

Direct Functionalization of Polyethylene Surfaces with High-Density Polymer Brushes

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ABSTRACT: Introducing functionality onto PE surfaces is a longstanding challenge in polymer science, driven by the need for polymer materials with improved adhesion and antifouling properties. Herein, we report surface-initiated hydrogen atom transfer-reversible addition–fragmentation chain transfer (SI HAT-RAFT) as a robust method to grow high-density brush polymers from PE surfaces. We demonstrate that, under mild conditions, direct initiation from the C–H bonds of PE surfaces allows for the graft polymerization of a variety of (meth)acrylate monomers. The resulting polymer brushes reached several hundred nanometers in thickness with densities of *ca.* 0.62 chains/nm², compared to the current standard of \sim 0.28 chains/nm². Finally, we show that our method is capable of dramatically improving the adhesive properties of PE surfaces. This work enables the preparation of PE with diverse surface functionalities for potential use in biomedical, industrial, and battery applications.

Polyethylene (PE) is ubiquitous in our society, with over 100 million tons produced annually.¹ The widespread use of PE is enabled by its superior bulk properties and low cost; PE is strong, tough, lightweight, and chemically resistant. Despite these advantages, poor surface properties such as low adhesivity and wettability limit its use in applications such as battery membranes, packaging, and automotive materials, all of which require interfacing with other plastics, metals, and solvents.^{2,3} Furthermore, the surface of PE contains only unactivated C–C and C–H bonds, making it challenging to modify.⁴ This difficulty in functionalization hampers the synthesis of PEs with high-performance surfaces such as antifouling biomedical implants, antibacterial high-touch surfaces, or chemically selective filtration membranes. A method to imbue PE surfaces with improved or novel properties would facilitate the development of next generation polymeric materials.

Previous attempts to modify the surface chemistry of PE have relied on either oxidation of the PE surface or impregnating PE films with a photosensitizer. In the first case, oxidative functionalization to yield carboxylic acids or free radicals on the surface is carried out under harsh conditions using strong acids or plasma.^{5–8} This approach requires specialized equipment and often leads to degradation of PE chains at the surface.⁹ Furthermore, the resulting small molecule functionality tends to migrate into the bulk of the polymer to lower surface energy, leading to a short lifetime of functionalization.⁹ In the second case, a PE film is first soaked in benzophenone photosensitizer, dried, and finally polymer is grafted from the sensitized surface under UV irradiation.^{10–13} While this method is often used to prepare biomedical materials,¹⁴ its multistep nature and frequently reported low grafting densities make it difficult to efficiently functionalize PE surfaces.

In 2020, our group reported hydrogen atom transfer reversible addition–fragmentation chain transfer (HAT-RAFT) polymerization, a method to directly initiate controlled polymerization from hydridic to neutral polarity C–H bonds.¹⁵ We demonstrated that using visible light, a benzophenone photocatalyst, and a disulfide, we can initiate controlled polymerization of acrylic monomers directly from a variety of H atom sources, including cyclohexane. We hypothesized that because both cyclohexane and PE have C–H bonds with similar polarities, our HAT-RAFT method could be applied to grafting polymers from PE substrates. In the proposed mechanism of HAT-RAFT, the photocatalyst performing HAT is turned over by the disulfide species, allowing each photocatalyst to abstract multiple hydrogen atoms. We envisioned that this turnover would generate high-density polymer brushes, and that the vast scope of acrylic monomers available would make possible a wide range of surface functionalities. Here, we report surface-initiated HAT-RAFT (SI HAT-RAFT) as a method for the synthesis of high-density brush polymers on PE surfaces (Figure 1).

