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Title

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Abstract

A light-mediated method for the facile removal of polymer end groups that are common to controlled radical polymerization techniques is presented. This metal-free strategy is general, being effective for chlorine, bromine, and thiocarbonylthio moieties as well as a number of different polymer families (styrenic, acrylic, and methacrylic). In addition to solution reactions, this process is readily translated to thin films, where light mediation allows the straightforward fabrication of hierarchically patterned polymer brushes.

Graphical Abstract
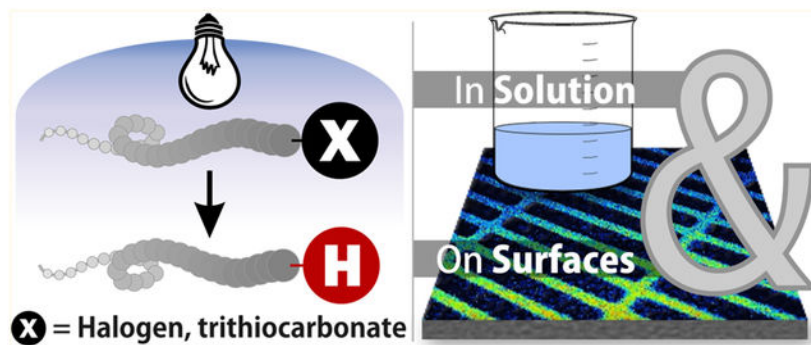
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INTRODUCTION

The ability to control molecular weight, architecture, and comonomer incorporation in the production of polymers has facilitated access to functional materials with diverse and targeted properties. Controlled radical polymerization techniques[1–4] such as atom transfer radical polymerization (ATRP)[1] and reversible addition–fragmentation chain transfer (RAFT)[5] polymerization have been successfully used to commercially produce polymers[1,6–8] from readily available starting materials under mild conditions. Both ATRP and RAFT processes require the presence of chain ends that can undergo reversible activation to give propagating radicals as a prerequisite for control. These chain ends are chemically reactive and thermally unstable, which negatively influences long-term stability and is problematic for polymer processing.[9–14] For example, the elimination of toxic and corrosive hydrobromic (HBr) or hydrochloric acid (HCl) during thermal decomposition of ATRP polymer chain ends leads to a range of issues, including acid-catalyzed ester degradation and corrosion.[10] Challenges related to polymerization-active chain ends also extend beyond solution-processed materials. The fabrication of patterned, functional polymer surfaces serves as an example where chain end removal with spatial control is often desirable for surface passivation and long-term stability.[15–17]

In previous work, spatial control has been achieved in the production of surface-grafted polymer brushes through deactivation by particle beams,[18] UV irradiation,[19–22] or light-mediated atom transfer radical addition (ATRA).[23,24] However, the former methods are considered high cost, low throughput, and destructive while the latter method (ATRA) does not remove the halogen, merely changing its reactivity.

Our group has recently described the use of a reducing photoredox catalyst—10-phenylphenothiazine (PTH)—for the dehalogenation of small molecule halides.[25,26] In this contribution, we apply this approach to efficiently remove the chain ends that are common to controlled radical polymerizations (see Figure 1). This mild, metal-free, and operationally simple method is applicable to a number of different polymer classes and is compatible with diverse chemical functionalities. Rigorous deoxygenation, anhydrous conditions, and elevated temperatures are all rendered unnecessary. In addition, the use of visible light as an external stimulus for catalyst activation allows spatial control and localized dehalogenation of surface-grafted polymer brushes. As a consequence, a much greater range of materials systems can be used in the preparation of soluble and grafted polymer chains.

DISCUSSION

To initially demonstrate this metal-free chain end removal strategy, PTH in the presence of formic acid and tributylamine was used to debrominate a linear polystyrene–Br derivative (PS-Br, Figure 2a). Efficient chain end removal was confirmed via analysis of the characteristic ^{1}H NMR signal at δ(CH-Br) = 4.5 ppm. As evident from Figure 2b,c, this key resonance, corresponding to the methine proton on the terminal styrene unit adjacent to the ω-end C–Br bond, was no longer detectable after 6 h of reaction. Size exclusion chromatography (SEC) showed no appreciable changes in molecular weight or polydispersity (see Figure S1), indicating the absence of undesired side reactions (e.g.,

polymer degradation, chain scission, chain–chain coupling) with field-desorption mass spectrometry (FD-MS) providing additional evidence for quantitative hydrogenation (see Figure 3). Prior to dehalogenation (Figure 3a), the absolute mass of each peak corresponds to a polystyrene chain with ethyl isobutyrate at the α-end and bromine at the ω-end. After reaction (Figure 3b), the spectrum was shifted by $m/z = 78.9$ (loss of Br and addition of H), reaffirming the successful removal of the bromine chain end and full retention of polymer structure. Control experiments under the same conditions, in the absence of either PTH or light, showed no dehalogenation, even after 24 h with analysis by ^{1}H NMR revealing only starting material (see Supporting Information).

