Impact of Added Tetraethylthiuram Disulfide Deactivator on the Kinetics of Growth and Reinitiation of Poly(methyl methacrylate) Brushes Made by Surface-Initiated Photoiniferter-Mediated Photopolymerization

Santosh B. Rahane,[†] Andrew T. Metters,[†,‡] and S. Michael Kilbey II*[,†]

Department of Chemical and Biomolecular Engineering and Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, South Carolina 29634, and Department of Bioengineering, Clemson University, Clemson, South Carolina 29634

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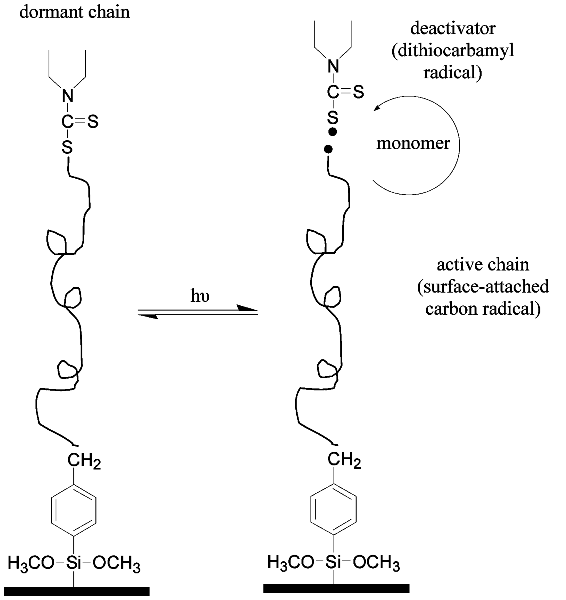
ABSTRACT: Without intervention, it has been found that surface-initiated photoiniferter-mediated photopolymerization (SI-PMP) of methyl methacrylate suffers from irreversible termination, which leads to cessation of polymerization. These irreversible termination reactions were successfully reduced by preaddition of tetraethylthiuram disulfide (TED). The poly(methyl methacrylate) layers were also reinitiated using styrene as a monomer to investigate the effect of TED concentration on the extent of irreversible termination. The reinitiation efficiency increased as [TED] was increased, indicating that extent of irreversible termination reactions can be reduced by increasing [TED]. It was also observed that dithiocarbamyl radicals generated from TED can initiate polymerization in solution, resulting in significant monomer consumption.

Introduction

Polymer brushes[1] grafted covalently to solid substrates are of great importance owing to their potential applications in food packaging, lithography, microelectronics, and design of corrosion resistant and biocompatible materials. Of the various methods by which polymer brushes can be made, the "grafting from" approach using controlled (free) radical polymerizations has become perhaps the most widely practiced.[2] Techniques such as atom transfer radical polymerization (ATRP),[3−9] nitroxide-mediated free-radical polymerization (NMP),[10−12] and reversible addition fragmentation transfer (RAFT)[13,14] have been used to produce polymer brushes. While the grafting-from approaches in general allow surface densities and molecular weights of the tethered chains to be independently manipulated, thereby allowing interfacial structure to be tailored, the controlled-polymerization methods have the additional advantage of being amenable to the synthesis of multiblock copolymers. The creation of such multifunctional layers springs from the preservation of the active end groups during the polymerization, brought about by establishing and maintaining an equilibrium between capped, dormant chains and active, free-radical species. Most often, this is accomplished by the addition of a deactivating species that reacts reversibly with the radical,[4,8,10,15−21] thereby allowing another block(s) to be added subsequently.[4,10,15,16,21]

In a recent publication, we described our interest in using surface-initiated, photoiniferter-mediated photopolymerization (SI-PMP) to create polymer brushes.[22] SI-PMP is advantageous for the fabrication of these interfacial layers because it is mediated by light, which permits polymerization to be carried out at room temperature and readily allows spatial and temporal control over layer growth. Photoiniferter-mediated photopolymerization was first discovered by Otsu et al.[23] and has been extensively used by several groups[24−30] to modify surface properties of various organic and inorganic substrates. Ideally, photoiniferter-mediated photopolymerization involves a dynamic equilibrium between growing chains with active free radicals and chains that exist in a "dormant" state, temporarily capped with the deactivating dithiocarbamyl radicals,[23] as depicted in Scheme 1. As predicted by persistent radical effect and mentioned previously, a sufficient concentration of these deactivating species must be present to provide reversible deactivation of chains during propagation to create an equilibrium between active and dormant chains that favors a low yet persistent concentration of free radicals, leading to controlled-radical polymerization behavior.[31,32] However, the extremely