We began our studies by layering a solution of benzophenone derivative (1), bis(trithiocarbonate) disulfide species (2), *tert*-butyl acrylate, and dioxane on top of a high-density polyethylene (HDPE) film and covering it with a glass slide before irradiating with visible light from a compact fluorescent light (Figure 2a, reaction setup depicted in the SI). We chose HDPE as a starting point due to its attractive bulk

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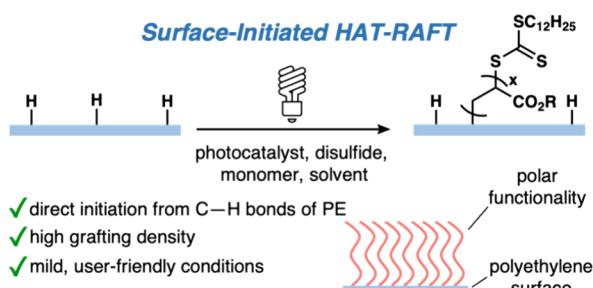


Figure 1. Surface-initiated HAT-RAFT leverages direct initiation from the surface of PE to allow for facile synthesis of high-density brushes.

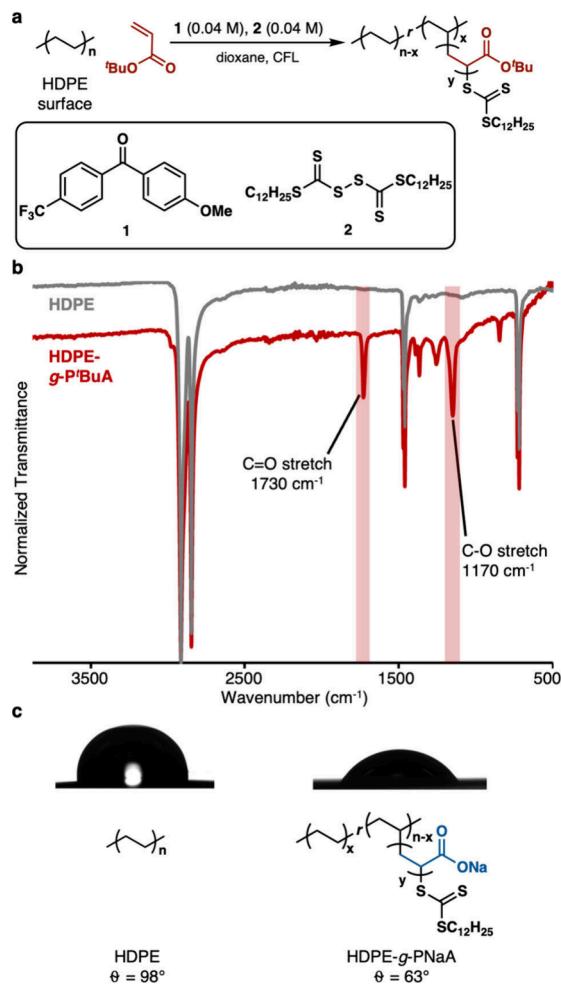


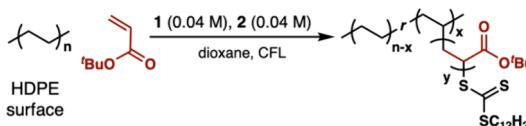
Figure 2. (a) Standard reaction conditions for SI HAT-RAFT from PE. (b) IR spectra of unfunctionalized HDPE and HDPE-g-P^tBuA. (c) Static water contact angle for HDPE and HDPE-g-PNaA.

properties and wide range of potential applications. Dioxane, a solvent with suitably hydridic C–H bonds for HAT-RAFT, was selected because surface-initiated RAFT systems typically require a sacrificial chain transfer agent; dioxane-initiated chains in solution likely promote surface polymerization by facilitating chain transfer in surface-bound polymer chains.^{16–18} Following irradiation, we detected carbonyl and C–O bond stretches in the IR, indicating that poly(tert-butyl acrylate) (P^tBA) was successfully installed on the surface of PE (Figure 2b). Upon basic hydrolysis of P^tBA to poly(sodium acrylate) (PNaA), the static water contact angle of the surface

decreased from 98° to 63°, indicating a dramatic increase in the hydrophilicity of the surface (Figure 2c).