The removal of dormant Br chain ends is not only of considerable importance for chemical but also for thermal stability and related polymer processing (vide supra). Indeed, thermogravimetric analysis (Figure 4) showed increased thermal stability for the dehalogenated PS-H when compared to the initial PS-Br. In direct contrast to PS-Br, which lost 7 wt % at $T = 215$ °C (corresponding to HBr) with the onset of complete decomposition at $T = 390$ °C, the dehalogenated PSH polymer was thermally stable even above 325 °C with the onset of degradation for PS-H being delayed until ~400–420 °C.

The versatility of PTH-based chemistry for chain end removal was reinforced by its successful implementation with other polymer families. For the dehalogenation of poly(*tert*-butyl acrylate)-Br, loss of the halogen chain end was confirmed by the disappearance of the ^{1}H NMR signal at $\delta = 4.4$ ppm (CH-Br) (Figure S4). Again, no precautions were taken to ensure an inert environment during the reaction. Similar reactivity was observed for the removal of chloro-based chain ends (Figure S6). Significantly, macromolecules synthesized via RAFT polymerization with thiocarbonylthio RAFT chain ends also underwent facile deactivation and conversion to hydrogen (see Scheme 1 and Figure S7). In the latter case, the UV activity of the thiocarbonylthio moiety (absorption maximum, $\lambda_{\max} = 310$ nm) served as a marker to monitor the progress of this reaction via SEC (Figure S8). Again, SEC indicated no appreciable change in molecular weight or dispersity for all samples studied, reaffirming the mild and nondestructive nature of this process.

Having demonstrated applicability to a wide range of polymeric starting materials in solution, our attention was drawn to the passivation of polymer brushes. The ability to pattern surfaces and remove reactive chains ends is useful for a variety of applications, and therefore we envisioned the translation of this chemistry to surfaces would be further enabled by the robust reaction conditions.

For the formation of complex 2-D and 3-D grafted polymer brushes, the selective termination of polymer chain ends allows for hierarchical patterning via surface-initiated ATRP (SIATRP).[16,17,23,27–29] Figure 5 summarizes the advantages and disadvantages of common techniques for modulating the reactivity of polymer brushes through nucleophilic substitution[15,30–32] and ATRA.[23,24] This comparison with the PTH-based dehalogenation strategy described above clearly illustrates the potential advantages of this robust and spatially controlled alternative for polymer brush deactivation.

Initial experiments were directed toward the uniform debromination of a silicon oxide substrate functionalized with the ATRP initiator undecyl 2-bromoisobutyrate (see Figure 6). X-ray photoelectron spectroscopy (XPS) was employed to detect the presence of bromine-containing functional groups on the substrate. For the substrate functionalized with immobilized ATRP initiators (Figure 6c), the bromine 3d orbital contains two components: the $3d_{5/2}$ and $3d_{3/2}$ doublet at binding energies BE = 69 eV and BE = 70 eV, respectively, as a result of spin–orbit splitting. Figure 6d illustrates disappearance of this Br 3d peak, confirming that irradiation at λ = 405 nm in the presence of PTH was capable of removing the halogen from the ATRP initiating layer.

To illustrate the spatial fidelity of this light-mediated process, localized debromination of ATRP-initiator functionalized wafers was investigated by irradiation through a photomask with 20×200 μm^2 clear rectangles. The photomask was subsequently removed, and poly(methyl methacrylate) (PMMA) polymer brushes were grown via light-mediated radical polymerization.[33,34] Optical microscopy, secondary ion mass spectrometry (SIMS), and atomic force microscopy (AFM) confirmed spatially confined growth of polymer brushes exclusively in areas which were not previously irradiated/dehalogenated in the presence of PTH (Figure 7).

The utility of this process was further demonstrated by transitioning from the debromination of monolayers to the dehalogenation of surface-grafted polymer brush chain ends. As illustrated in Figure 8a, a uniform PMMA brush layer was initially grown (thickness 39 ± 2 nm), followed by spatially controlled dehalogenation by irradiation through a binary photomask with 2.5×25 μm^2 clear rectangles. Removal of the photomask and homogeneous polymerization of a second monomer, 2,2,2-trifluoroethyl methacrylate (TFEMA), resulted in a chemically patterned surface composed of PMMA homopolymer and PMMA-*b*-PTFEMA diblock brushes. Both optical microscopy (Figure 8b) and SIMS (Figure 8c) confirmed successful patterning via spatially controlled dehalogenation and subsequent polymer brush extension. Detection of fluorine (^{19}F) and carbon (^{12}C) fragments in SIMS confirmed the spatial confinement of TFEMA exclusively in areas with PMMA-*b*-PTFEMA diblock copolymer brushes (Figure 8c).

