and stability of the living radical initiator.

Grafting from Pendant Initiators within Photopolymerized Networks. A relatively simple monomer system was chosen to demonstrate the principle of grafting from pendant living radical initiators within a photo-cross-linked network. Figure 2 is a schematic of the experiment to demonstrate controlled grafting capability within a photopolymerized network containing pendant living radical initiators (**2** or **3**). After photopolymerization of a comonomer formulation containing MEMA, MA, **2** or **3**, and the photoinitiator, DMPA, the network was swollen in a mixture of styrene monomer, DMF, and additional nonmethacrylic initiator (**4** or **5**). A control network, which did not contain pendant initiator functionality (i.e., **2** was not included in the photopolymerizable monomer formulation) was swollen in the grafting monomer solution as well. The grafting reaction was carried out at 125 °C for 18 h. Unattached polymer (created from **4** or **5** present in the graft monomer formulation) and unreacted monomer were extracted from the grafted and control networks. Finally, the covalently grafted network, the control network, an ungrafted network, and an ungrafted control network were degraded by transesterification with methanol. Specifically, the anhydride cross-links and ester linkages (between the methoxyethyl groups or alkoxyamine initiators and the photopolymer kinetic chains) were degraded by sulfuric acid-catalyzed methanol addition. Complete transesterification of the cross-links and pendant ester bonds resulted in low molecular weight compounds and linear polymer chains. Specifically, linear poly(methyl methacrylate) (PMMA) was formed from the loosely cross-linked poly(2-methoxyethyl methacrylate) (PMEMA) kinetic chains of the original network, and linear polystyrene (PS) from the graft polymerization was cleaved from the network backbone.

The polymeric degradation products were isolated and analyzed by GPC. Figure 3a contains GPC traces for the degradation products of control networks, which did not contain any alkoxyamine initiator, **2**, in their backbone kinetic chains. In one case (dotted line), the network was degraded without performing any further steps. In the other case (solid line), before degradation, the control network was subjected to the grafting procedure, which involved swelling it in a monomer solution containing **4** and polymerization of the solution by maintaining the swollen network at 125 °C for 18 h. Alternatively, Figure 3b shows GPC results for degradation products from ungrafted (dotted) and grafted (solid) networks which contain the pendant alkoxyamine initiator, **2**. Each plot also contains a curve corresponding to ca. 13 kDa PS formed from polymerization of the reaction solution (i.e., styrene, DMF, and **4**) in the absence of the network (dashed line). The degradation product curves in Figure 3a are very similar, which suggests that styrene does not graft from the network backbone without **2**. Furthermore, the curve corresponding to the degradation products from the ungrafted network containing **2** (Figure 3b, dotted) is the same as the curves in Figure 3a (corresponding to the control networks). In contrast, the GPC trace of the degradation products for the grafted network in Figure 3b is unique. First, for the grafted network (solid), a peak appears at ca. 28 min, which is approximately the same elution time as the solution polymerized PS (dashed curve). Prep GPC and NMR confirm that this peak is linear PS that was cleaved from the kinetic chains of the photo-cross-linked network. These cleaved chains are slightly lower in molecular weight than the reaction solution PS because the concentration of initiator was slightly higher in the network samples containing **2**. Finally, the distinct shoulder peak (at shorter elution time—larger hydrodynamic volume—than the kinetic chains) results from partially degraded kinetic chains from the grafted network. In other words, transesterification of the anhydride cross-links has occurred, but cleavage of all ester linkages along the backbone is not complete. Hence, PS grafted to