We then carried out a series of control experiments to verify that the polymer observed on the surface was in fact grafted covalently via the HAT-RAFT process. Free P^tBA drop-cast onto an HDPE surface washed away easily, suggesting no adhesion of P^tBA to HDPE in the absence of covalent bonds between the surface and the grafted polymer (Table 1).

Table 1. SI HAT-RAFT Controls



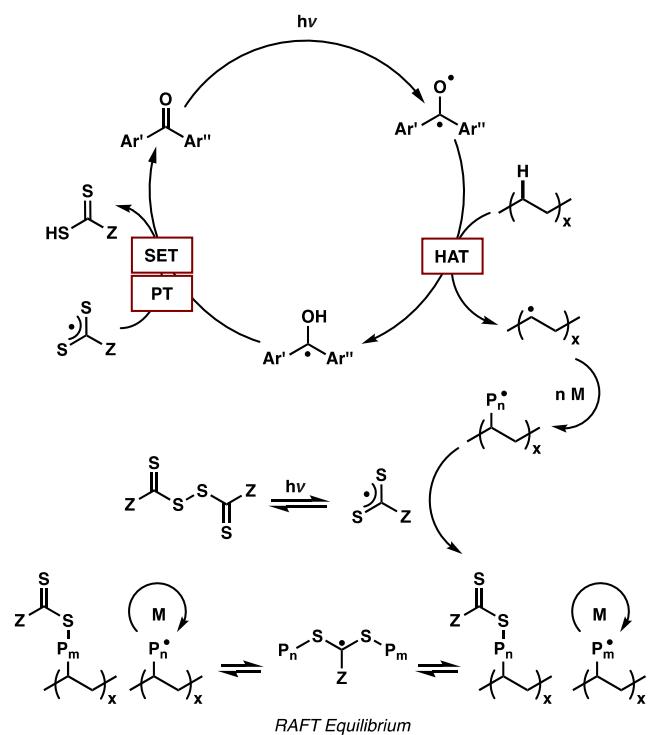
Conditions	Strong IR stretch at 1730 cm⁻¹
Standard Conditions	+
Drop cast P ^t BuA onto HDPE	-
Thermal RAFT	-
No light	-
No disulfide	-
PET instead of HDPE	-

Additionally, subjecting HDPE to thermal RAFT polymerization conditions yielded no polymer on the surface, confirming that generation of radicals alone is not enough to graft from HDPE. We also found that under standard SI HAT-RAFT conditions but in the absence of light, polymerization does not proceed.

Interestingly, under normal SI HAT-RAFT conditions but in the absence of disulfide, negligible polymer is observed by IR (Table 1). This suggests that despite the relatively high concentration of photocatalyst as compared to surface C–H bonds, the presence of disulfide to turn over the photocatalyst is crucial to attain significant amounts of brush polymer on the surface. In our proposed mechanism, the photocatalyst initiates chains both from the PE surface and from the dioxane in solution. Due to its ether functionality, the C–H bonds of dioxane are better polarity matched to the electrophilic photocatalyst than the C–H bonds of the PE surface. It is likely that in absence of the disulfide species, the photocatalyst does a small amount of initiation from the surface which is difficult to observe by IR, as well as a significant amount of the more kinetically favorable initiation from dioxane. Without the disulfide species to turn over the photocatalyst, it is not possible to achieve a significant amount of hydrogen atom abstraction from the PE surface. The X-ray-photoelectron spectroscopy (XPS) data showed sulfur from the disulfide in the grafted PE, supporting the presence of chains capped by the disulfide as in the solution HAT-RAFT process (SI). Finally, we subjected PET (polyethylene terephthalate) to our standard surface polymerization conditions. Because the C–H bonds present in PET are acidic, we anticipated that the kinetic barrier to HAT would be too high for functionalization. As expected, we were unable to graft P^tBA from a PET surface due to the electron-poor nature of the polyester. Together, these results suggest that surface-initiated HAT-RAFT is likely to proceed through our proposed mechanism and operates with similar kinetic selectivity to the solution polymerization. Visible light from the CFL excites the benzophenone photocatalyst, which abstracts a hydrogen atom from PE to generate a carbon centered radical. This radical adds into

monomer before being capped by half of the disulfide (previously homolyzed under visible light). As chains continue to form on the surface, they enter the RAFT equilibrium, likely assisted by chains in solution initiated by dioxane. The consumed photocatalyst is turned over by single electron transfer (SET) and proton transfer (PT) to half of the disulfide species to begin the catalytic cycle again (Scheme 1).

