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Surface-Initiated Photopolymerization of Poly(ethylene glycol) Methyl Ether Methacrylate on a Diethyldithiocarbamate-Mediated Polymer Substrate

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ABSTRACT: Grafting efficiency and graft conversion have been investigated for poly(ethylene glycol) methyl ether methacrylate (m-PEGMA) polymerized on the surface of diethyldithiocarbamate-containing polymer substrates. The substrate is prepared by copolymerization of a mixture of methacrylic monomers with a methacrylic diethyldithiocarbamate molecule, which serves as a photoiniferter that is chemically anchored on the surface of and throughout the substrate. Surface initiation was revealed by FTIR measurements of m-PEG200MA monomer conversion for two different monomer layer thicknesses; however, side reactions including chain transfer to PEG units affect surface-initiated polymerization of m-PEG200MA monomer significantly. Chain transfer causes a sharp decrease in the measured grafting efficiency at the beginning of this surface-mediated polymerization. Addition of N,N,N',N'-tetraethylthiuram disulfide (TED), which suppresses chain transfer to PEG units, and the use of octyl methacrylate as the grafting monomer result in an increase in graft efficiency at early stages of the polymerization. Specific polymerization events that relate the chain transfer of PEG units to the graft properties of the photoiniferter-mediated polymerization are discussed.

Introduction

Interest in techniques to produce thin, chemically bound, polymeric layers on solid surfaces has increased over the past decade. Chemical bonding between sequential layers enhances the polymer with chemical and environmental stability over a wide range of conditions (e.g., pH, solvents, and temperature). The unique coupling of stability and versatility of the surface chemistry has been the impetus for novel polymeric material development for microdevices and microelectronics applications,[1−3] membrane technology,[4,5] chemical separations,[6] and biomedical materials.[7−10]

Two general approaches are followed to fabricate thin, covalently bound, polymeric layers: *grafting to* and *grafting from* the solid substrate. In the *grafting to* technique, end-functionalized polymer is reacted with a solid surface to form an anchored polymer layer. Steric hindrance and macromolecular diffusion (through the developing polymer layer to reach reactive surface sites) limit this approach; as a result, thick and/or dense polymer layers are difficult to achieve.

In contrast, low molecular weight monomers diffuse to reactive sites more readily than macromolecules. Thus, the *grafting from* approach is an attractive method. A key concept in controlling the fabrication of a thin polymer layer on the surface with the *grafting from* approach is introducing initiating groups on substrate surfaces. When surface initiation is combined with living radical polymerization, via nitroxide-mediated polymerization,[2] atom transfer radical polymerization (ATRP),[3] or photoiniferter-controlled

polymerization,[7−13] the thickness of the thin polymer layer is controlled by the polymerization time.[7,10,13] Additionally, utilizing highly branched grafted layers or block−graft copolymer layers facilitates enhanced control of the chemical and mechanical properties of the thin polymer layer.

Methods reported for chemically attaching initiating groups to substrate surfaces are divided into two categories. The first category includes irradiation techniques such as plasma,[14] γ-ray,[15] and ozone[16] pretreatment methods as well as chemically anchoring a photoactive copolymer coating by γ-ray irradiation.[9,11] The second category is by chemical reactions including surface modification of functionalized molecules,[4,7,10,12,13] self-assembled monolayer (SAM) techniques,[17,18] and photochemically introducing chemical groups by exposure to short wavelength ultraviolet light in the presence of reducing agents.[5,19] Irradiation methods are suitable for introducing initiator groups on polymeric substrates; however, specialized equipment is required for these techniques. Therefore, they are not convenient for many general laboratory environments. The chemical reaction methods are not well suited to polymeric substrates because they are based on specific reactions of functional groups such as silane or thiol groups with particular surfaces, such as glass, silicon, gold, or silver.
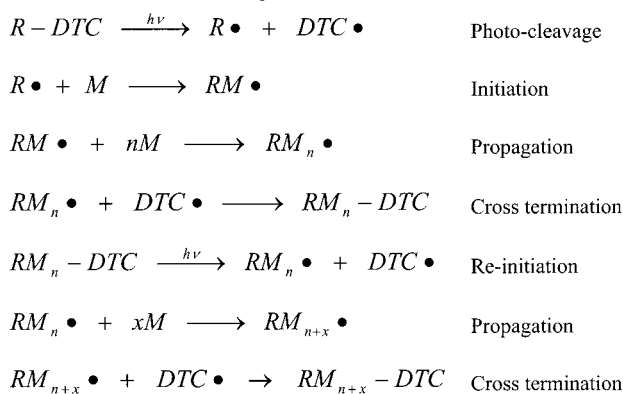
Photoiniferter-mediated polymerizations have been employed extensively in the past decade to produce well-defined block and graft copolymers.[20] The ability to incorporate distinctly different chemistries within the same macromolecule has led researchers to pursue photoiniferters for grafting from polymeric surfaces. Typically, photoiniferter molecules include a diethyldithiocarbamate functionality, which contains bonds that cleave upon exposure to light.[20] One of the radicals resulting from the cleavage, the diethyldithiocarbamyl

