

Kinetic Characterization of Surface-Initiated Photoiniferter-Mediated Photopolymerization in Presence of Tetraethylthiuram Disulfide

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Introduction.

Modification of surfaces with covalently grafted polymer brushes is a widely used technique to tailor surface properties such as wettability, biocompatibility, corrosion resistance and lubricity. In the current work, surface-tethered poly(methyl methacrylate) (PMMA) layers were produced via surface-initiated photoiniferter-mediated photopolymerization (SI-PMP). Photoiniters, based on dithiocarbamate chemistries are often utilized as photoinitiators for “living” radical polymerizations in bulk or solution.¹ However; it has been found that, due to a low concentration of deactivating radicals, SI-PMP of methyl methacrylate suffers from irreversible termination reactions, which lead to cessation of polymerization.² Therefore, to suppress the extent of irreversible termination reaction, a source of deactivating dithiocarbamyl species, tetraethylthiuram disulfide (TED), was added to the reaction mixture. The presented work is focused on investigating the impact of TED on the surface-tethered chain growth and the ability of this strategy to preserve active ends during brush formation to allow creation of block copolymers.

Experimental Section

Materials. Purities of methyl methacrylate (MMA), solvents and reagents are described in detail previously.² 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 characterization² 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.²

Photopolymerization. The photopolymerization procedure that includes solution preparation, assembly of the reaction cell, photopolymerization, and post-photopolymerization treatments are described previously.² Solutions of MMA and TED in anhydrous toluene were prepared in airfree 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, 2 mM. The reinitiation of the PMMA layers synthesized at various photopolymerization conditions used styrene as a monomer ([Styrene] = 4.34 M in all cases). The synthesized polymer layers were characterized using contact angle goniometry and variable-angle ellipsometry. The reaction solutions recovered after polymerization were characterized using nuclear magnetic resonance (NMR) spectroscopy.

Results and Discussion.

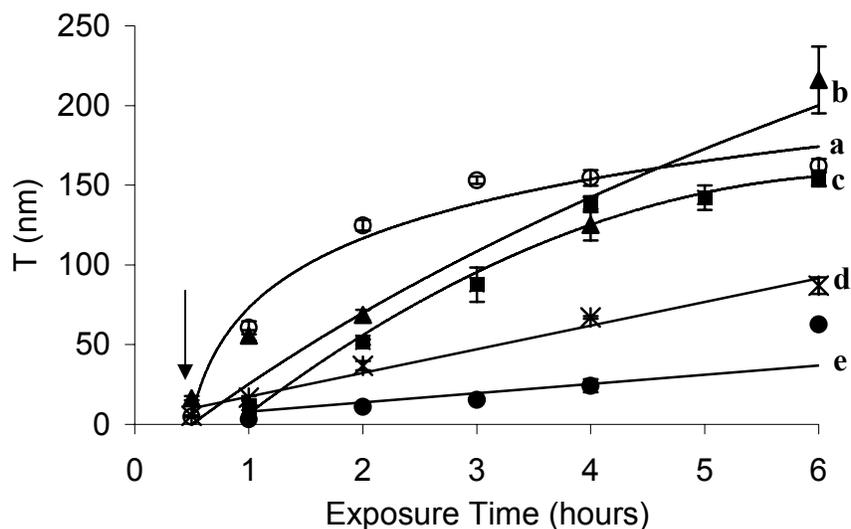


Figure 1. Dry PMMA layer thicknesses at TED concentrations of (a) 0 mM, (b) 0.02 mM, (c) 0.2 mM, (d) 1 mM and (e) 2 mM. The thin lines are only to guide the eye. In these experiments, MMA concentration of 4.68 M and light intensity of 5 mW/cm² were used.

Figure 1 shows how the dry layer thicknesses of grafted PMMA layers increase with polymerization time for various TED concentrations, [TED]. For all measured data sets an initial lag period is observed, after which the PMMA layers grow rapidly. In absence of any TED (curve labeled **a**), this rapid increase is followed by a sharp decline in growth rate, which has been attributed to the loss of active ends by bimolecular termination.² At [TED] = 0.02 mM, the maximum growth rate is slower than that in absence of TED. However, the thickness of this PMMA layer after six hours of exposure (209±5 nm) exceeds that of the sample polymerized without TED (162±4 nm), suggesting 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 non-linear 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, indicating a further decrease in irreversible termination as [TED] is increased. This decrease in irreversible termination results from a shift in the surface-tethered radical equilibrium towards the dormant state at higher [TED] values.

However, we also observed that at long times when [TED] = 2 mM, the viscosity of the bulk solution increased. This increase in viscosity was a result of formation of PMMA chains in bulk through the propagation of dithiocarbamyl radicals. This PMMA formation in bulk was confirmed by quantifying the monomer conversion using NMR spectroscopy. 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.