Scheme 1. Idealized Scheme for the Growth of a Surface-Tethered Polymer Chain by Surface-Initiated Photoiniferter-Mediated Photopolymerization; Several Such Chains Grow Simultaneously To Form a Polymer Brush



[†] Department of Chemical and Biomolecular Engineering and Center for Advanced Engineering Fibers and Films.

[‡] Department of Bioengineering.

* To whom correspondence should be addressed. E-mail: mkilbey@clemson.edu.

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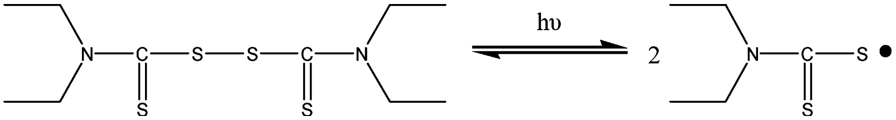
Scheme 2. Formation of Two Identical Dithiocarbamyl Radicals by Homolytic Cleavage of Tetraethylthiuram Disulfide (TED) Mediated by Ultraviolet (UV) Light



low concentration of deactivating radicals produced by surface-initiated photoiniferter-mediated photopolymerization (SI-PMP) from flat surfaces leads to irreversible termination, primarily by bimolecular termination, and cessation of layer growth.[22] Analogous "nonliving" behavior is also observed in the synthesis of polymer brushes by surface-initiated ATRP[4,8,33−35] and NMP[10−12] from low area, flat substrates.

Because of the problem of cessation of layer growth brought about by bimolecular termination, in this work we investigate the impact of adding a source of deactivating species, tetraethylthiuram disulfide (TED), to the reaction mixture. As shown in Scheme 2, when irradiated with UV light, TED undergoes a homolytic cleavage, yielding two dithiocarbamyl (DTC) radicals. Previously, TED has been used by Doi et al.[36] to prevent bimolecular termination during photoiniferter-mediated photopolymerization of methyl acrylate in bulk or in benzene. Lovell et al.[37] used TED in combination with conventional initiator, 2,2-dimethoxy-2-phenylacetophenone, to create cross-linked polymers without trapped radicals. Similarly, in studies of SI-PMP of poly(ethylene glycol) methyl ether methacrylate from diethyldithiocarbamate-modified polymer substrates, Luo et al.[38] inferred that chain transfer to poly(ethylene glycol) units can be suppressed by addition of TED to the reaction mixture. Otsu et al.[39] were able to synthesize di- and triblock copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA) layers using surface-initiated photopolymerization from photoiniferter-modified PS beads in the presence of TED.

However, to date, synthesis of block copolymer brushes from flat surfaces using SI-PMP in the presence of TED has not been reported. Additionally, the impact of added TED on the kinetics of surface-tethered chain growth and the ability of this strategy to preserve active ends during brush formation to allow block copolymers to be created has not been adequately investigated. To better understand the kinetics of SI-PMP in the presence of TED, we have studied the impact of TED concentration on the growth of surface-tethered PMMA layers by SI-PMP. Additionally, reinitiation experiments were conducted using PMMA layers photopolymerized in the presence of varying amounts of TED. These studies provide additional insight into the reinitiation efficiency (ability of PMMA layers to restart growth) and, therefore, the extent of irreversible termination reactions occurring during SI-PMP of MMA in the presence of TED.

Experimental Section

Materials. Purities and preparations of methyl methacrylate (MMA), solvents, and reagents are described in detail in a previous publication.[22] Additional compounds used here were styrene (Acros, 99%), which was dehibited by passing it through a neutral alumina column prior to use, and tetraethylthiuram disulfide (TED) (Sigma, 97%), which was used as received. The synthesis and characterization[22,28] of the photoiniferter, *N*,*N*-(diethylamino)dithiocarbamoylbenzyl(trimethoxy)silane (SBDC), and procedures used to make self-assembled monolayers (SAMs) of this iniferter on silicon surfaces are discussed elsewhere[22] and therefore not repeated here.