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Scheme 1. Mechanism of a Photoiniferter-mediated Polymerization[a]

$$R - DTC \xrightarrow{h\nu} R\bullet \ + \ DTC\bullet \qquad \text{Photo-cleavage}$$

$$R\bullet \ + \ M \ \longrightarrow \ RM\bullet \qquad \text{Initiation}$$

$$RM\bullet \ + \ nM \ \longrightarrow \ RM_n\bullet \qquad \text{Propagation}$$

$$RM_n\bullet \ + \ DTC\bullet \ \longrightarrow \ RM_n - DTC \qquad \text{Cross termination}$$

$$RM_n - DTC \xrightarrow{h\nu} RM_n\bullet \ + \ DTC\bullet \qquad \text{Re-initiation}$$

$$RM_n\bullet \ + \ xM \ \longrightarrow \ RM_{n+x}\bullet \qquad \text{Propagation}$$

$$RM_{n+x}\bullet \ + \ DTC\bullet \ \rightarrow \ RM_{n+x} - DTC \qquad \text{Cross termination}$$

[a] R is a benzyl group, DTC represents a diethyldithiocarbamyl radical, and M is a monomer unit.

(DTC) radical, is relatively unreactive (i.e., it does not rapidly initiate a chain polymerization). In general, photoiniferters dissociate into a reactive carbon radical in addition to the less reactive DTC moiety. This type of photoiniferter acts as a controlled radical initiator without the addition of any other initiating species. Under the correct conditions, the DTC radical will cross-terminate with propagating macroradicals (initiated from the carbon radical). In this way, diethyldithiocarbamate groups are re-formed as the terminal groups on the polymer chains. Upon further exposure to light, the terminal iniferter species will cleave again. The reinitiation allows more monomer units to be inserted into the growing chain before another cross termination event occurs. A brief, idealized description of the overall mechanism of a photoiniferter-mediated polymerization is shown in Scheme 1.

Photoiniferter sites located on the surface of a substrate are used to initiate a covalently bound layer when exposed to light in the presence of monomer. Furthermore, the ability to reinitiate the polymerization promotes highly controlled thickness and chemistry of the grafted layer. We have developed a functionalized photoiniferter molecule: (methacryloylethylene–dioxycarbonyl)benzyl *N,N*-diethyldithiocarbamate (HEMA-E-In).[21]
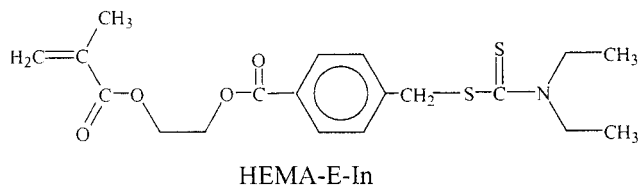
HEMA-E-In

HEMA-E-In is copolymerized with a suitable mixture of methacrylic monomers to produce a cross-linked polymeric substrate with a photoactive surface. The advantages of this novel method include cost, chemical versatility, layer thickness control, and suitability for facile preparation of micropatterned polymer surfaces.

We have been especially interested in grafting poly(ethylene glycol) monomethyl ether monomethacrylate (m-PEGMA) to polymer substrates. For biomedical applications, surface-grafted poly(ethylene glycol) (PEG) molecules are known to prevent protein adsorption.[22] The nonadhesive nature of proteins to PEG-coated surfaces is maximized by covalent grafting of the PEG layer.[23–25] Previous attempts at immobilizing PEG on

surfaces of materials involved functionalized derivatives of PEG (e.g., silanated PEG,[23] thiol-terminated PEG,[25] amino-terminated PEG[26]) or functionalized substrate surfaces for coupling reactions involving two or more steps.[26–31] Most of the derivatized PEG agents are very expensive. The drawbacks of cost and reaction complexity are largely overcome by grafting PEG macromonomers on the surface of materials.

