

Mechanophore Activation at Heterointerfaces

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S Supporting Information

ABSTRACT: Silica nanoparticles grafted with poly-(methyl acrylate) (PMA) chains anchored by a maleimide–anthracene cycloadduct were synthesized to demonstrate mechanochemically selective activation of mechanophores at heterogeneous interfaces. By quantifying the anthracene-containing cleaved PMA polymers, which are generated via retro-[4 + 2] cycloaddition reactions, the first-order kinetic coefficient was determined. Activation characteristics of mechanophores anchored to a nanoparticle exhibit behavior similar to mechanophore-linked polymers, e.g., threshold molecular weight and linear increase in rate coefficient with molecular weight above the threshold. This model system is thus valuable as a probe to test stress activation of interfacially bonded mechanophores relevant to the design of fiber-reinforced polymer composites.

Mechanical failure of polymeric materials is often closely related to physical and chemical changes to the polymer molecules.¹ When stress builds along the polymer backbone, scission of chemical bonds occurs, leading to degradation of the molecular weight and the mechanical properties of the material.² Within the past decade, mechanochemical reactions were studied to better understand these damage events and to potentially utilize force as a stimulus for mechanochemical-responsive materials.^{3–5} For example, by attaching two polymer chains on specific positions of a substituted benzocyclobutene, our group demonstrated the production of forbidden ring opening products, driven by the unique directionality of the mechanical-force-driven reaction.⁶ This concept was also used to study the distribution of forces in materials using mechanochromic molecules.^{7–9} To date, research on mechanophores has focused on homopolymer systems,¹⁰ where bond scission occurs near the center of the chain. The nature of polymer mechanochemistry at interfaces, which are arguably more important considering the prevalence of composite materials in industrial applications,^{11–13} remains mostly unexplored. Herein, we demonstrate for the first time the selective activation of mechanophores anchored at the heterointerface of polymer chains and inorganic nanoparticles. The prerequisite for mechanochemical activation in mechanophore-linked polymers is that the mechanophore resides near the center of the chain. The new mode of activation demonstrated here is a starting point to understand interface-selective mechanochemical reactions thus broadening the utilization of polymer mechanochemistry. We believe this

work is a significant first step toward designing self-sensing, self-repairing composite materials.

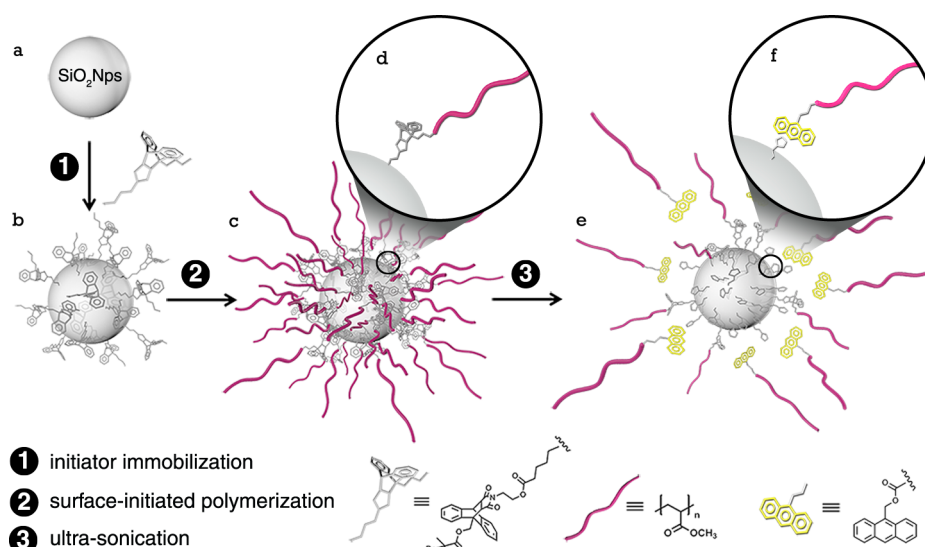
The model mechanophore used in this work is a [4 + 2] cycloadduct of maleimide–anthracene (MA) that has been first demonstrated by the Bielawski^{14,15} group and independently researched by the Boydston¹⁶ group to undergo a mechanically induced retrocycloaddition. The mechanophore-anchored poly-(methyl acrylate) (PMA) grafted silica nanoparticles (SiO₂NPs-MA-PMA) were prepared by immobilizing triethoxysilane-terminated MA-containing initiators to SiO₂NPs (avg diameter = 16.9 nm before grafting) and subsequent surface-initiated living radical polymerization (SI-LRP)^{17,18} (Scheme 1; see Supporting Information for details). The orientation of the MA mechanophore (i.e., whether the anthracene or maleimide side is connected to the SiO₂NPs/PMA) was deliberately designed to accommodate characterizations of polymer released by retro-[4 + 2] cycloaddition.