Photopolymerization. The protocols used in these photopolymerization studies, including solution preparation, assembly of the reaction cell, photopolymerization, and post-photopolymerization treatments, were also described in our previous paper[22] and therefore are not repeated here. The only significant change in these studies is the addition of TED to the photopolymerization solutions. Solutions of MMA and TED in anhydrous toluene were prepared in air-free Schlenk tubes. MMA concentration of 4.68 M in toluene was used for all experiments. The concentrations of TED (based on the volume of the solution of MMA in toluene) used were 0.02, 0.2, 1, and 2 mM. The reinitiation of the PMMA layers synthesized at various photopolymerization conditions used styrene as a monomer. Styrene concentration of 4.34 M in toluene was used for all reinitiation experiments, and for all of these reinitiation studies, the preparations, photopolymerization, and postpolymerization treatment were analogous to those followed for MMA photopolymerizations.

Characterization. A Beaglehole Instruments phase-modulated Picometer ellipsometer (He−Ne laser, $\lambda = 632.8$ nm) was used to measure the dry layer thicknesses of the SBDC SAMs, PMMA layers, and PMMA−PS block copolymer layers. Refractive indices of 1.45, 1.48, and 1.59 were used for the SAMs of SBDC, PMMA, and PS, respectively. The ellipsometric angles ψ and Δ, measured by changing the angle of incidence from 80° to 35°, were fitted using a Cauchy model (Igor Pro. software package) to determine the thickness. Thickness measurements were taken at five different points on every sample in ambient air. The SAMs, PMMA layers, and PMMA−PS block copolymers were also characterized by measuring the static water contact angle. The details of contact angle instrument and measurement method are discussed elsewhere[22] and therefore not repeated here. Monomer conversions were estimated from the ^{1}H nuclear magnetic resonance (NMR) spectra of aliquots of reaction cell solutions before and after photopolymerization. These ^{1}H NMR spectra were recorded on a Bruker AC300 Fourier transform NMR spectrometer. Monomer conversion was calculated as the ratio of the peak integral corresponding to the double bond proton ($CH_2{=}C$) of MMA after SI-PMP to the peak integral corresponding to the double bond proton of MMA before SI-PMP. For the comparison of peak integrals, peaks corresponding to the constant concentration of solvent (toluene) protons were used as internal controls.

Results and Discussion

Growth of the PMMA Layers. Figure 1 shows how the dry layer thicknesses of grafted PMMA layers measured using variable-angle ellipsometry increase with polymerization time for various TED concentrations, [TED]. All data sets show an initial period of slow increase in thickness followed by a rapid increase. This initial lag has been previously attributed to the "mushroom-to-brush" transition[22] (indicated by the arrow). Therefore, the kinetic analysis of the variation of PMMA layer thickness with time at all [TED] is done after this initial lag period (after the exposure time marked by the arrow). As seen by the curve labeled **a** in Figure 1, when no TED is added to the polymerization solution, the thickness of the PMMA layer increases rapidly after the initial lag period but is followed by a sharp decline in the growth rate. Through complementary kinetic modeling studies, this cessation of layer growth has been primarily attributed to loss of active ends by bimolecular termination.[22]

The data sets labeled **b**−**e** in Figure 1 show the effect of increasing [TED] on the growth of the grafted PMMA layers. As seen in Figure 1, when [TED] = 0.02 mM (data set **b**), the maximum growth rate (observed between 30 min and 1 h exposure time) is slower than when no TED is added; however,

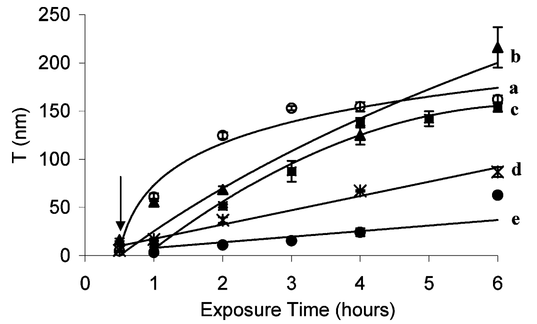


Figure 1. Poly(methyl methacrylate) dry layer thicknesses as a function of exposure time at tetraethylthiuram disulfide (TED) concentrations of (a) 0, (b) 0.02, (c) 0.2, (d) 1, and (e) 2 mM. The thin lines are only to guide the eye. In these experiments, a methyl methacrylate concentration of 4.68 M and a light intensity of 5 mW/cm^2 were used. Error bars represent the standard deviation calculated from repeat measurements using three identical samples (and five thickness measurements per sample).