m-PEGMA is often used to create PEG-modified surfaces. For example, Wang et al. grafted m-PEGMA monomer onto the surface of a segmented poly(ether–urethane) material by ozone-induced polymerization.[16] Chen et al. grafted m-PEGMA macromer by UV-induced copolymerization on the surface of an emeraldine film,[24] while Wang et al. grafted m-PEGMA macromonomer to a plasma-pretreated PTFE surface by UV-induced polymerization.[14] Because of its propensity for chain transfer, polymerization of PEG macromonomers is very sensitive to reaction conditions, and insoluble cross-linked gels often result.[32] These important issues are further examined in this contribution.

Specifically, using substrates containing the HEMA-E-In photoiniferter, we previously demonstrated a procedure to photograft covalently bound layers of polymer that are greater than 100 μm thick.[21] In particular, incorporation of divinyl monomers as cross-linking agents in the grafted layer allowed for relatively thick layers that are useful for high aspect ratio patterning and/or three-dimensional modifications. To advance this application, a better understanding of the surface initiation of m-PEGMA is necessary. Factors that affect the surface initiation and thickness of the m-PEGMA grafted layer are examined experimentally and discussed in this paper. Specifically, graft efficiency and graft conversion are measured for m-PEGMA layers initiated from a HEMA-E-In-containing polymer substrate. Results are discussed with regard to chain transfer mechanisms that lead to the observed behavior.

Experimental Section

Materials. All monomers were passed through a column containing weakly acidic, basic, and neutral 150 mesh Brockmann I aluminum oxide particles (Aldrich, Milwaukee, WI) to remove inhibitor and impurities prior to polymerization. Poly(ethylene glycol) (200) monomethyl ether monomethacrylate (m-PEG200MA), poly(ethylene glycol) (600) dimethacrylate (PEG600DMA), and *n*-octyl methacrylate (99+%, OctMA) were purchased from Polysciences (Warrington, PA). Methyl methacrylate (99%, MMA), 2-ethylhexyl methacrylate (98%, EHMA), 1,6-hexanediol dimethacrylate (HDMA), poly(ethylene glycol) (550) monomethyl ether (PEG550), and *N,N,N',N'*-tetraethylthiuram disulfide (TED) were purchased from Aldrich (Milwaukee, WI). 2-Hydroxyethyl methacrylate (99+%, HEMA) was purchased from Sigma (St. Louis, MO).

Instruments. Near-FTIR spectroscopy (Fourier transform infrared, Magna-IR 750, series II, Nicolet Instruments, Madison, WI) was used to follow the photoiniferter-mediated polymerization at 4 cm^{-1} resolution. A horizontal mounting unit, which redirects the IR beam vertically, was used in conjunction with an ultraviolet light source of 365 nm (Efos Ultracure, EIT, Sterling, VA) to facilitate polymerization of the monomer samples within the IR unit.[33,34] Series scans (DTGS detector) were performed to monitor the conversion of the methacrylic double bond (6165 cm^{-1}) as a function of time. ^{1}H NMR spectra of the functionalized iniferter were collected on a Varian VXR3000S Unity spectrometer. NMR samples were dissolved in CDCl$_3$ containing 1% TMS as an internal reference.

Synthesis of the Functionalized Iniferter, (Methacryloylethylene–dioxycarbonyl)benzyl *N,N*-Diethyldithio-

carbamate. 4-(Chloromethyl)benzoyl chloride (1 equiv, 5 g), HEMA (1.5 equiv, 5.1 g), triethylamine catalyst (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 °C). The esterification proceeded at low temperature until the ice melted and then continued overnight at ambient temperature. The intermediate product was isolated from the reaction mixture. Then, 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 °C in ethanol. The final product was dissolved in dichloromethane, washed with water, and dried with anhydrous $MgSO_4$, and the correct structure was confirmed by ^{1}H NMR.