CONCLUSIONS

This report describes a fully organic, light-mediated approach for the efficient removal of ATRP (Br, Cl) or RAFT (thiocarbonylthio) polymer chain ends from a variety of different polymer backbones. The facile and robust nature of this approach does not require elevated temperatures or inert reaction conditions, occurring with high efficiency under ambient conditions. Further, dehalogenation of both ATRP initiator monolayers and surface-grafted polymer brushes affords a novel and versatile procedure for surface patterning. Soluble and supported polymers with improved thermal and chemical stability can now be obtainable under mild, metal-free conditions and with external regulation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGMENTS

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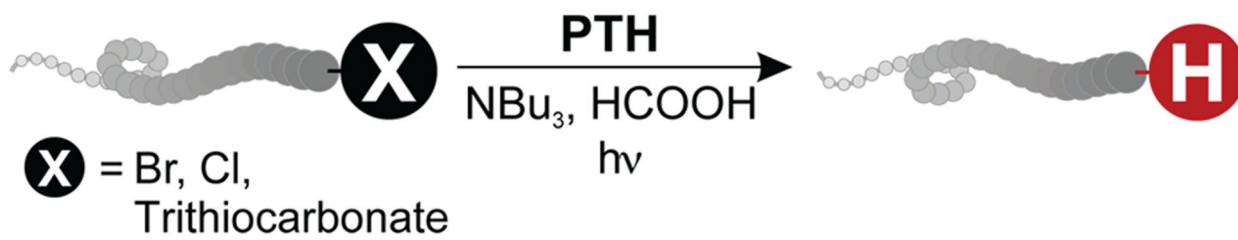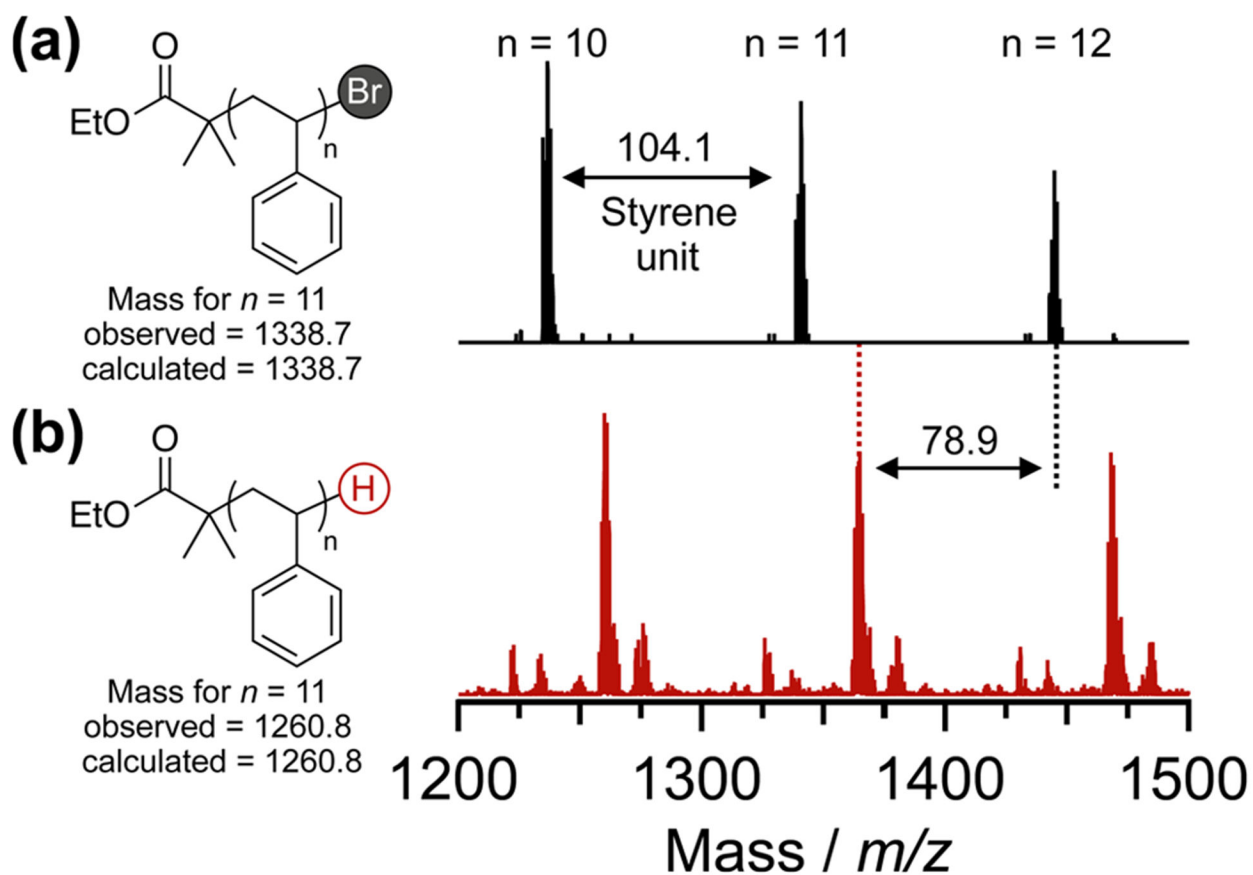