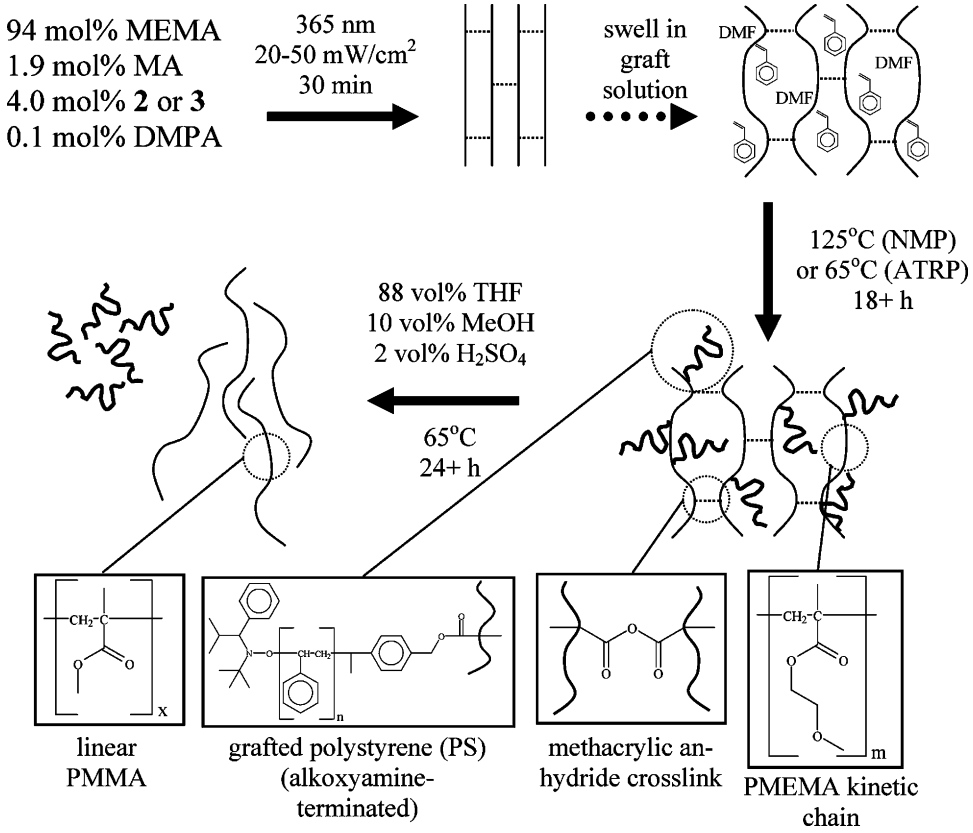


Figure 2. Schematic of methodology to demonstrate grafting *within* networks. The proof-of-concept experiment to demonstrate grafting from living radical initiators within photo-cross-linked networks is accomplished in three steps. First, a formulation containing a methacrylic living radical initiator (**2** or **3**) and other mono- and divinyl monomers is photopolymerized to form a loosely cross-linked network. Next, the network is swollen in monomer solution and the living radical initiators are activated to produce linear polymers grown from the network backbone. Finally, to validate the grafting methodology, the network is degraded to linear graft chains and linear kinetic chains that are analyzed with GPC.

PMMA or PMEMA chains are observed at higher molecular weight.

Figures 3c and 3d, which are the control and ATRP-grafted networks, respectively, are analogous to 3a and 3b. However, shorter grafted chains of PS (ca. 7000 Da) were created by addition of extra "free" ATRP initiator (**5**). Furthermore, this less hydrophobic system allowed complete degradation of the networks. Therefore, in Figure 3d, the ratio of the low-polydispersity peak at 29 min (corresponding to PS cleaved from kinetic chains) to the broad peak between 22 and 28 min (corresponding to the kinetic chains from the photopolymerized networks) is much larger than the same ratio of peak areas observed in Figure 3b. For the same reason, no shoulder peak at shorter elution time appears in Figure 3d.

Application of Methodology To Prepare Chemically Functional Networks. β-Dicarbonyl moieties act as strong bidentate ligands that coordinate with many different metals and metal ions.[36] In fact, a number of investigations on complexation of metals with monomers containing β-dicarbonyl functionality have been reported.[32−34,36] These inorganic−organic hybrid materials (e.g., polymer-supported metal complexes) find utility in a number of applications including catalysis,[32−34] separations,[35] wastewater treatment, and water-based coatings.[37] Primarily, metal-coordinated polymers are synthesized to create insoluble heterogeneous catalysis resins. However, recent interest in the self-assembly