Synthesis of *N,N*-Diethyldithiocarbamated Polymer Substrates. Substrates of varying monomer composition were polymerized with the functionalized iniferter (HEMA-E-In). Two formulations are used as follows. Formulation 1: HEMA-E-In (2.0 wt %), MMA (30 wt %), HEMA (18 wt %), EHMA (40 wt %), HDMA (10 wt %). Formulation 2: HEMA-E-In (0.5 wt %), MMA (30 wt %), HEMA (19.5 wt %), EHMA (40 wt %), HDMA (10 wt %). The main difference between these formulations is the resulting concentration of the functionalized iniferter that is incorporated into the final polymer network. On the basis of these compositions and assuming a uniform distribution of the 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. Monomer solutions were cast into a glass mold and exposed to 365 nm UV light at ∼2 mW/cm² (BlakRay) for 2 h. Near-infrared spectroscopy (NIR, 7000−4000 cm⁻¹) measurements of the methacrylic double bond (6165 cm⁻¹) showed that the double-bond conversion was greater than 95%. Upon polymerization, the surface density of active dithiocarbamate end groups is estimated from the initial concentration of HEMA-E-In. However, this contribution refers only to the initial bulk density of HEMA-E-In for comparison of surface functional group density.

Grafting from the Functionalized Substrates. In the context of this contribution, "graft" refers to initiation and subsequent formation of covalent linkages between the substrate and a second polymer layer. This definition is somewhat different from traditional definitions, which refer to macromolecular architectures that include polymer chains attached to other backbone chemistries or pure linear grafts grown from a controlled surface initiation.

Purified monomers were grafted on substrates using ∼5 mW/cm² of 365 nm radiation. The graft area was controlled by clamping a Viton O-ring (10.6 mm diameter; ca. 2.0 mm thick) onto the substrate and filling it with the monomer to be grafted. The sample was enclosed in a vessel with a quartz exposure window and ports for continuous flow of nitrogen.

Measurement of Graft Efficiency and Graft Conversion. Graft efficiency (GE) and graft conversion (GC) were calculated according to the following equations.

$$GE = \frac{W_g}{W_p} = \frac{W_{g,s} - W_s}{W_0 X} \tag{1}$$

$$GC = \frac{W_g}{W_0} = \frac{W_{g,s} - W_s}{W_0} \tag{2}$$

W_g, W_p, W_0, and W_s are the weights of the graft, polymer, monomer, and substrate, respectively. X is the monomer conversion, and $W_{g,s}$ is the weight of the sample after grafting and extraction by deionized water or ethanol. The monomer conversion was determined using NIR spectroscopy with a horizontal transmission accessory[33,34] that was described above.

Results and Discussion

Polymerization kinetics, initiated by covalently bound HEMA-E-In within the substrate network, were ob-
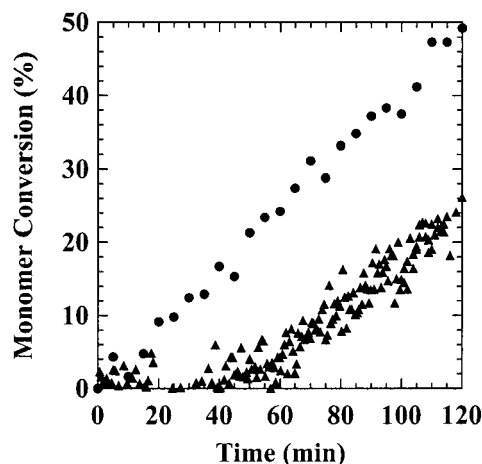

Figure 1. Monomer conversion as a function of time for m-PEG200MA polymerized from the surface of substrates containing two different concentrations of photoiniferter: (●) 2.0 wt % HEMA-E-In; (▲) 0.5 wt % HEMA-E-In.

served using real-time NIR spectroscopy. Figure 1 plots the monomer conversion as a function of time and shows that the m-PEG200MA polymerization rate increases as the concentration of iniferter incorporated in the substrate increases. The iniferter-mediated polymerization is more complex than traditional radical polymerizations due to the initiation, termination, and reinitiation roles of the iniferter and associated radicals. Therefore, the dependence of reaction rate on initiator concentration offers only qualitative evidence that the surface-bound iniferter groups mediate the polymerization.

Figure 2 reveals that the kinetics also depend on the thickness of the monomer layer on top of the iniferter-containing substrate. Because the surface area probed by the infrared spectrometer is identical for each thickness, the number of observed surface-bound iniferter molecules should be the same for each thickness. Therefore, the rate of monomer consumption should be identical for any thickness; however, the total number of monomer molecules varies linearly with thickness. The rate of monomer conversion, which is the ratio of the rate of monomer consumption to the total number of monomer molecules, has an inverse relationship with thickness. One expects the thickness effect to be eliminated by multiplying the conversion data for a monomer film by its thickness. The results of this calculation are shown in Figure 2b, but the conversion data do not collapse to a single rate after correcting for thickness.

