

Synthesis of a Novel Methacrylic Monomer Iniferter and Its Application in Surface Photografting on Crosslinked Polymer Substrates

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ABSTRACT: (Methacryloyl ethylenedioxy carbonyl) benzyl *N,N*-diethyldithiocarbamate (HEMA-E-In) was synthesized and used as a monomer iniferter to develop a novel, photopatternable grafting technology. This molecule functions as both a methacrylic monomer and a photoiniferter (photoinitiator–transfer agent–terminator). The structure of HEMA-E-In was characterized by ¹H NMR, Fourier transform infrared, and ultraviolet–visible spectroscopies. In the presence of the monomer iniferter, methyl methacrylate was polymerized by exposure to 365-nm ultraviolet radiation, confirming the initiation capability of HEMA-E-In. After the copolymerization of HEMA-E-In into a methacrylate-based polymer, attenuated total reflectance Fourier transform infrared spectra revealed that the photoiniferter functionality was present at the surface of this polymeric substrate. Photografting of poly(ethylene glycol) monomethacrylate monomer from the surface caused a significant change in the hydrophobicity of the surface as demonstrated by contact angle measurements. The novel monomer photoiniferter HEMA-E-In initiates the polymerization of bulk monomer and provides a reactive functionality that facilitates further initiation and polymer modification by the polymerization of different monomers. © 2002 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 40: 1885–1891, 2002

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INTRODUCTION

The modification of solid surfaces by grafted polymers is a versatile and effective technique for tailoring surface chemistry and properties. Commonly, surface grafting is performed with monomers different from the substrate to render a specific, desired surface property.¹ For example,

grafting can be used to produce cell-adhesive or anticoagulant layers for biomaterials. Alternatively, covalent bonding between adjacent layers of different polymers is critical for the fabrication of three-dimensional polymeric microdevices and microfluidic assemblies.

Current trends in polymeric surface modification include the preparation of dense grafts, specifically polymer brushes,^{2,3} block copolymer grafts,⁴ the design of complex surface-grafted macromolecular architectures such as hyperbranched polymers,^{5–8} and micropatterning of surface-grafted layers.^{9–12} Self-assembled mono-

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layers (SAMs)¹³ and living radical polymerization techniques^{2,3,9,10,13} have also been demonstrated for preparing highly controlled polymer surface chemistries. Initiator molecules are anchored to the substrate surface with SAM technology,¹⁴ whereas living radical polymerization enables the fabrication of low-polydispersity block copolymer grafts.^{15–17} The use of living radical polymerizations for surface grafting represents a significant advance because the surface physicochemical properties are dependent not only on the chemical composition but also on the secondary polymer structure.

Ultraviolet (UV)-induced polymerization^{1,18} is a desirable method for the surface modification of polymers for a number of reasons. First, photochemically produced triplet states of carbonyl compounds facilitate hydrogen abstraction, so graft polymerization is initiated without prior modification of a surface with conventional or living radical initiators. Second, a high concentration of active species is produced locally at the interface between the substrate polymer and the monomer solution. Third, the procedure is relatively simple, energy-efficient, and cost-effective. Fourth, UV-induced polymerization is well suited for integration with other technologies, such as microcontact printing and photolithography, to produce desired surface chemistry changes in well-defined two-dimensional regions on a surface.^{11–13}

Most current photografting methods do not allow strict control of graft density, length, and chemistry. However, photoiniferter-mediated living radical polymerization has enabled the synthesis of grafted block copolymers with controlled chain lengths.¹¹ The desired polymerization control results from the unique mechanism of the photoiniferter-mediated polymerization. That is, the end group on the polymer graft has the ability to reinitiate readily upon absorption of an additional photon.¹⁹ Molecules containing diethyldithiocarbamate groups are the most common compounds that serve as photoiniferters. Photolysis of these species forms a carbon radical and a diethyldithiocarbamyl (DTC) radical; the carbon radical readily initiates polymerization of the monomer, and the DTC radical primarily participates in cross-termination with propagating radicals. After cross-termination, the diethyldithiocarbamate end group can redissociate (upon absorption of an additional photon) and, therefore, increase the length of the polymer graft by inser-