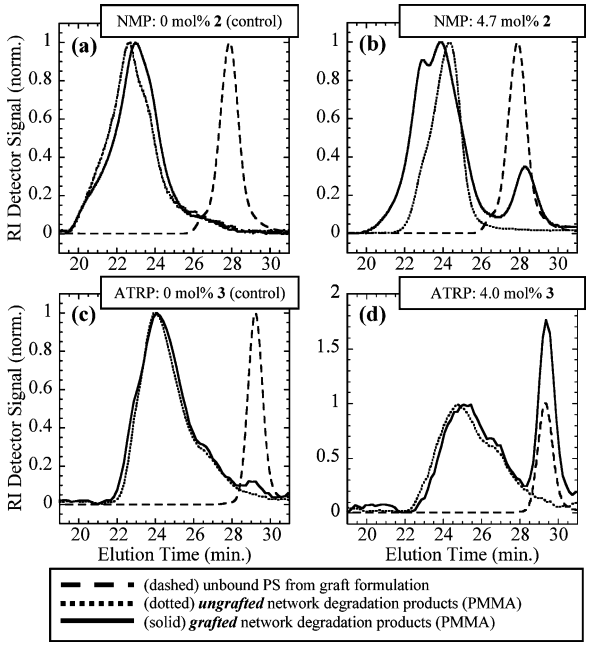


Figure 3. GPC analysis of degradation products from grafted and control networks. (a) The lines are GPC traces of the degradation products of "grafted" (solid line) and ungrafted (dotted line) *control* networks. (b) GPC results for grafted (solid) and ungrafted (dotted) alkoxyamine-containing networks are shown. Each plot also contains a curve corresponding to ca. 13 kDa PS formed from polymerization of the reaction solution with neither type of network present (dashed line). (c) and (d) The bottom figures represent analogous results for control and ATRP-grafted networks, respectively. In this case, the linear PS trace (dashed) corresponds to ca. 7000 Da.

(36) Krasia, T.; Soula, R.; Borner, H. G.; Schlaad, H. *Chem. Commun.* **2003**, 538−539.

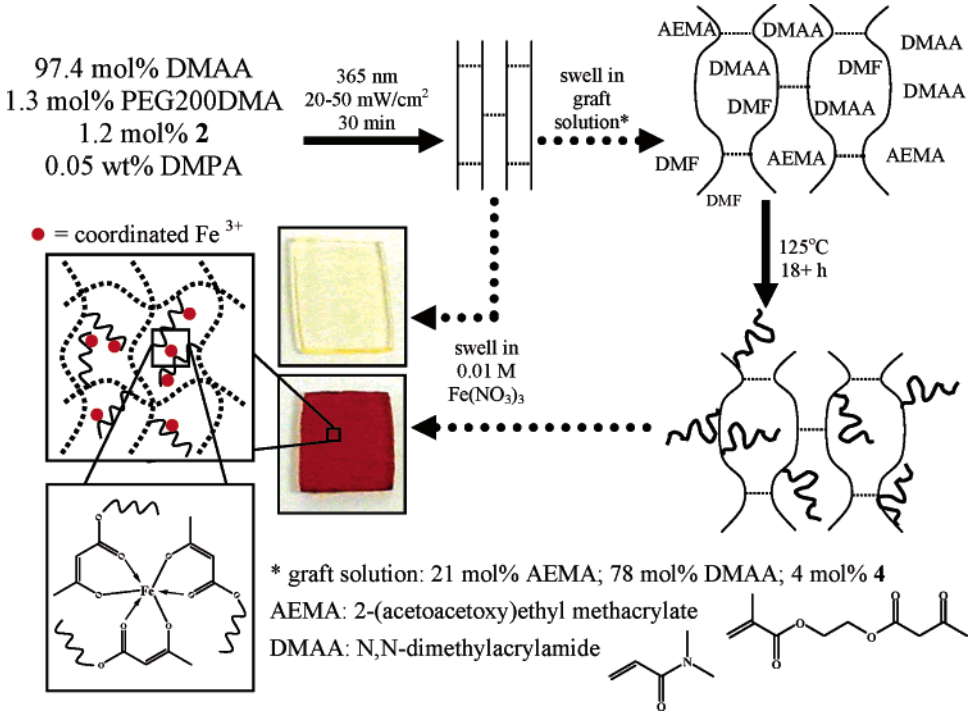
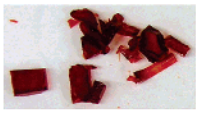
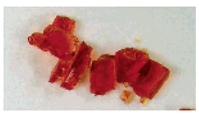
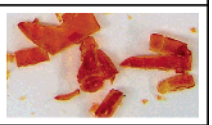


