Direct Functionalization of Polyethylene Surfaces with High Density Polymer Brushes

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Primary CNF Tools Used: Ramé-Hart Goniometer

Abstract:

Introducing functionality into 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 ~ 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.

Summary of Research:

Polyethylene (PE) is ubiquitous in our society, with over 100 million tons produced annually. The widespread use of PE is enabled by its superior bulk properties and low cost; PE is strong, tough, light weight, 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. Furthermore, the surface of PE contains only unactivated C-C and C-H bonds, making it challenging to modify.

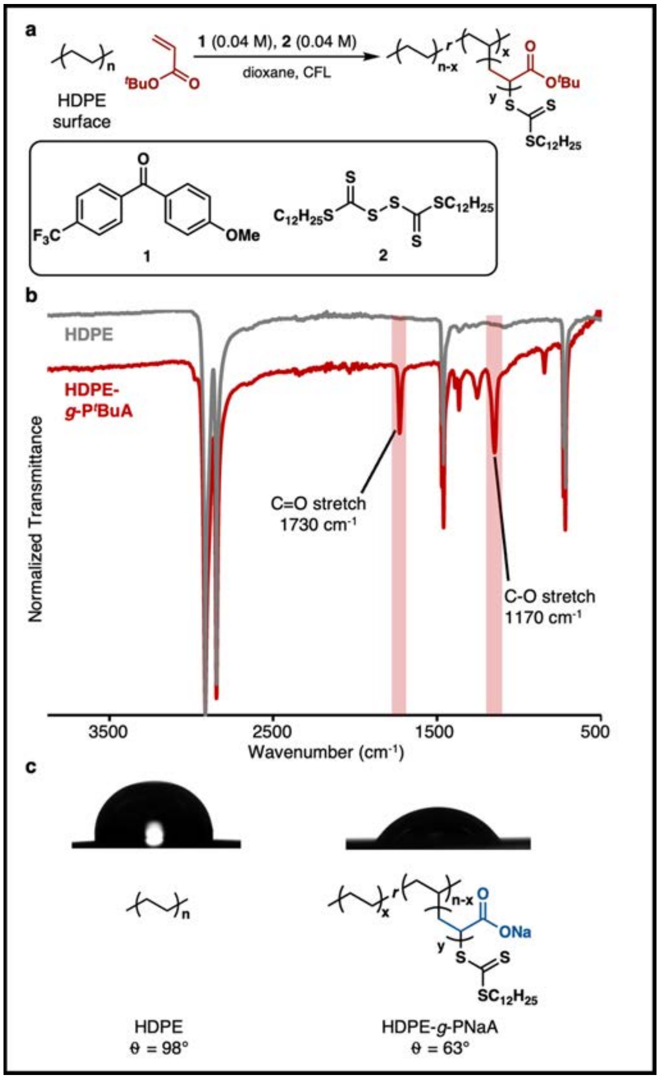
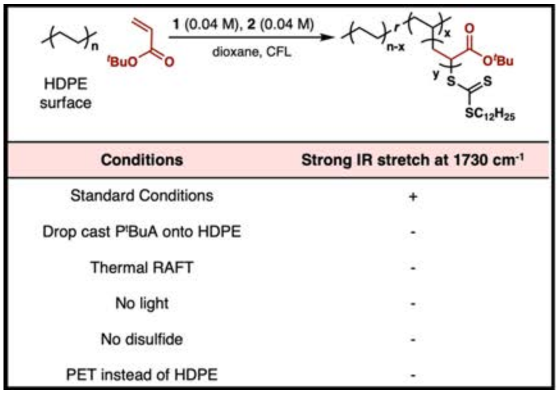
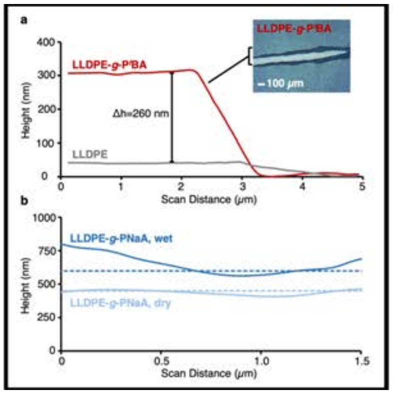


Figure 1: (a) Standard reaction conditions for SI HAT-RAFT from PE. (b) IR spectra of unfunctionalized HDPE and HDPE-g-PtBuA. (c) Static water contact angle for HDPE and HDPE-g-PNaA.

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.



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



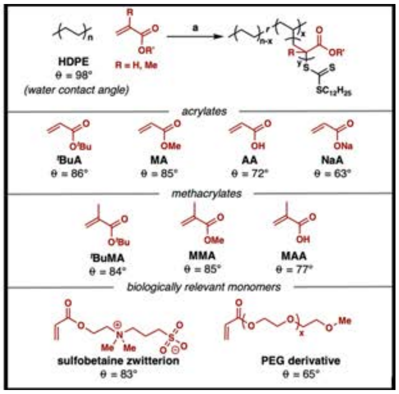


***Table 1, left:** SI HAT-RAFT Controls.* ***Figure 2, middle:** (a) AFM measurement of LLDPE-g-PtBuA brush thickness. Brush thickness is assessed by comparing the depth of a scratch (pictured here by optical microscopy) in an LLDPE film before and after graft-ing. (b) AFM swelling study of LLDPE-g-PNaA in pH 9 buffer solu.tion shows the wet film swells 63% relative to the dry film. The dashed lines denote the average film height over the scan distance.* ***Figure 3, right:** 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 hours. 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.*

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 SI). Following irradiation, we detected carbonyl and C-O bond stretches in the IR, indicating that poly(tert-butylacrylate) (PtBA) was successfully installed on the surface of PE (Figure 1). Upon basic hydrolysis of PtBA 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 1).

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 PtBA drop-cast onto an HDPE surface washed away easily, suggesting no adhesion of PtBA to HDPE in the absence of covalent bonds between the surface and the grafted polymer (Table 1). 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.

Having shown that we can grow acrylates 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 PtBA. Atomic force microscopy (AFM) was used to assess brush thickness (Figure 2). For our LLDPE.g-PtBA sample, we achieved a brush thickness of 260 nm. We also used AFM to characterize brush density. Our SI HAT-RAFT method achieves a grafting density of 0.62 chains/nm2. 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 3). 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.

Conclusions and Future Steps:

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. 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.