the thickness of this PMMA layer after 6 h of exposure (209 ± 5 nm) exceeds that of the sample polymerized without TED (162 ± 4 nm). The presence of a thicker layer suggests that the extent of irreversible termination is lower in the presence of TED. At a [TED] of 0.2 mM (data set labeled **c** in Figure 1), a nonlinear increase in PMMA layer thickness is still observed. However, at [TED] of 1 and 2 mM (data sets **d** and **e**, respectively), the measured thicknesses of PMMA layers increase linearly throughout the experiment, albeit the layers grow more slowly compared to the other three cases. A linear increase in PMMA layer thickness throughout the photopolymerization provides evidence that the extent of irreversible termination is less than at the lower TED concentrations studied. These simultaneous decreases in extent of irreversible termination and PMMA layer growth rate are consistent with a shift in the equilibrium of the surface-tethered radicals toward the dormant state.

Thus, on the basis of behaviors exhibited in Figure 1, we conclude that TED decreases the extent of irreversible termination reactions that occur during SI-PMP; however, we also observed that at long times when [TED] = 2 mM, the viscosity of the bulk solution increased. In comparison, we observed no thickening of the solution in control experiments in which a bare silicon substrate was immersed in monomer solution without TED and irradiated for 6 h. These pieces of information suggest that monomer consumption caused by propagation of dithiocarbamyl radicals occurs in solution. This dithiocarbamyl-initiated photopolymerization of MMA has been previously observed by Otsu et al.,[23] Lambrinos et al.,[40] and Turner et al.[41] in their studies of photoiniferter-mediated photopolymerization. NMR analysis was used to quantify the consumption of monomer in solution as a function of exposure time and [TED]. Figure 2 shows monomer conversion as a function of exposure time when no TED was added and at [TED] = 2 mM. As can be seen, monomer conversion becomes significant when TED is added to the system. In the presence of TED, monomer conversion increases with exposure time. Increased monomer conversion, in addition to irreversible termination, reduces the rate of PMMA layer growth at long exposure times.

Because monomer conversion is not significant at short exposure times, even at high TED concentrations, the shift in the equilibrium of the surface-tethered radicals toward the dormant state as a function of increasing [TED] can be inferred by comparing the maximum PMMA layer growth rates obtained during early stages of photopolymerization. As can be seen from Figure 3a, the maximum rate of PMMA layer growth decreases with increasing [TED], implying that the instantaneous concentration of active, surface-tethered radicals decreases as [TED] is increased. As a result, because of the shift in the equilibrium of the surface-tethered radicals toward the dormant state, propagation and extent of irreversible termination are both decreased.

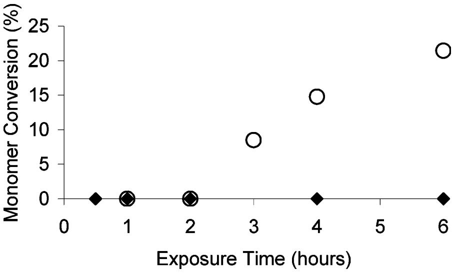


Figure 2. Effect of exposure time on the conversion of methyl methacrylate (MMA) when no tetraethylthiuram disulfide (TED) was added (filled diamonds, ◆) and at a TED concentration of 2 mM (open circles, ○).