Reasons for this discrepancy are a combination of experimental and mechanistic factors. For example, experimental uncertainties regarding the light intensity at the substrate−monomer interface and the thickness of the monomer layer affect the expected agreement. More importantly, however, is the assumption that the polymerization is initiated only from the substrate surface. Initiation in the bulk of the monomer layer, from radicals not generated from iniferter molecules, leads to a dependence of conversion on thickness that is less than the theoretical inverse relationship. In fact, the corrected rate curves shown in Figure 2b have a larger range of slopes than the ones in Figure 2a, which means that nonideal behavior is a very important aspect of the iniferter-mediated grafting of m-PEG200MA. A more detailed exploration of mechanistic characteristics is required.
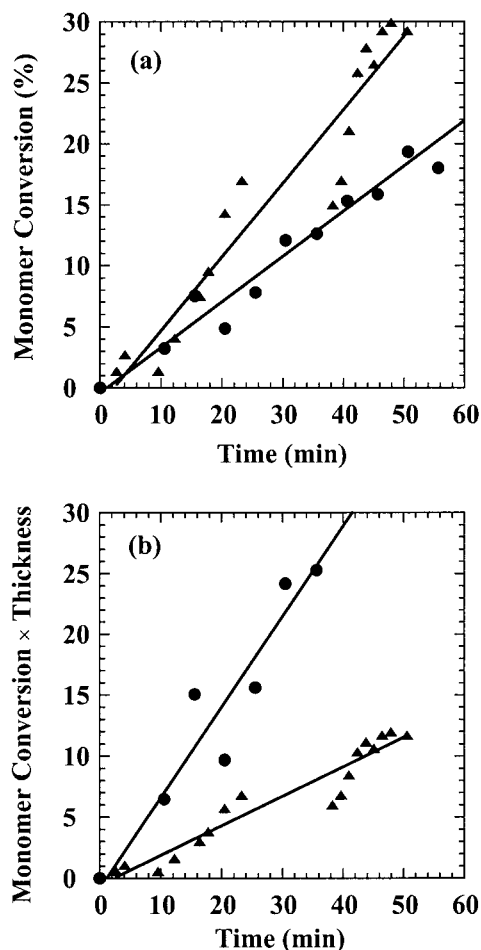
Figure 2. **(a)** Monomer conversion as a function of time for two thicknesses of m-PEG200MA polymerized from the surface of a substrate containing 2.0 wt % HEMA-E-In. **(b)** The same monomer conversion data corrected to account for thickness. (●) 0.4 mm; (▲) 0.1 mm.

Table 1 contains a list of some of the possible reactions that may take place in the iniferter-mediated system described in this work. In particular, the different chain transfer reactions are listed, as well as their effects on graft properties (GE and GC) and the type of polymer architecture that would form on the surface. Figure 3 shows a schematic of a likely scenario during the surface-initiated controlled polymerization of a monomer that will chain transfer easily (e.g., m-PEGMA). At early stages, linear chains grow from the substrate surface, some initiation in the bulk occurs, and chain transfer leads to some branching. At higher conversion, chain transfer results in bonding between surface-attached polymer and unattached polymer. Eventually, a highly branched and cross-linked network forms.

Figure 4 displays GE and GC for m-PEG200MA initiated from the surface of a HEMA-E-In-containing surface. Graft efficiency decreases significantly between 0 and 20% monomer conversion. This result is attributed to the chain transfer propensity of the grafted PEG monomer. The chain transfer coefficient to a PEG unit, which accounts for reacted monomer that is not incorporated via double-bond propagation, is 0.0017 in the polymerization of vinyl acetate[35] and on the order of $1.36-4.7 \times 10^{-4}$ during the polymerization of styrene.[35] This value is an order of magnitude higher than the chain transfer coefficient of many other typical methacrylic monomers (e.g., 1.2×10^{-5} for MMA[36]) and

relates to the presence of ethylene glycol units with abstractable hydrogen atoms. Chain transfer can create chains that are not bound to the evolving network. In addition, creation of PEG radicals (from chain transfer) rather than methacrylic radicals leads to a series of reactions that decrease the graft efficiency at low conversion. A PEG radical is less stable than a methacrylic radical, so chain transfer and bimolecular termination compete with cross termination (i.e., by combination with a diethyldithiocarbamate group). Furthermore, diffusion of the DTC radical is severely limited as conversion and viscosity increase. In contrast, radicals propagating through unreacted double bonds have higher mobility via reaction diffusion.[35] The separation of propagating and DTC radicals decreases the cross termination frequency relative to bimolecular termination. Therefore, the living or controlled nature of the polymerization is dramatically reduced.