Figure 1.
Graphical representation of the metal-free removal of terminal polymer chain end groups common to controlled radical polymerizations.
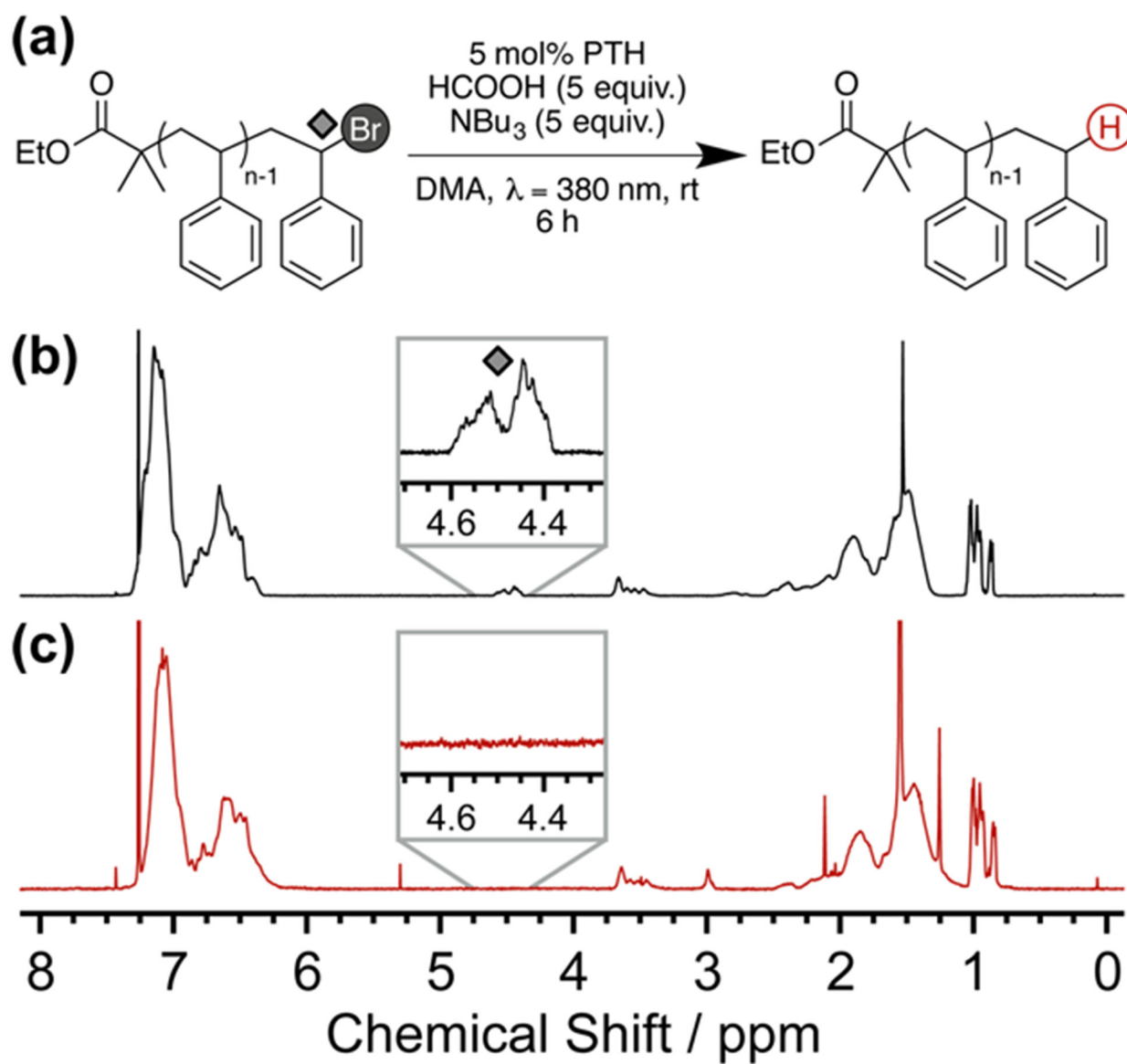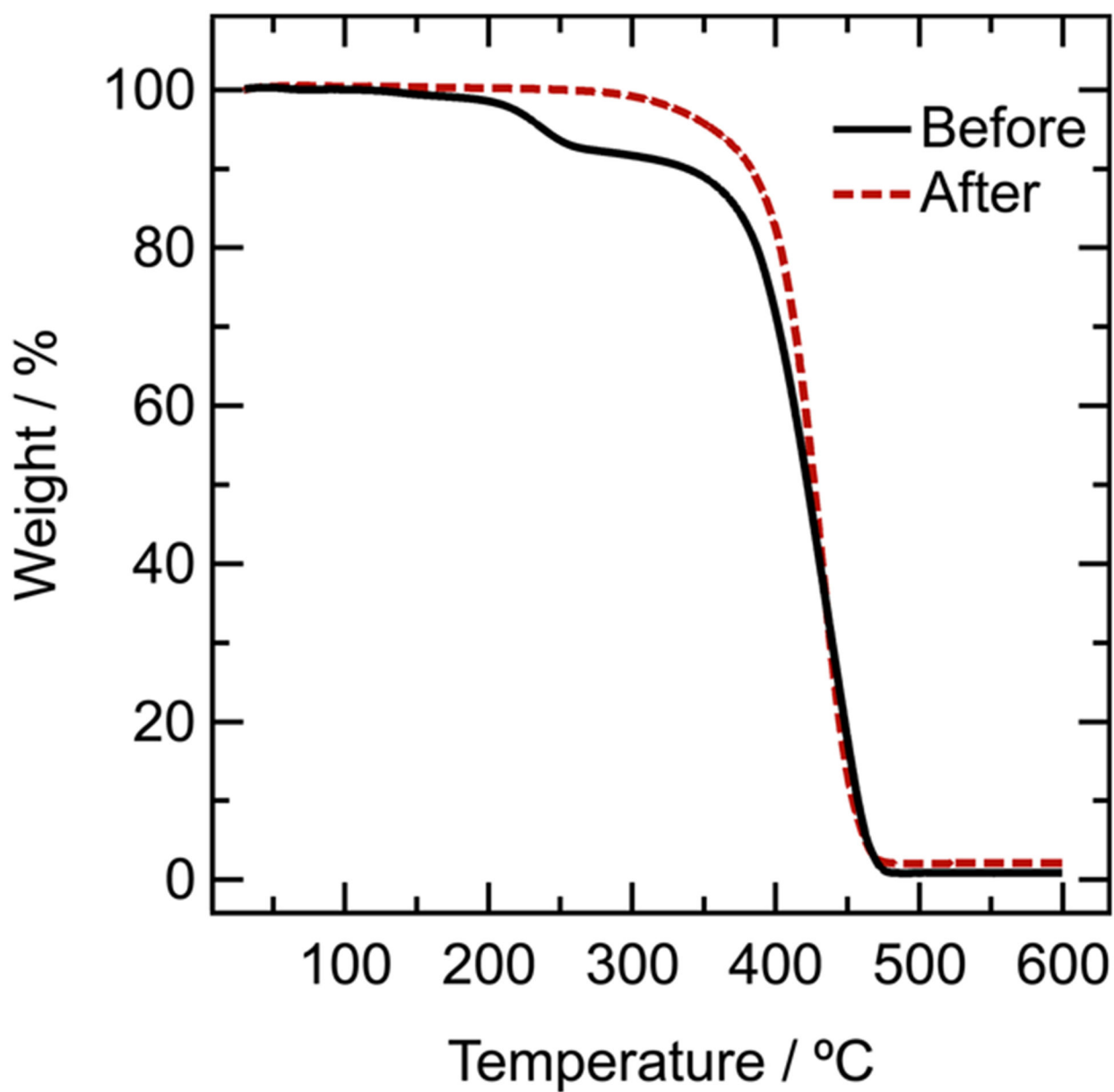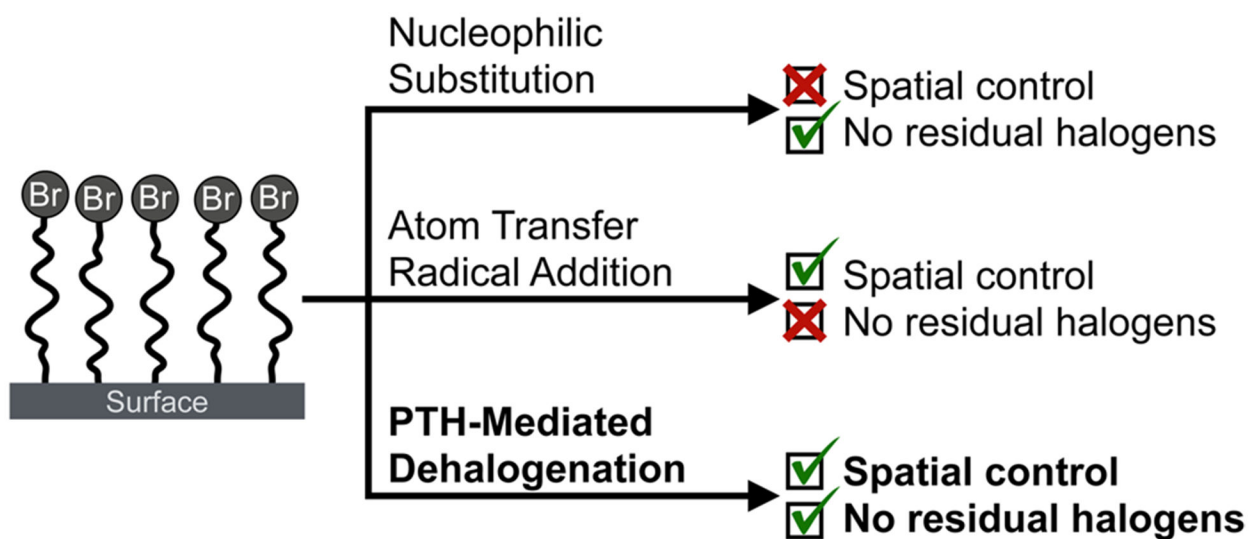
Figure 2.
(a) Synthetic strategy for debromination of linear polystyrene. (b) ^{1}H NMR spectrum of polystyrene-Br and (c) ^{1}H NMR spectrum of the dehalogenated polymer. Insets