Figure 4. Demonstration of metal-coordinating networks. A cross-linked poly(dimethylacrylamide) (PDMAA) network was synthesized via photopolymerization and internally grafted with 2-(acetoacetoxy)ethyl methacrylate (i.e., a ketoester-containing monomer) via nitroxide-mediated polymerization. The preswollen hydrogel was placed in aqueous 0.01 M $Fe(NO_3)_3$ for less than 2 min. The resulting red network (bottom) is due to coordination of the iron to ketoester moieties grafted within the network. The light-colored network (top) is a PDMAA hydrogel control (i.e., without grafted metal-coordinating functionality) that has been swollen in the same 0.01 M $Fe(NO_3)_3$ solution for more than 24 h without eliciting any color change.

Table 2. Comparison of Iron-Coordinating Hydrogels[a]

	Sample Composition			C/H/N Analysis		Iron Analysis		
	conc. of 2 (mol%)	graft length (M_n)	AEMA (mol% in grafts)	calculated (wt%)*	Elem. Analysis (wt%)	max. (wt%)**	TGA (wt%)	Picture
(A)	3.0	7500	58	C: 58.2 H: 7.8 N: 6.6	C: 59.06 H: 8.66 N: 7.50	4.3	4.1	
(B)	1.0	8000	59	C: 59.0 H: 8.3 N: 8.9	C: 58.97 H: 8.37 N: 9.31	2.9	2.9	
(C)	3.0	5600	30	C: 59.2 H: 8.4 N: 9.6	C: 59.88 H: 9.08 N: 11.19	2.5	2.2	
(D)	1.0	5200	32	C: 59.7 H: 8.7 N: 11.1	C: 59.47 H: 8.39 N: 12.15	1.5	1.3	

[a] (*) The expected mass fractions of C, H, and N are computed from the network and graft compositions. (**) The maximum iron content corresponds to the total mass fraction of iron if each Fe^{3+} binds to three AEMA units.

of block copolymers has prompted synthesis of controlled architecture polymers that contain metal-coordinating pendant functionality.[36] Finally, water-based coatings have been designed from linear polymers containing β-dicarbonyl groups because they react with primary amines (i.e., diamines) to create a cross-linked film.[35,37]

The method described in this contribution (i.e., living radical grafting within photopolymerized networks) is ideally suited for preparation of polymer-supported metal catalysts and separation media. Figure 4 contains the approach and results to demonstrate this application. First, a water-swellable network (i.e., hydrogel) was created by photopolymerization of *N*,*N*-dimethylacrylamide and **2** cross-linked with poly(ethyleneglycol) dimethacrylate. Then, comonomer solutions, containing ca. 20% (mol/mol) 2-(acetoacetoxy)-

(37) Esser, R. J.; Devona, J. E.; Setzke, D. E.; Wagemans, L. *Prog. Org. Coat.* 1999, *36*, 45−52.

ethyl methacrylate and ca. 80% *N*,*N*-dimethylacrylamide were grafted via NMP. The functional gel pictured on the bottom in Figure 4 is a metal-coordinating hydrogel after swelling in a 0.01 M $Fe(NO_3)_3$ solution for approximately 2 min. The red color indicates the complexation of Fe^{3+} with the grafted acetoacetoxy (i.e., ketoester) moieties. A picture of a control network, which contained no ketoester functionality, is also shown in Figure 4. The control gel has a yellow tint due to swelling in the light yellow $Fe(NO_3)_3$ solution.

Table 2 contains the results of a comparison between four networks containing 1 or 3 mol % of **2** and internally grafted with random copolymers containing ca. 30 or 60% AEMA. Pictures of the swollen, metal-coordinated hydrogels (after removing unbound metal) indicate that the red color intensity, which corresponds to iron complexation with three ketoester groups, differs for each hydrogel network. NMR analysis of unbound chains grown during the graft copolymerization provides information about molecular weight and composition of the grafted chains. This information, in conjunction with the compositions of the photopolymerized networks, translates into specific mass fractions of the atomic species C, H, and N in the grafted network. Results from elemental analysis of the dried networks confirm that the mass fractions of C, H, and N calculated from the NMR results and network compositions are reasonably accurate. Discrepancies between the composition information and the elemental analysis results can be attributed to the uncertainty in the composition information from the FTIR and NMR measurements required to calculate the conversion of the photopolymerized network and grafted chains, respectively.