Scheme 1. Hypothesized SI HAT-RAFT Mechanism



Having shown that we can grow polyacrylates from a PE surface, we set out to better characterize the brush polymers produced through microscopy experiments. A silicon wafer was spin-coated with linear low-density polyethylene (LLDPE) to form the substrate and then grafted with P'BA. LLDPE was used for brush characterization due to its greater solution processability relative to HDPE. Atomic force microscopy (AFM) was used to assess brush thickness (Figure 3). For our LLDPE-g-P'BA sample, we achieved a brush thickness of 260 nm. In uncontrolled, photosensitized systems, brush thicknesses up to 160 nm have been achieved,¹⁴ and in ATRP polymerizations from PE copolymers, only ~50 nm of polymer brush have been attained.¹⁹ Excitingly, we are also able to tune film thickness by controlling the reaction time; after 1 h, we achieve a brush thickness of 34 nm, and after 4 h, we reach 108 nm of brush thickness (SI).

To investigate the brush density achieved by SI HAT-RAFT from PE, we carried out a swelling study of an LLDPE-g-PNaA surface (Figure 3b). According to classic scaling laws for polyelectrolyte brushes, the ratio of swollen to dry brush thickness can be described as a function of grafting density, independent of molecular weight.²⁰ After incubation in a pH 9 buffer solution for 10 min, the film thickness increased from 450 to 600 nm. This swelling ratio corresponds to a brush density of 0.62 chains/nm² (see the SI for calculation). In comparison, Takahara and co-workers estimate that their SI-ATRP system from HDPE copolymers has a grafting density of

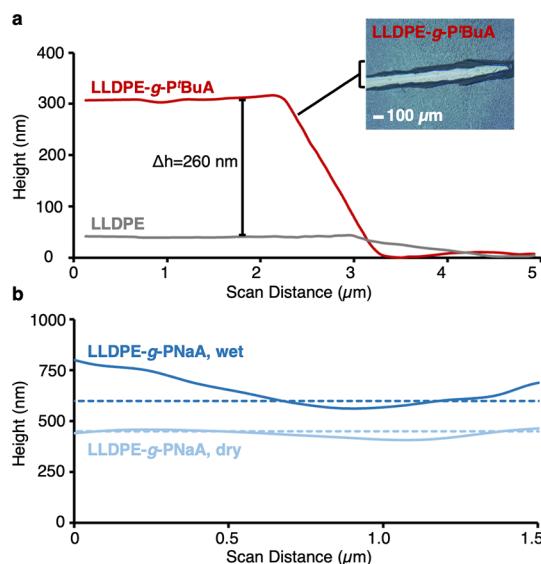


Figure 3. (a) AFM measurement of LLDPE-g-P'BuA brush thickness. Brush thickness is assessed by comparing the depth of a scratch (pictured here by optical microscopy) in an LLDPE film before and after grafting. (b) AFM swelling study of LLDPE-g-PNaA in pH 9 buffer solution shows the wet film swells 63% relative to the dry film. The dashed lines denote the average film height over the scan distance.

0.28 chains/nm.¹⁹ Other reports employing uncontrolled, photosensitized polymerization strategies from PE typically do not quantify brush density.^{5,11–15,21} This high grafting density is also supported by following the water contact angle as polymerization proceeds. After an initial decrease over the first hour of polymerization, the water contact angle remains relatively constant (SI). This behavior is consistent with brush polymers in the high-density regime.²¹ We believe that the high grafting density is due to the photocatalyst turnover by the CTA, allowing for multiple cycles of hydrogen atom transfer. Currently, there are no other methods for grafting from PE surfaces that report such a high grafting density.