tion of monomer units before a subsequent cross-termination event.^{20,21}

A number of authors have reported results related to the control of copolymer structures synthesized via photoiniferter-mediated polymerizations,^{4,7,9,11,12,21–23} and sequential addition of monomer units is used routinely for block copolymer production. Otsu et al.²⁴ synthesized vinylbenzyl diethyldithiocarbamate (VBDC) and used this compound to make copolymers of various chemistries and architectures. Nakayama and Matsuda⁴ developed 2-(ethylxanthate)ethyl methacrylate as a photoiniferter and also used VBDC to make photoactive copolymers. These photoactive copolymers were coated onto a polystyrene (PET) surface so that block graft copolymers and surface graft copolymers were prepared. Finally, Qiu and coworkers synthesized polymerizable photoiniferter macromonomers^{25–27} and demonstrated photoinitiated atom transfer radical polymerization of methyl methacrylate (MMA).²⁸

This contribution introduces a methacrylic photoiniferter molecule that is integral to a novel photopatternable grafting technology used for facile modification of polymer surfaces and networks. The presence of a polymerizable methacrylate group enables tethering of the photoiniferter functionality to the network backbone. Therefore, the initiator functionality exists both on the surface and throughout the bulk of the polymer network, which makes possible both surface grafting and internal grafting. Simply changing the polymer substrate composition controls the concentration of the photoactive group, that is, the diethyldithiocarbamate. The synthesis of this novel methacrylic monomer iniferter and the ability to facilitate surface grafting are presented in this contribution. Further investigations of photoiniferter-mediated and/or patterned modification of crosslinked networks have been published elsewhere.²⁹

EXPERIMENTAL

Materials

Poly(ethylene glycol) (200) monomethyl ether monomethacrylate (mPEG200MA) and *n*-octyl methacrylate (OctMA; >99%) were purchased from Polysciences (Warrington, PA). MMA (99%), 2-ethylhexyl methacrylate (EHMA; 98%), 1,6-hexanediol dimethacrylate (HDMA), 4-(chloromethyl)benzoyl chloride (97%), and sodium diethyl-

dithiocarbamate trihydrate (>99%) were purchased from Aldrich (Milwaukee, WI). Inhibitor was removed from all monomers with Dehibit 100 ion-exchange resin before polymerization. Furthermore, 2-hydroxyethyl methacrylate (HEMA; Sigma, St. Louis, MO), styrene (Aldrich), and MMA (Aldrich) were distilled before use. mPEG200MA was washed with a 30 wt % aqueous sodium hydroxide solution.

Instruments

^1H NMR spectra were collected on a Varian VXR3000S Unity spectrometer. Samples were dissolved in CDCl_3 containing 1% tetramethylsilane as an internal reference. Ultraviolet-visible spectra were collected on a PerkinElmer Lambda 40 spectrometer with ethylene glycol monoethyl ether as the solvent. Infrared (IR) spectra and near-infrared (NIR) spectra were recorded with a Fourier transform infrared (FTIR) spectrometer (Nicolet Instruments Magna-IR 750 II) at a 4-cm^{-1} resolution. For surface characterization, the attenuated total reflectance (ATR) mode was used. The conversion of methacrylate double bonds by bulk- or surface-initiated polymerization was monitored by quantification of the double-bond peak in the NIR region (6165 cm^{-1}). A horizontal mounting unit,^{22,30} which redirected the IR beam vertically, was used in conjunction with an EFOS Ultracure ultraviolet light source, providing about 5 mW/cm^2 at 365 nm, to facilitate surface- or bulk-initiated polymerization within the IR unit. Purified monomers were used for grafting, and the graft area was controlled by a Viton rubber o-ring (10.6 mm in diameter) clamped onto the substrate and filled with monomer. Samples were enclosed in a vessel with a quartz exposure window and ports for continuous purging with nitrogen.