The maximum iron content was computed by assuming that every bound iron cation coordinates with three ketoester groups. Thermal gravimetric analysis (TGA) on the dried, iron-coordinated networks provides a quantitative experimental measure of the iron mass fraction. The amounts of iron in the dried networks correspond very well to the maximum amounts of iron possible in each gel if every Fe^{3+} coordinates with three ketoester groups. In fact, each network contains 84% or more of the maximum expected iron content. This result indicates that the efficiency of iron binding is very high in the grafted networks. Interestingly, the iron binding occurs at a higher efficiency in the A and B networks, which were grafted with longer copolymer chains (ca. 8000 Da) and a higher concentration of ketoester groups (ca. 60% of the repeat units). Finally, the qualitative trend in red color intensity matches the quantitative TGA results.

The example shown in Figure 4 and the comparison of networks in Table 2 are simply demonstrations. In fact, one can imagine incorporating any of a large number of coordinated metals or metal ions within a network optimized for specific chemical and mechanical properties, including swelling and mesh size. Furthermore, facile control of the concentration and architecture of the grafted chains, as well as the concentration of the desired functional graft monomer, is afforded by the living radical polymerization process. The metal-coordinating network highlights a number of desirable features of this technology: (1) the network is photopolymerized, which facilitates spatial and temporal control but does not affect the living radical initiator; and (2) functional monomers are tethered to the network via a linear chain to afford maximum mobility and activity while still covalently attached to the highly swollen gel.

Perhaps most importantly, this technology is not limited to metal-coordinating grafts and/or networks formed with specific chemistry. Nitroxide-mediated polymerization and ATRP have been implemented in the synthesis of complex macromolecules with low polydispersity from a large variety of different monomers as well as well-defined block and graft architecture.[13,14] Furthermore, sequential activation of nitroxide and ATRP polymerizations within the same linear polymer system has been demonstrated. Therefore, by incorporating *both* **2** and **3** within a photo-cross-linked network, two distinct grafts could be prepared in a straightforward manner. The ability to control both graft density and length may be very important for networks where grafted chain interactions provide specific function or properties.[38] Additionally, exchange of nitroxide initiator-terminated chain ends with functional TEMPO derivatives offers a method for tethering specific functionality within a network that could be very useful for a multitude of applications in sensors, functional gels, and other advanced cross-linked materials.[39−42] Finally, further development of initiating systems for water-soluble monomers[43,44] facilitates more robust application of this methodology to various biomaterials and biosensors.

Conclusions

A methacrylic alkoxyamine initiator and a methacrylic tertiary bromide initiator were synthesized and the living radical initiators were stable during photopolymerization of comonomer formulations containing them and other mono- and divinyl monomers. After incorporation into loosely cross-linked networks and upon subsequent activation of the living radical initiators, linear polymer chains were covalently grafted throughout the network. This concept was demonstrated by grafting polystyrene within a network cross-linked with methacrylic anhydride, degradation of the grafted network to soluble, linear polymers (i.e., polystyrene chains and poly(methyl methacrylate) kinetic chains), and analysis of the degradation products by gel permeation chromatography. Linear grafts within the network exhibited low polydispersity and well-controlled molecular weight (based on the ratio of monomer to living radical initiator). Finally, a network with different chemical and physical properties was synthesized and grafted in the same manner. Specifically,

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linear chains containing ketoester functionality were grafted within a hydrophilic network. Swelling the network in an aqueous $Fe(NO_3)_3$ solution resulted in a color change of the network as Fe^{3+} coordinated with the grafted ketoester moieties. Although the metal-coordinating network illustrates an important application for this technology, combination of the advantages of photopolymerizations for synthesizing an array of networks and the wide variety of monomers and techniques developed for NMP and ATRP provides a robust technology for producing highly functional cross-linked polymeric materials for numerous advanced materials applications.

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