emphasize the loss of the a-Br proton signal, indicative of successful dehalogenation.
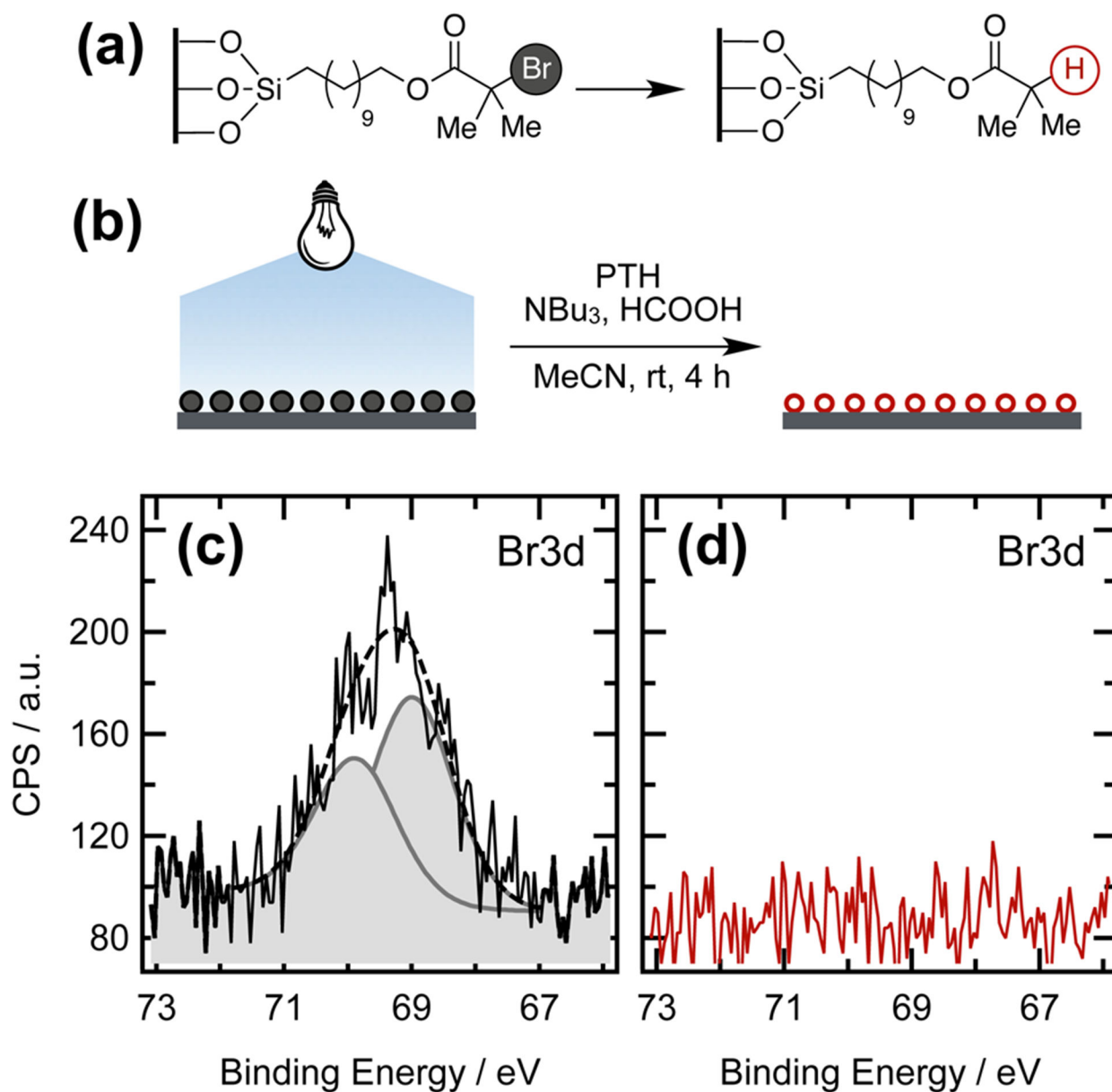
Figure 3.
FD-MS spectra of (a) the unmodified PS-Br polymer and (b) dehalogenated PS-H confirmed the loss of bromine chain ends.
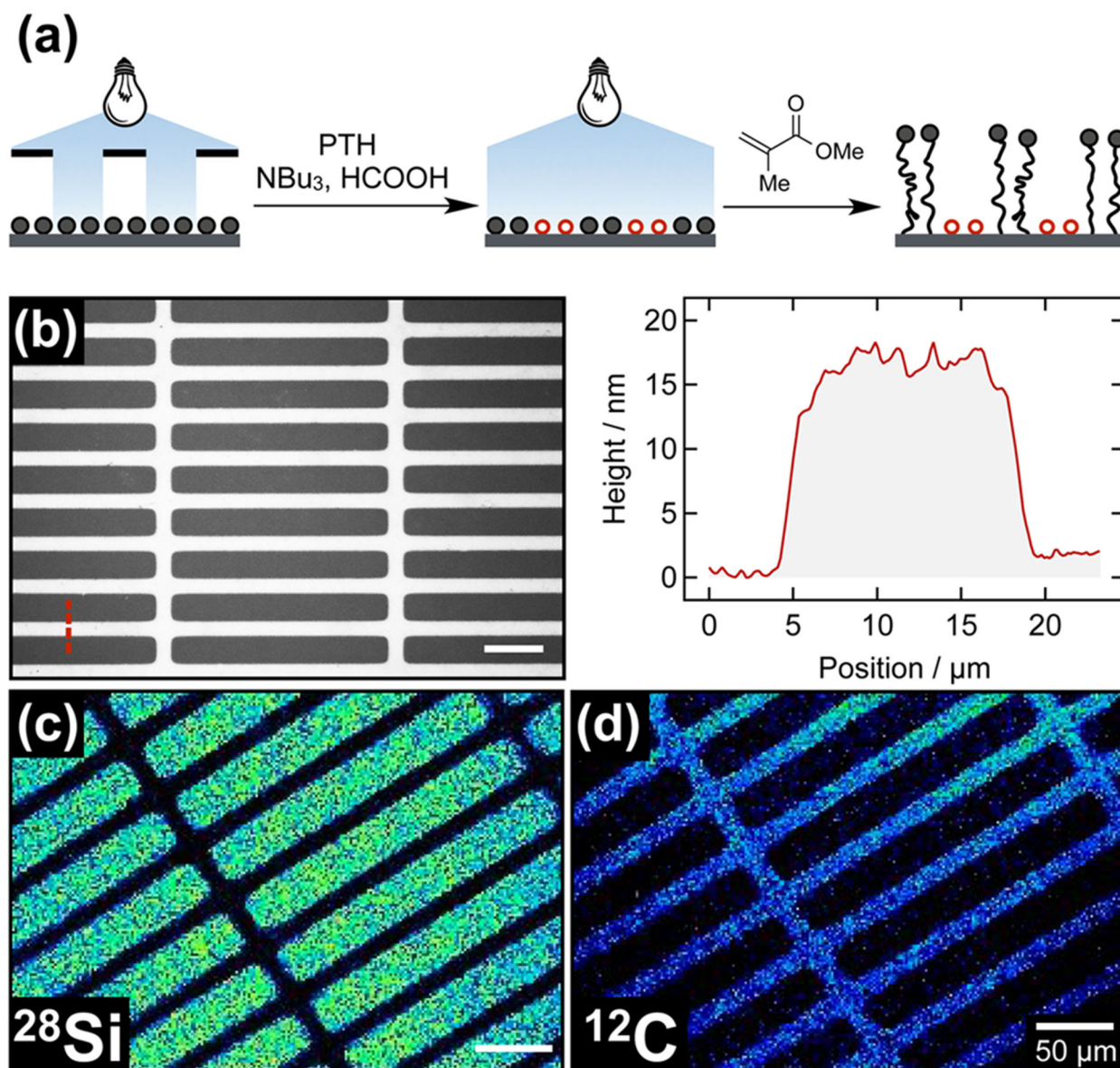
Figure 4.
Thermogravimetric analysis (TGA) of polystyrene with bromine chain end (solid black line)
and after dehalogenation (red dashed line).