Synthesis of the Monomer Photoiniferter (Methacryloyl ethylenedioxy carbonyl) Benzyl *N,N*-Diethyldithiocarbamate (HEMA-E-In)

The synthesis of the methacrylated iniferter HEMA-E-In, which is illustrated in Figure 1, was accomplished as follows. First, 4-(chloromethyl) benzoyl chloride (1 equiv, 5 g), HEMA (1.5 equiv, 5.1 g), triethylamine (1.1 equiv, 3 g), and 50 mL of ethyl acetate were added to a 250-mL, round-bottom flask with a magnetic stir bar. The flask was purged with dry N_2 gas, sealed, and placed in a salt-ice bath ($<0\text{ }^\circ\text{C}$). The esterification pro-

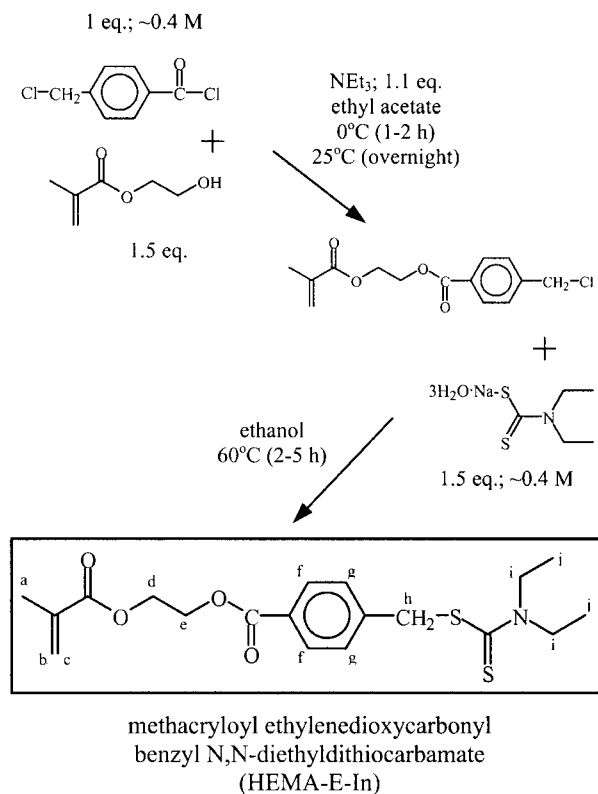


Figure 1. Synthesis and structure of a novel functionalized photoiniferter, HEMA-E-In.

ceeded at a low temperature until the ice melted and then continued overnight at ambient temperature. The intermediate product was isolated from the precipitated triethylamine salt and the solvent by filtration and evaporation of the solvent. Sodium diethyldithiocarbamate trihydrate (1.5 equiv, 9 g) was added to the intermediate product, and the substitution reaction was carried out for 5 h with continuous stirring at $60\text{ }^\circ\text{C}$ in ethanol. The final product was dissolved in dichloromethane, washed with water, and dried with anhydrous MgSO_4 . A brown oil was recovered ($\sim 90\%$ yield) and characterized by ^1H NMR and FTIR.

^1H NMR (250 MHz, CDCl_3 , δ): 1.3 (t, 6H, j), 1.98 (s, 3H, a), 3.7 (d, 2H, d), 4.0 (d, 2H, e), 4.45 (q, 2H, i), 4.55 (q, 2H, i), 4.6 (s, 2H, h), 5.6 (d, 1H, b), 6.15 (d, 1H, c), 7.45 (d, 2H, g), 8.0 (d, 2H, f).

A FTIR spectrum revealed absorbances at 1270 and 1485 cm^{-1} (dithiocarbamate group^{24,31}), 1637 cm^{-1} (methacrylate double bond), and other frequencies corresponding to characteristic carbonyl, methyl, and benzyl absorbances.

Substrate Network Synthesis

Substrates of various monomer compositions were polymerized with the methacrylated iniferter HEMA-E-In. Two formulations were used. Formulation 1 consisted of HEMA-E-In (2.0 wt %), MMA (30 wt %), HEMA (18 wt %), EHMA (40 wt %), and HDMA (10 wt %). Formulation 2 consisted of HEMA-E-In (0.5 wt %), MMA (30 wt %), HEMA (19.5 wt %), EHMA (40 wt %), and HDMA (10 wt %). On the basis of these compositions and assuming a uniform distribution of HEMA-E-In, formulation 1 contains 1.3×10^{-5} mol/cm² of HEMA-E-In and formulation 2 contains 3.2×10^{-6} mol/cm² HEMA-E-In. The monomer solutions were cast into glass molds (0.1–1 mm thick and 1–4 cm² in area) and exposed to 365-nm UV light at 2 mW/cm² (BlakRay, United States) for 2 h. The resulting substrates were slightly rubbery at ambient temperature and transparent to visible light. NIR measurements showed that the double-bond conversion was nearly quantitative. The substrates did not swell in the monomers used for grafting, so only HEMA-E-In accessible at the substrate surface was used for initiating the graft polymerization.