When the monomer conversion reaches ca. 20%, the measured graft efficiency increases significantly. This increase is due to incorporation of the previously ungrafted homopolymer. Nonideal reactions such as coupling and branching due to chain transfer lead to the formation of a cross-linked network. In this situation, a higher fraction of polymer (including some polymer initiated by radicals other than those generated from iniferter cleavage) is bound to the initiating surface, and the measured graft efficiency is higher, though the actual formation of polymer chains attached via iniferter-mediated grafting is likely decreasing.

Figure 5 plots the graft efficiency and conversion of m-PEG200MA monomer in a 50 wt % PEG550 solution. PEG550, which does not contain a double bond, acts as a diluent of double bonds in the graft monomer solution placed on the substrate surface. In this case, no measurable graft is formed until the monomer conversion reaches ~20%. Noh et al.[19] reported a study on the photografted polymerization of m-PEG acrylates onto photochemically reduced PTFE surfaces. In the reported study, PTFE films were photochemically reduced by exposure to a short wavelength ultraviolet source in the presence of reducing agents, such as diphenylketyl radical anions generated from a solution of benzophenone and sodium hydride in dimethylformamide. The authors showed that the extent of m-PEG acrylate grafting decreased with increasing m-PEG acrylate molecular weight. No evidence of grafting of m-PEG acrylates with molecular weights greater than 1000 was observed. In the cases of the previous publication and the current contribution, grafting decreases and the relative frequency of chain transfer to PEG units increases as the concentration of reactive double bonds decreases.

Figure 6 plots the monomer conversion as a function of time for m-PEG200MA initiated from a HEMA-E-In-containing surface in the presence or absence of TED. TED cleaves upon exposure to UV light to form two identical DTC radicals. As discussed previously, the DTC radicals repeatedly combine, cleave, and recombine with primary radical chains during UV exposure. Control in iniferter-mediated polymerization is a result of the relatively low initiation reactivity of the DTC radical. Since the DTC radical primarily terminates the growing radical chain, the measured polymerization rate is reduced. Figure 6 confirms a reduction in polymerization rate due to the presence of additional diethyldithiocarbamate groups.

Table 1. Effects of Various Chain Transfer Reactions on the Graft Efficiency and Graft Conversion in the Photoiniferter-Mediated Polymerization of m-PEGMA Monomer

| situation	chain transfer	graft conversion	graft efficiency	architecture of surface-anchored chains	schematic depicted in Figure 3
ideal mechanism	none	increases with monomer conversion	100%, constant	linear	chain 1
chain transfer case I	from surface-anchored chain to monomer	increases	reduced	linear	chain 7
chain transfer case II	between surface-anchored chains	increases with monomer conversion	100%, constant	branched	chains 2, 3, and 8
chain transfer case III-A	from grafted chain to ungrafted chain	increases	reduced	linear	chain 6
chain transfer case III-B	from un-grafted chain to surface-anchored polymer chain	increases	increased	branched	chains 2 and 3
chain transfer case IV	between ungrafted polymer chains	no effect	no effect	no effect	chain 6
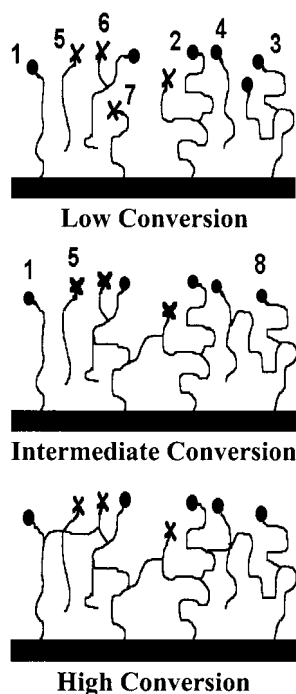
Figure 3. Illustration of surface-initiated polymerization associated with chain transfer reactions: (●) DTC end group with reinitiation capability. (×) end groups without reinitiation capability. At low monomer conversion, both iniferter-mediated polymerization and chain transfer reactions occur. Chain 1 represents ideal grafting by the iniferter-mediated polymerization. Chains 2 and 3 represent branching chains generated from a transferred PEG macroradical. Chains 4−6 are the polymer chains generated from PEG radicals by chain transfer to monomer. However, chain 6 transferred to a polymer backbone. At intermediate monomer conversion, several chain transfer events occur on the same polymer chain (chain 8), which results in a highly branched polymer. Radical coupling may form cross-links as well. Finally, at high monomer conversion, most polymer chains are associated by radical coupling reactions. In this case, high apparent graft efficiency and apparent graft conversion are observed.