To demonstrate the diversity of PE surfaces accessible with SI HAT-RAFT, grafted polymer surfaces were prepared using a variety of acrylate and methacrylate monomers (Figure 4). Static water contact angles ranging from 63° to 86° are accessible, showing that hydrophilicity is tunable by the choice of monomer. Hydrophilicity can also be tuned by protonating or deprotonating the brushes. For example, in their protonated form, PAA brushes have a water contact angle of 72°. In their deprotonated, water-soluble PNaA form, the water contact angle falls to 63°. In the interest of synthesizing biomedically relevant surfaces, we examined a sulfobetaine zwitterion acrylate and a PEG acrylate. The sulfobetaine monomer has previously been shown to prevent bacteria from adhering to surfaces,²² making it a promising candidate for creating antifouling PEs. While the water contact angle observed for this monomer is relatively high compared to other sulfobetaine brushes,²³ likely due to low grafting density, we anticipate that further optimization of SI HAT-RAFT for zwitterionic monomers will facilitate the synthesis of more hydrophilic surfaces. Poly(PEG) acrylates are currently of interest as a replacement for traditional linear PEG polymers, where they may be used to minimize nonspecific binding or to aid in drug delivery.²⁴ PEG coated PEs are also desirable for their use in Li ion battery separators, where they have been shown to improve

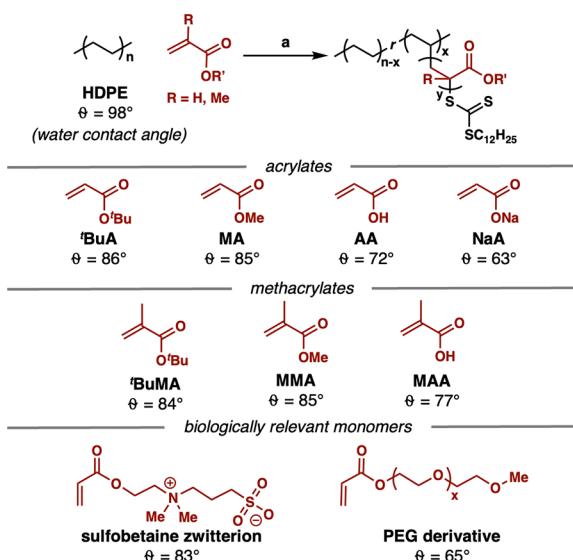


Figure 4. Monomer scope of SI HAT-RAFT, where a is the standard reaction condition: photocatalyst **1** (1 equiv), CTA **2** (1 equiv), monomer (200 equiv), and dioxane (0.04 M in CTA) irradiated with a CFL at room temperature in a nitrogen atmosphere for 16 h. For the sulfobetaine zwitterion and the PEG derivative, water was used in place of dioxane. For the sulfobetaine zwitterion, the reaction was run at half the overall concentration due to poor monomer solubility.

conductivity relative to HDPE alone.²⁵ Excitingly, surface polymerization of a PEG acrylate from HDPE decreased the water contact angle of the surface to 65°, providing a highly hydrophilic surface. HDPE-g-poly(PEG acrylate) surfaces could be promising candidates for applications in biomedical or battery science.

Finally, an important implication of modifying the surface properties of PE is improving its adhesion to other materials such as plastics, metals, or paint. To probe the ability of surface functionalized PE to adhere to paint, we prepared an HDPE-g-[PMMA-*co*-PⁿBuA] brush polymer surface and an unfunctionalized HDPE surface and coated both substrates with acrylic paint (Figure 5). Although the exact composition of most acrylic paints is proprietary, acrylic paint is most commonly composed of PMMA and PⁿBuA copolymers.²⁶ For this reason, we selected PMMA-*co*-PⁿBuA as brushes for our paint test. Using a simple tape test, we observed a dramatic improvement in the ability of HDPE-g-[PMMA-*co*-PⁿBuA] to adhere to paint, in stark contrast with the unfunctionalized HDPE. We propose that the grafted surface was better able to interact with acrylic paint because of its similar chemical structure. In addition to adhesion to paint, we performed lap shear testing to probe the adhesion of surface modified PE to aluminum. Unfunctionalized LDPE is unable to form a lap joint with aluminum (SI). In contrast, LDPE-g-PMMA adheres to aluminum with a shear strength of 1.1 ± 0.2 MPa (SI). Improved adhesion of HDPE to paint and aluminum demonstrates the utility of SI HAT-RAFT as a platform for tuning the surface properties of PE.