Static contact angles on grafted surfaces were measured with digital images of deionized water drops with samples soaked in deionized water for at least 10 h before measurements. The acute angle between the drop base and the surface is reported.

RESULTS AND DISCUSSION

Synthesis of the Monomer Photoiniferter HEMA-E-In

Covalently tethered diethyldithiocarbamate groups on a polymer surface are photolyzed readily upon UV irradiation to generate surface-attached carbon radicals, as well as DTC radicals. The carbon radicals spontaneously react with monomer in contact with the surface to generate propagating polymer chains. However, the DTC radicals do not initiate polymerization efficiently; they preferentially combine with the propagating radical to reform a diethyldithiocarbamate end group (i.e., cross-termination). After a series of such reactions, polymer chains are covalently bound to the polymer surface, and the graft length is readily controlled by the exposure time.

The synthesis of one such functional iniferter, HEMA-E-In, is described in the Experimental

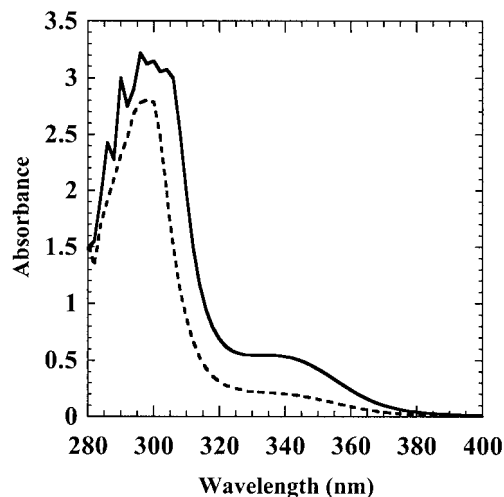


Figure 2. UV spectrum for HEMA-E-In: (—) 5×10^{-3} M XDT and (---) 5×10^{-3} M HEMA-E-In in ethylene glycol monoethyl ether.

section and depicted in Figure 1. The unique feature of the synthesized product is that the molecule contains a methacrylate group (derived from the HEMA unit) and a diethyldithiocarbamate group. IR and DSC experiments indicate that this compound self-polymerizes when exposed to UV light because of its unique functionality. When a polymer network is formed, the diethyldithiocarbamate group exists throughout the bulk polymer and on its surface.

Molecular absorption in the ultraviolet region of the spectrum is dependent on the electronic structure of the chromophore groups present in the monomer iniferter: the methacrylic group, benzyl group, and carbamate group. The characteristic absorptions of methacrylic and benzyl groups are at 210 and 230 nm (K-band) and 270 nm (B-band), respectively. In addition, Liang et al.³¹ reported that an absorption at 280 nm was attributable to the N—C—S and S—C=S conjugation present in aliphatic dithiocarbamate molecules.

Figure 2 reveals two characteristic absorption peaks around 300–308 and 340 nm in the UV spectrum of HEMA-E-In in an ethylene glycol monoethyl ether solution. In contrast to many photoiniferter structures reported in the literature, the HEMA-E-In molecule contains a unique conjugation of carbonyl and diethyldithiocarbamate groups with its benzyl ring, which leads to absorption at 340 nm. A similar absorbance peak is generated by the symmetrical aromatic carbamate, *p*-xylylene bis(*N,N*-diethyldithiocarbam-