Figure 5.
Comparison of the visible-light-mediated dehalogenation strategy, which combines both spatially and chemically controlled removal of reactive halogens, with traditional approaches based on nucleophilic substitution and ATRA chemistry.
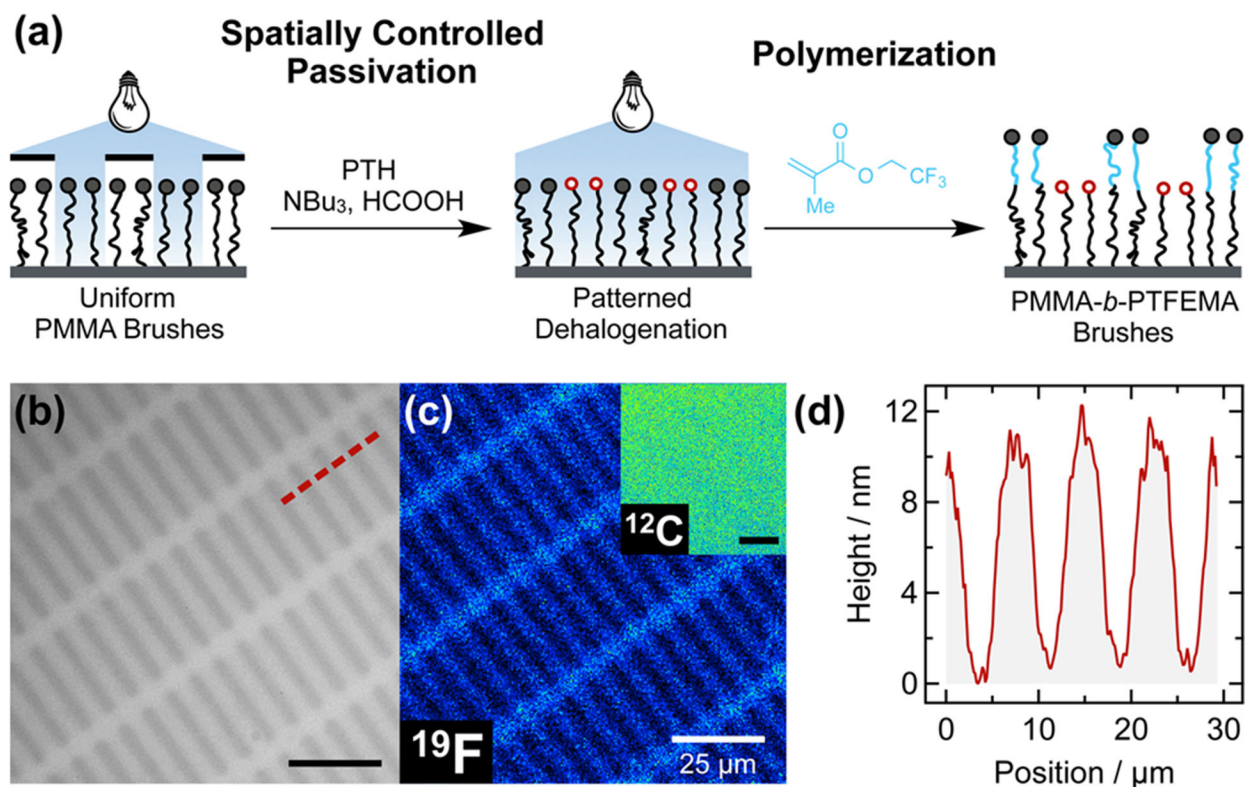
Figure 6.
(a) Synthetic strategy and (b) schematic representation showing the uniform dehalogenation of a-bromoisobutyrate functionalized silicon surfaces. High-resolution XPS scans provided evidence for (c) the brominated ATRP initiator for the untreated substrates and (d) the absence of Br signals after PTH-catalyzed dehalogenation. Gaussian bell curves (c) correspond to the Br $3d_{5/2}$ and Br $3d_{3/2}$ orbitals. The dashed line represents the sum of both bell curves.