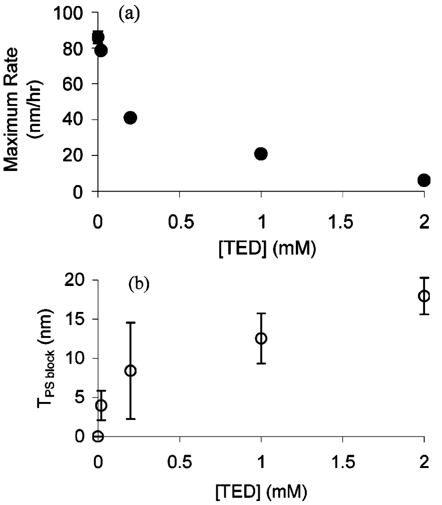


Figure 3. Effect of tetraethylthiuram disulfide concentration [TED] on (a) maximum rate of poly(methyl methacrylate) (PMMA) layer growth and (b) the thickness of poly(styrene) blocks synthesized by reinitiating the PMMA layers that were synthesized at the various TED concentrations shown. The maximum rates were obtained by plotting a straight line through the first two data points for thickness of PMMA layers after the initial lag period (after the exposure time marked by the arrow in Figure 1) for each TED concentration. Error bars in the maximum rates, which are of the size of the datum points or smaller, represent the standard error obtained using linear regression of the multiple measurements. Reinitiation of the PMMA layers (synthesized at a light intensity of 5 mW/cm^2, a methyl methacrylate concentration of 4.68 M, and an exposure time of 6 h) was carried out at an intensity of 5 mW/cm^2, a styrene concentration of 4.34 M, and an exposure time of 4 h.

To support the inference that the extent of irreversible termination decreases upon preaddition of TED, PMMA layers synthesized with 6 h of UV exposure in the presence of TED were reinitiated using styrene as a monomer. All the reinitiation polymerizations were conducted for 4 h in toluene using a light intensity of 5 mW/cm^2 ($\lambda = 365$ nm) and a styrene concentration of 4.34 M without preaddition of TED. Also, a control experiment in which synthesis of a PS layer directly tethered to photoiniferter-modified silicon wafer at the reinitiation conditions was carried out. The thickness of this control PS layer was found to be 76 ± 2 nm. Because all of the reinitiation experiments were conducted under exactly the same conditions, the molecular weights of the PS chains grown during reinitiation of PMMA layers should be approximately constant. Therefore,

Table 1. Static Water Contact Angle of Poly(methyl methacrylate)−Polystyrene (PMMA−PS) Layers along with the Individual Thicknesses of PMMA and PS Layers as a Function of Tetraethylthiuram Disulfide Concentration [TED] Used for the Synthesis of PMMA Layers[a]

[TED] (mM)	PMMA block thickness (nm)	PS block thickness (nm)	static water contact angle (deg)
0	162 ± 4	0	74.3 ± 1.9
0.02	216 ± 21	4 ± 2	90.6 ± 0.3
0.2	154 ± 5	8 ± 6	92.3 ± 2.2
1	87 ± 5	13 ± 3	91.3 ± 3.2
2	63 ± 1	18 ± 2	95.2 ± 0.6

[a] Uncertainties in the reported contact angles represent the standard deviation calculated from three identical samples with three repeat measurements per sample.

owing to steric crowding effects, the ellipsometric thickness of the PS block formed will be a function of the number of PS chains per unit area, which in turn depends on the number of PMMA chains per unit area capable of reinitiating.

Figure 3b shows how the PS block thickness (dry layer) increases as a function of [TED] used during formation of the initial PMMA layer. When no TED was added to the polymerization solution, the PMMA layer could not be reinitiated, indicating the complete loss of active chain ends via irreversible termination reactions during the initial 6 h MMA polymerization. As [TED] increases, the PS block thickness increases, suggesting that the extent of irreversible termination reactions during PMMA layer formation decreases with increasing [TED]. Even at [TED] = 2 mM, however, a significant degree of termination is still believed to occur since the PS block thickness of the sample polymerized under these conditions (18 ± 2 nm) is still significantly less than that of the PS control layer (76 ± 2 nm). These results suggest that TED, which provides deactivating DTC radicals, helps to at least partially preserve DTC-capped PMMA chains that are capable of reinitiation in the presence of PS.

Contact angle measurements were made to confirm that the observed thickness increases seen after reinitiation with styrene are due to the formation of surface-tethered PMMA−PS block copolymers and not due to the formation of PS chains tethered directly to photoiniferter-modified silicon wafer. If surface-tethered PS chains instead of PMMA−PS block copolymers are created, a mixed polymer brush containing individual PMMA and PS chains tethered to the surface would be formed. In this case, because static water contact angles of PMMA and PS are significantly different,[42] a mixed PMMA−PS brush contact angle will reflect the presence of (i) a PMMA surface if PMMA chain length is greater than PS chain length, (ii) a PS surface if PS chain length is greater than PMMA chain length, or (iii) a mixed PMMA−PS surface if PMMA and PS chains are of approximately equal length. Alternatively, a PMMA−PS block copolymer exposed to toluene, which is a better solvent for PS than PMMA, will exhibit contact angle that corresponds to PS.