Figure 7 shows the effect of adding TED to the bulk monomers so that excess DTC radicals are formed. First, the grafting reaction is dramatically slowed by the addition of TED to the bulk. This change occurs because the additional DTC radicals further limit the polymerization and grafting rates. Additonally, the graft efficiency is lowered relative to grafting without excess TED. This result, though initially surprising, is likely
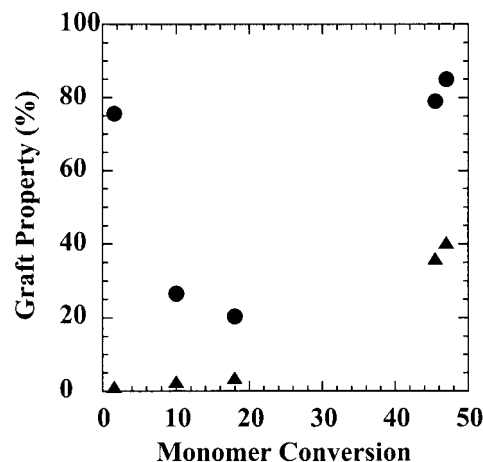

Figure 4. Graft properties, graft efficiency (●) and graft conversion (▲), as a function of monomer conversion for m-PEG200MA polymerized on the surface of a substrate containing 2.0 wt % HEMA-E-In.
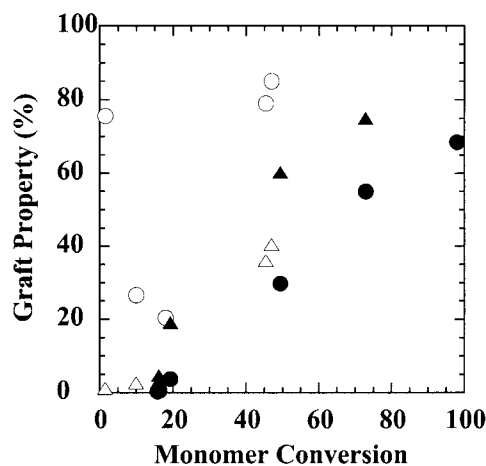

Figure 5. Graft properties, graft efficiency (●) and graft conversion (▲), as a function of monomer conversion for 50 wt % m-PEG200MA in PEG550 polymerized on the surface of a substrate containing 2.0 wt % HEMA-E-In. The unfilled symbols represent the properties of m-PEG200MA grafted in bulk (described in Figure 4).

caused by additional side reactions that occur in the bulk because of the presence of TED and the additional exposure time.

To further examine the impact of chain transfer, OctMA was used as the graft monomer to decrease the
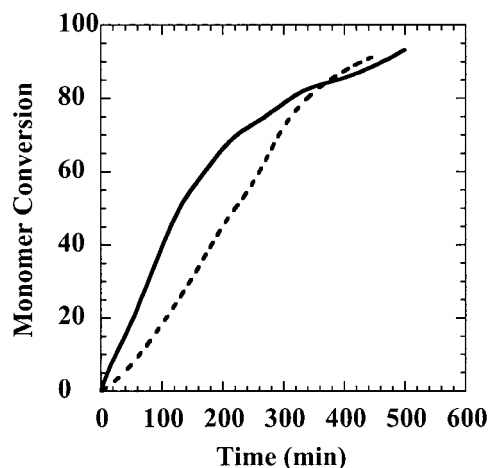
Figure 6. Monomer conversion as a function of time for m-PEG200MA polymerized from the surface of a substrate containing 2.0 wt % HEMA-E-In in the presence of 0.5 wt % TED (dashed line) and without TED (solid line).
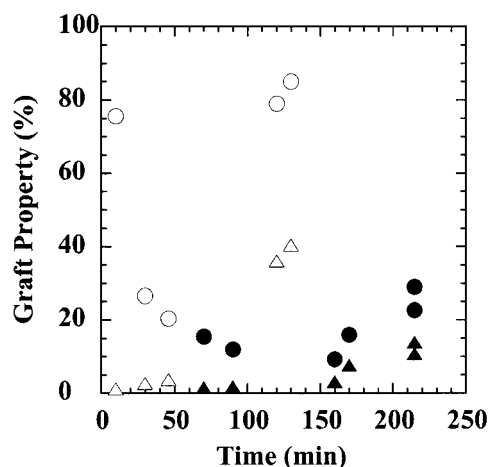