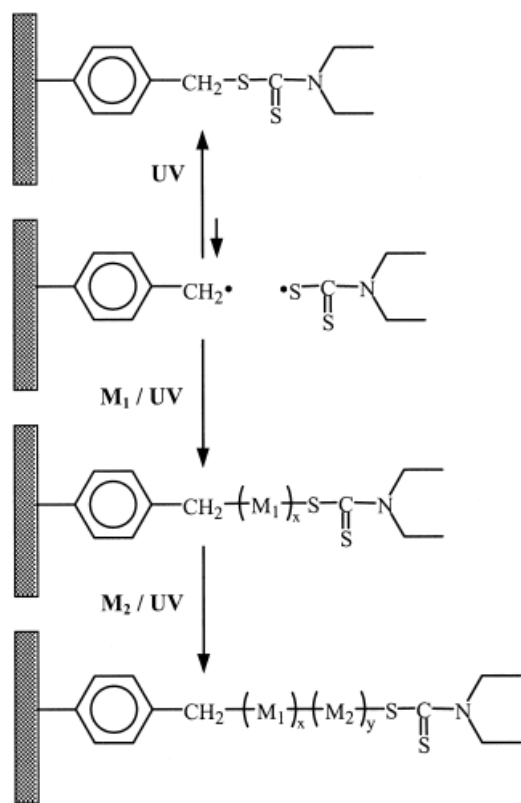


Figure 3. Schematic mechanism of graft photopolymerization by diethyldithiocarbamate chemistry: M_1 = first monomer and M_2 = second monomer.

ate) (XDT). In the XDT molecule, two diethyldithiocarbamate groups are associated with a central benzyl group. A similarity of absorption profiles for XDT and HEMA-E-In in Figure 2 suggests that the 340-nm absorption is contributed by the conjugated aromatic and dithiocarbamate groups. UV light sources with wavelengths near 365 nm are widely used in the photopolymer industry. Therefore, the existence of the 340-nm absorption band in the HEMA-E-In molecule yields greater compatibility with longer wavelength UV light sources in comparison with other chemistries reported previously, which necessitate short-wave UV light.^{4,7,12,31}

Surface Characterization

Figure 3 shows a schematic of an idealized process of photoiniferter-mediated surface graft polymerization. A dithiocarbamate group that is incorporated into a polymer substrate cleaves upon exposure to UV light. The resulting carbon radicals propagate through methacrylic monomers; this re-

sults in linear polymers grafted (i.e., covalently bound) to the substrate. Dithiocarbamate radicals cross-terminate growing polymer chains in a cycle that facilitates relatively low-polydispersity polymers and well-defined multiblock copolymers in comparison with traditional photoinitiation mechanisms.

ATR FTIR spectroscopy was used to determine the chemical composition of modified polymer surfaces and the presence of reactive dithiocarbamate groups. After copolymerization of the monomer iniferter with the other monomers comprising the substrate, diethyldithiocarbamate groups are attached covalently throughout the bulk of the substrate. The ATR FTIR spectra in Figure 4 reveal the surface chemistry of substrates synthesized with two different concentrations of HEMA-E-In. The diethyldithiocarbamate unit and benzene ring are unique to the HEMA-E-In molecule in the substrate formulations. Characteristic peaks from the diethyldithiocarbamate functionality are observed in the ATR FTIR spectra at 1485 and 1270 cm^{-1} . In addition, peaks corresponding to the aromatic ring present in HEMA-E-In are located at 1603 and 850 cm^{-1} . Finally, quantitative analysis of the two ATR FTIR spectra indicates a direct relationship between the concentration of monomer iniferter used in the substrate formulation and the IR signal from the diethyldithiocarbamate and aromatic groups on the substrate surface.

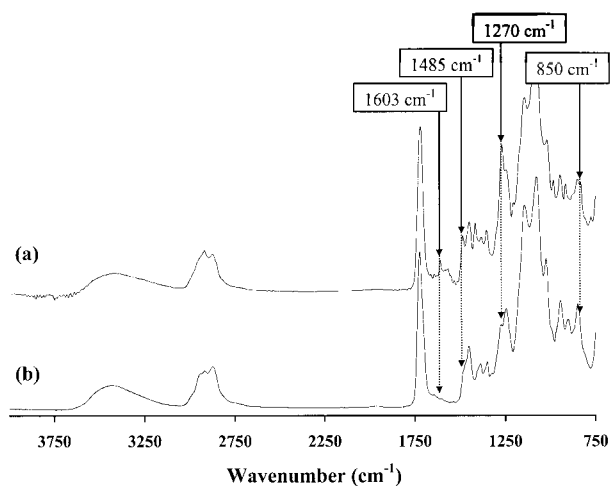


Figure 4. ATR FTIR spectra of the substrates with various concentrations of the HEMA-E-In photoiniferter: (a) 2.0 wt % HEMA-E-In and (b) 0.5 wt % HEMA-E-In.