Figure 7.
(a) Spatially confined dehalogenation of a-bromoisobuty-rate-functionalized silicon substrates by irradiation through a binary photomask with $20 \times 200 \ \mu m^2$ clear rectangles, followed by subsequent homogeneous irradiation and light-mediated polymerization of MMA. (b) Optical micrograph (left) of the resulting patterned PMMA brushes confirmed the absence of polymer growth within the dehalogenated rectangles. AFM (right) indicated 15 nm polymer brush height and provided additional evidence for the absence of polymer in dehalogenated areas. SIMS chemical maps for (c) silicon and (d) carbon fragments confirmed spatially confined polymerization. All scale bars are 50 μm.

Figure 8.
(a) Patterned diblock copolymer brush formation via spatially controlled dehalogenation and subsequent uniform polymerization of TFEMA. (b) Optical micrograph of the patterned polymer brushes. (c) ^{19}F fluorine and (inset) ^{12}C carbon SIMS scans confirmed localized presence of fluorine (PMMA-*b*-PTFEMA brushes) atop a uniform MMA polymer brush layer. (d) AFM height profile of the patterned PTFEMA brushes along the dashed line in (b) confirmed patterning and allowed quantification of brush height increase after block copolymerization. Scale bars in (b, c) are 25 μm.
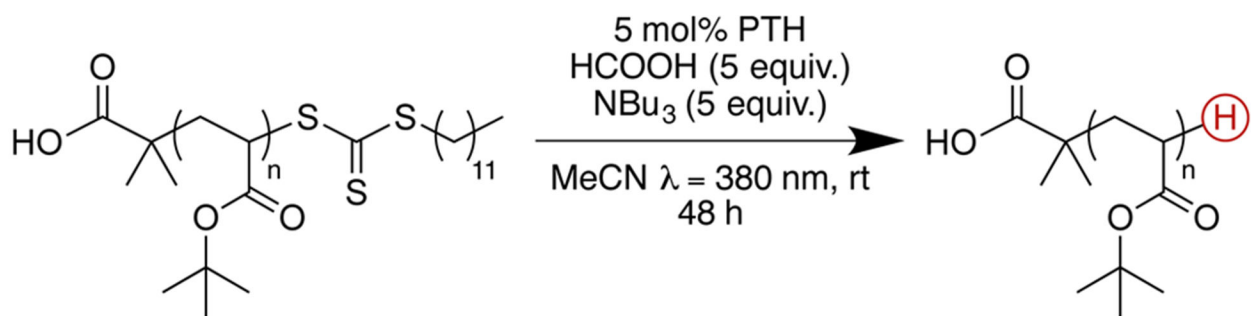
Scheme 1.
Synthetic Strategy for the Facile Deactivation and Conversion of Thiocarbonylthio RAFT
Chain Ends to Hydrogen