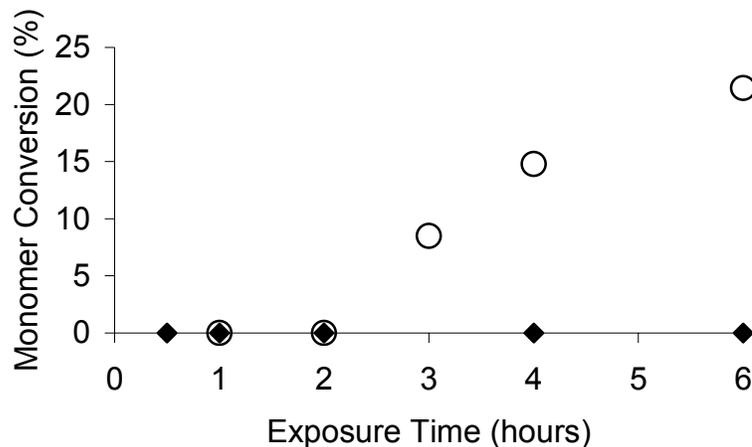


Figure 2. Effect of exposure time on the conversion of MMA when no TED was added (filled diamonds; \blacklozenge) and at a TED concentration of 2 mM (hollow circles; \circ).

To support the inference that increasing [TED] shifts the equilibrium of the surface-tethered radicals towards the dormant state the maximum PMMA layer growth rates obtained during early stages of photopolymerization are plotted as a function of [TED] (Figure 3a). As can be seen, 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. This shift in the equilibrium of the surface-tethered radicals towards the dormant state results a decrease in both the propagation rate and extent of irreversible termination.

To support the conclusion that the extent of irreversible termination decreases upon preaddition of TED, PMMA layers synthesized with 6 hours of UV exposure in the presence of TED were reinitiated using styrene monomer. All the reinitiation polymerizations were conducted for four hours in toluene using a light intensity of 5 mW/cm² ($\lambda = 365$ nm) and a styrene concentration of 4.34 M without TED. Figure 3b shows how the PS-block thickness (dry layer) increases as a function of [TED] used during formation of the initial PMMA layer. As can be seen from Figure 3b, as [TED] increases, the PS-block thickness increases, suggesting that the extent of irreversible termination reactions during PMMA layer formation decreases with increasing [TED].

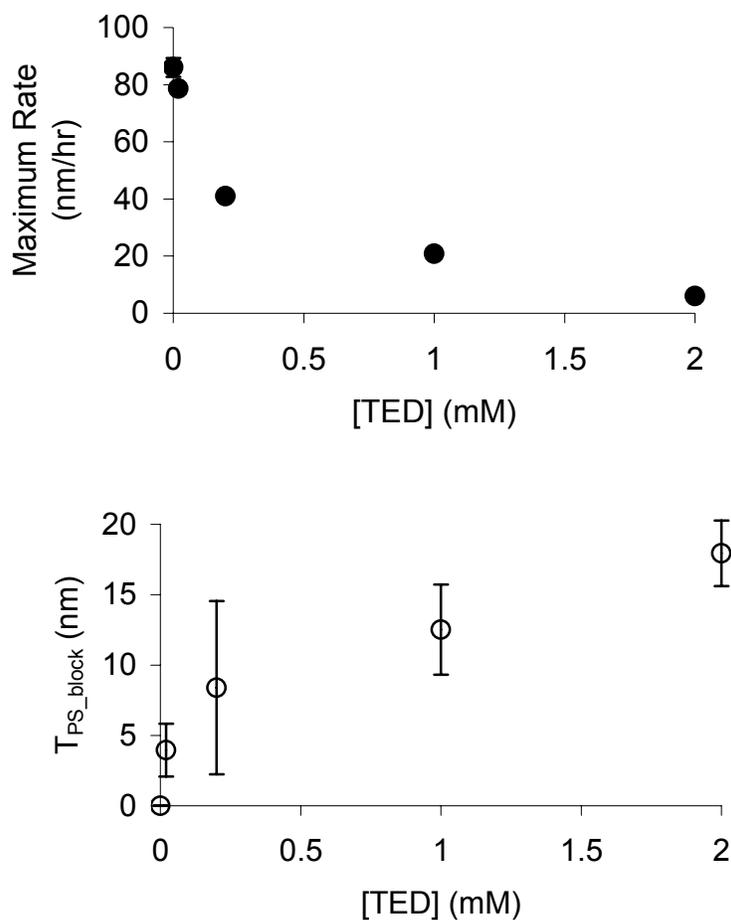


Figure 3. Effect of TED concentration on (a) maximum rate of PMMA layer growth and (b) the thickness of poly(styrene) blocks synthesized by reinitiating PMMA layers previously synthesized at various TED concentrations.

Conclusion.

These studies of the impact of TED on the growth of PMMA by SI-PMP 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. Our results indicate that to achieve high layer growth rates via SI-PMP while maintaining the high percentage of active chain ends necessary for block copolymer formation, moderate concentrations of TED must be combined with large photoiniferter concentrations and light intensities.

References.

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2. Rahane, S. B.; Kilbey, S. M., II; Metters, A. T. *Macromolecules*, **2005**, *38*, 8202-8210.