Figure 7. Graft properties, graft efficiency (●) and graft conversion (▲), as a function of monomer conversion for m-PEG200MA polymerized on the surface of a substrate containing 2.0 wt % HEMA-E-In in the presence of 0.5 wt % TED. The unfilled symbols represent the properties of m-PEG200MA grafted without TED (described in Figure 4).

significance of chain transfer in the development of a surface-initiated graft. Figure 8 indicates a major difference in the graft efficiency as a function of monomer conversion for OctMA compared to m-PEG200MA. Since chain transfer is reduced, the initial decrease in graft efficiency for the m-PEG200MA graft is not observed for the OctMA system, but rather an increase in efficiency is observed. Furthermore, branching during the grafting of OctMA and cross-linking are not significant enough to cause an upturn in the graft efficiency curve at moderate monomer conversion. This result indicates that high graft efficiency, i.e., a value not including the contribution of cross-linking, can be obtained, depending on the monomer chemistry.

Finally, the feasibility of grafted, macromolecular design is demonstrated by sequential grafting of m-PEG200MA followed by OctMA on a substrate containing 2.0 wt % HEMA-E-In. m-PEG200MA is grafted to the substrate, and then the dithiocarbamate-terminated chains present near the surface of the first graft layer are used to initiate the polymerization of OctMA. Table 2 contains information about the graft properties of both layers in the sequential grafting demonstration.
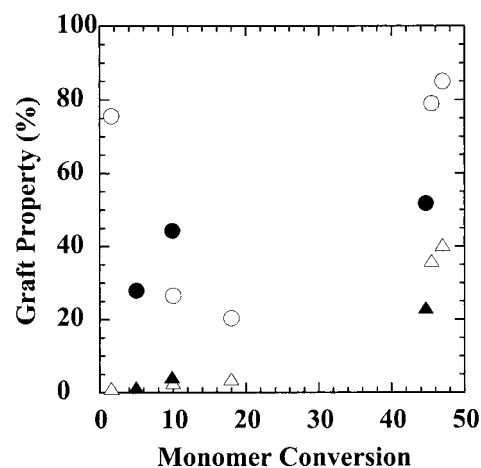

Figure 8. Graft properties, graft efficiency (●) and graft conversion (▲), as a function of monomer conversion for OctMA polymerized on the surface of a substrate containing 2.0 wt % HEMA-E-In. The unfilled symbols represent the graft properties of m-PEG200MA (described in Figure 4).

Table 2. Graft Properties for Sequentially Grafted m-PEG200MA (the First Layer) and OctMA (the Second Layer) on a Substrate Containing 2.0 wt % HEMA-E-In

	monomer conversion (%)	GC^a (%)	GE^b (%)
first monomer (m-PEG-200MA)	1.6	1.21	75.6
	10.0	2.66	26.6
	18.0	3.68	20.3
second monomer (OctMA)	25.8	3.121	12.1
	25.9	2.98	11.5
	37.2	14.4	38.7

^{a} $GE = W_g/W_p = (W_{g,s} - W_s)/W_0 X$. ^{b} $GC = W_g/W_0 = (W_{g,s} - W_s)/W_0$.

Conclusions

Chain transfer to PEG chains affects surface-initiated photopolymerization of m-PEG200MA monomer significantly. Chain transfer causes a sharp decrease in the measured graft efficiency at the beginning of surface-mediated polymerizations. Then, chain transfer leads to branching and cross-linking at ca. 20% monomer conversion. Addition of diethyldithiocarbamate functionality (e.g., TED) suppresses chain transfer so the onset of the increase in GE is delayed to ca. 30% monomer conversion. High graft efficiency (that is not influenced by branching and cross-linking) is attained when using OctMA instead of m-PEG200MA as the graft monomer because chain transfer is reduced significantly. Grafted linear chains of PEG may be fabricated by limiting the conversion and suppressing chain transfer. In addition, multiblock macromolecular architectures are created using the diethyldithiocarbamate-mediated controlled polymerization method applied to sequentially grafted layers. Finally, nonideal chain transfer reactions enable fabrication of thick layers of surface-bound polymer. For instance, high monomer conversion has been used to achieve well-adhered, micron-order thick polymer layers on an iniferter-containing surface.

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