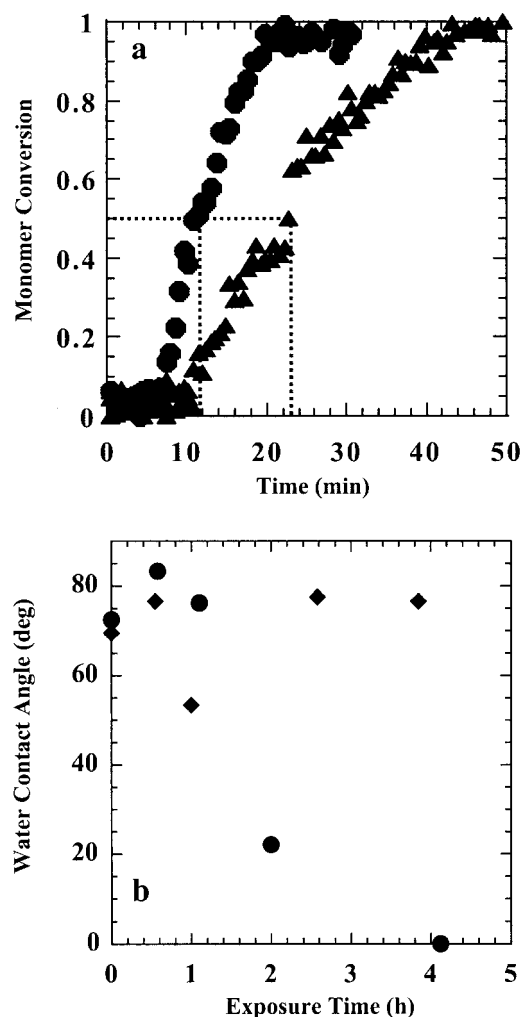


Figure 5. (a) Bulk photopolymerization of MMA initiated with (●) 2.0 wt % HEMA-E-In and (▲) 0.5 wt % HEMA-E-In and (b) (●) grafting mPEG200MA and (◆) OctMA from a hydrophobic substrate containing HEMA-E-In.

Photoactivity and Surface Initiation from HEMA-E-In

MMA was used to characterize the initiation ability of the monomer iniferter, and the conversion profile, measured by FTIR spectroscopy, is shown in Figure 5(a). MMA reaches 50% conversion in about 12 min when initiated with 2.0 wt % HEMA-E-In. Furthermore, MMA is polymerized to 50% in about 23 min with only 0.5 wt % monomer iniferter. The difference in times for different HEMA-E-In concentrations is evidence of the initiation capability of the monomer iniferter.

In addition to monitoring of the conversion of monomer initiated by the monomer iniferter, ex-

periments were performed to evaluate the surface initiation properties of a substrate initiated from and containing HEMA-E-In. Changes in the hydrophobicity of the substrate surface due to grafting of a hydrophilic monomer (mPEG200MA) and a hydrophobic monomer (OctMA) were characterized. The grafting reaction was allowed to proceed for various lengths of time, and the water contact angle was measured.

The profiles in Figure 5(b) indicate that the grafted mPEG200MA causes a significant change in the surface hydrophobicity: the hydrophobic substrate surface becomes hydrophilic after UV exposure. In contrast, the grafting of OctMA does not lead to a significant change in the surface wetting. Gravimetric results (not shown) reveal that the mass of the grafted substrate increases, so the absence of a change in the contact angle is due to the grafted surface having a similar hydrophobicity to that of the ungrafted substrate. The change in contact angle is not affected by subsequent solvent extraction of the polymer, which confirms the presence of covalently bound polymer.

CONCLUSIONS

A novel methacrylic monomer iniferter was synthesized to mediate photoinduced surface grafting and modification. A methacrylate functionality allows the monomer iniferter to be chemically tethered to a polymeric backbone, whereas a strong absorbance around 340 nm facilitates initiation of the monomer iniferter by exposure to 365-nm UV light. Photografting on the surface of polymer networks containing various concentrations of HEMA-E-In was demonstrated. Elevating the concentration of the monomer iniferter increases the rate of graft polymerization, and differences in water contact angles reveal surface-bound functionality. The results suggest that the novel methacrylic monomer iniferter is suitable for use in producing photopatternable grafted polymer networks.

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