We developed a robust, highly diversifiable method to grow high density brush polymers from PE surfaces. The SI HAT-RAFT method presented achieved the highest reported brush thicknesses and densities grafting from PE surfaces, and we can access brush polymer surfaces composed of a wide variety of (meth)acrylate monomers. Finally, we demonstrated the improvement in adhesion, an important surface property,

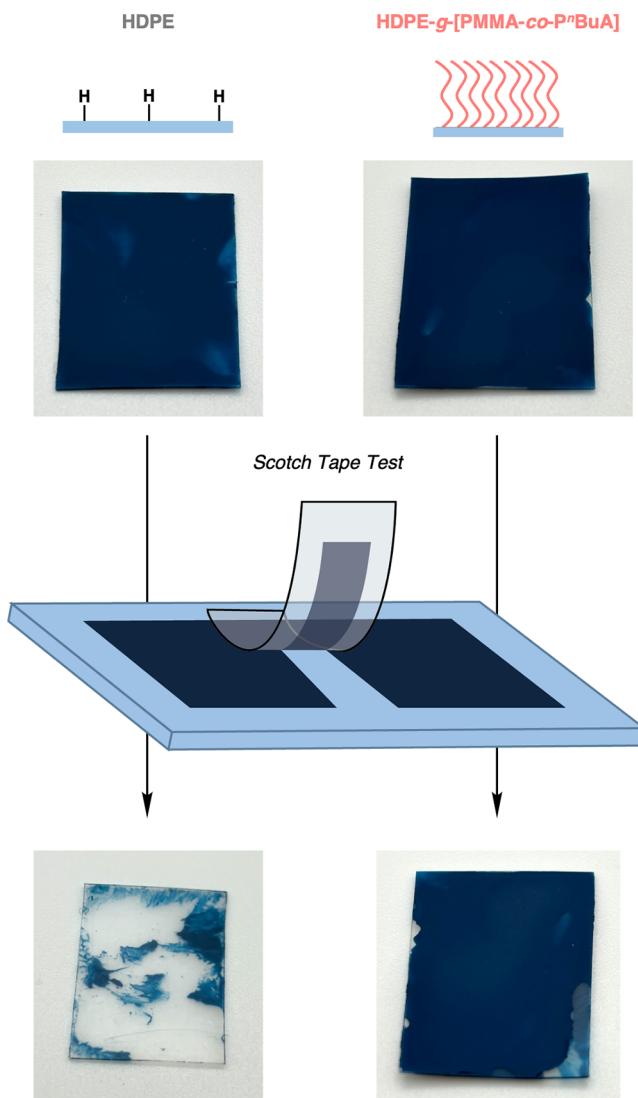


Figure 5. Tape test for acrylic paint adhesion of HDPE (left) and HDPE-g-[PMMA-*co*-PⁿBuA] (right).

upon grafting brush polymers from PE. We envision that this method will also be amenable to curved surfaces and the interior of tubes with flow technology, while functionalization of the interior of closed vessels may be challenging. Improving the surface properties of PE opens the door to using PE in applications including battery science, antimicrobial surfaces, and filtration. This work addresses the long-standing challenge in polymer science of facile and robust access to PEs with enhanced surface properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.4c06924>.

Reagent and analytical information, general procedures, and additional studies (PDF)

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Notes

The authors declare no competing financial interest.

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