Table 1 lists the water contact angle of the photopolymerized PMMA−PS layers along with the individual thicknesses of PMMA and PS layers. All measurements were taken after the layers were sonicated in toluene and vacuum-dried. As can be seen from Table 1, a water contact angle of 74.3 ± 1.9°, which corresponds to that of PMMA,[42] was observed when no TED was added to the polymerization solution. This result is expected because no increase in the PMMA layer thickness was observed upon reinitiation with styrene. For TED concentrations of 0.02, 0.2, 1, and 2 mM, static water contact angles of 90.6 ± 0.3°, 92.3 ± 2.2°, 91.3 ± 3.2°, and 95.2 ± 0.6°, respectively, were measured. These contact angles correspond to the static water contact angle of PS.[42] At [TED] of 0.02, 0.2, and 1 mM, the PMMA thicknesses are greater than the thickness of PS layer synthesized at reinitiation conditions, suggesting that the PMMA chain lengths at these [TED] are greater than the length of PS chains formed upon reinitiation. As hypothesized earlier, this comparison of chain lengths and contact angle data indicate that the PMMA layers synthesized at [TED] = 0.02, 0.2, and 1 mM, when reinitiated in the presence of styrene produce PMMA−PS block copolymer, rather than a mixed brush of individual PMMA and PS chains. We note that at [TED] = 2 mM the thickness of the initial PMMA layer is smaller than that of the PS layer grown under control conditions. Nevertheless, on the basis of behaviors observed in the reinitiation studies of PMMA layers made at lower TED concentrations, we believe that reinitiation of PMMA layers grown at [TED] = 2 mM also produce a PMMA−PS block copolymer.

It should be noted that these studies to quantify the impact of TED on PMMA layer growth kinetics and reinitiation capability only prove that preaddition of TED helps reduce the extent of irreversible termination reactions. This decrease in irreversible termination reactions, however, is not sufficient to conclude that preaddition of TED improves the control over SI-PMP. Such a contention requires additional information about the molecular weight (MW) and molecular weight distribution (MWD) of the surface-tethered PMMA chains. To obtain these MW and MWD data, it is necessary to first degraft the PMMA chains from the surface and subsequently characterize them with gel permeation chromatography (GPC) or an analogous technique. Unfortunately, application of any degrafting strategy to low-area substrates is rather impractical because of the insufficient amount of polymer synthesized. Previous efforts to degraft polymer chains synthesized by surface-initiated polymerizations have involved the use of high area substrates such as silica gel.[10,43−44] However, a uniform SI-PMP from photoiniferter-modified silica gel is difficult to achieve because of high solution opacities that can lead to nonuniform exposure of all initiating sites. In addition, molecular weight data obtained from such systems may not accurately reflect the molecular weight distribution of chains grown from flat substrates due to important differences in surface geometry, chain conformation, and ratio of surface to bulk radical concentrations. Therefore, degrafting of PMMA chains to obtain MW and MWD data was not included in this work.

Conclusion

These studies of the impact of TED, a source of deactivating dithiocarbamyl radicals, on the growth of PMMA by SI-PMP reveal interesting tradeoffs: As expected, TED reduces the rate of growth of the layers and decreases the extent of irreversible termination reactions that lead to cessation of polymerization; however, at long times the DTC radicals generated from TED can initiate polymerization in solution, resulting in monomer consumption, which can further retard the rate of propagation. Reinitiation studies using styrene support the contention that preaddition of TED helps to preserve the active ends, leading to an increase in reinitiation efficiency and block copolymer formation, as manifest by increasing PS block thicknesses with increasing [TED]. These studies show that it is necessary to supply a source of deactivating radicals to decrease the extent of irreversible termination reactions during SI-PMP, but this benefit comes at the cost of reducing the rate of polymerization and layer growth. These insights into the kinetic behavior and reinitiation efficiency of SI-PMP in the presence of an added deactivating species highlight the impact and importance of reaction conditions, including amount of TED, on the engineering of soft material interfaces by SI-PMP.

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