Ultrasonication was employed to generate elongational flow that presumably stretches the grafted chains and transduces mechanical force.¹⁹ As it is near the center of mass, the polymer–nanoparticle interface is likely to be the point where maximum stress concentrates.^{20,21} Once sufficient stresses accumulate, the attached PMA chain should cleave from the surface of SiO₂NPs generating an anthracene-end-capped PMA chain as depicted in Scheme 1c–1f. The predicted cleavage of the polymer was confirmed by gel permeation chromatography (GPC) using a UV detector set at 254 nm, shown in Figure 1a with a SiO₂NPs-MA-PMA 50 kDa sample (see Supporting Information for molecular weight determination). Using 254 nm as the detection wavelength for MA activation precludes the observation of nonspecific chain detachment. Furthermore, mechanochemical-selective cleavage was identified by its unique UV absorption using a photodiode array UV detector coupled with the GPC. The characteristic UV absorption patterns of anthracene at the elution time corresponding to the 50 kDa polymer confirm that anthracene is bounded to the expected-size macromolecule (Figures S2, S3, and S4, Supporting Information). A control experiment, where an ester (EE) linkage was substituted for MA as the anchor point at the interface, did not exhibit similar spectroscopic signatures (Figure S5, Supporting Information).

In mechanophore-centered homopolymers, longer chains transduce greater mechanical force to the mechanophores and as a result a molecular weight dependence of mechanophore

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Scheme 1. Illustration of the Synthetic Approach to Mechanophore-Anchored Polymer Brush-Grafted Nanoparticle and Its Response to Mechanical Activation^a

^a(a) Bare silica nanoparticle, (b) mechanophore-anchored silica nanoparticle, (c, d) silica nanoparticles grafted with PMA chains anchored by the maleimide-anthracene cycloadduct, and (e, f) interfacial retrocycloaddition-induced detachment of PMA chains and generation of anthracene-end-capped PMA. Note: e is only a cartoon representation and may not convey the actual dynamics.

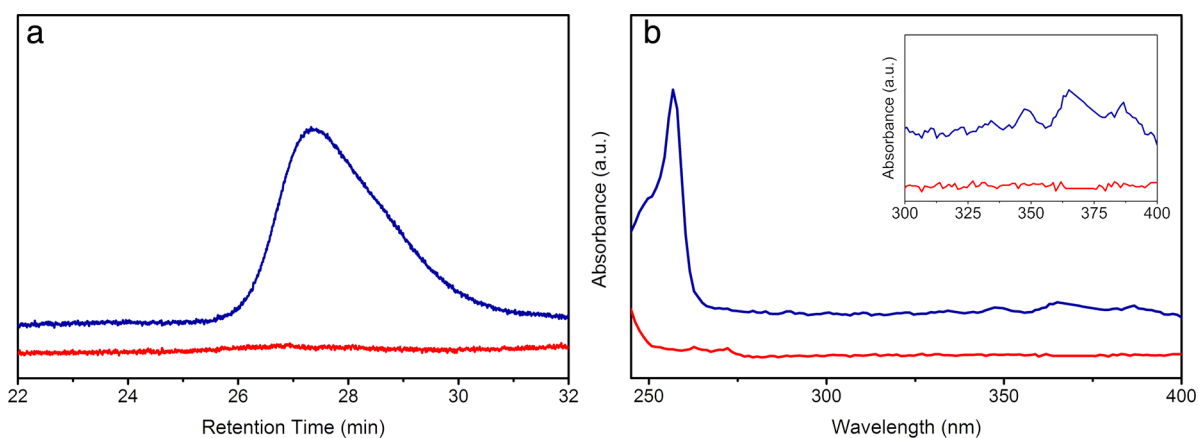


Figure 1. (a) GPC trace of SiO₂NPs-MA-PMA-50k, 2 mg/mL in THF, after 3 min (red) and 120 min (blue) ultrasonication. (b) UV spectra from the retention time = 27.6 min slice after 3 min (red) and 120 min (blue) ultrasonication. The inset is the magnification of the 300–400 nm area.

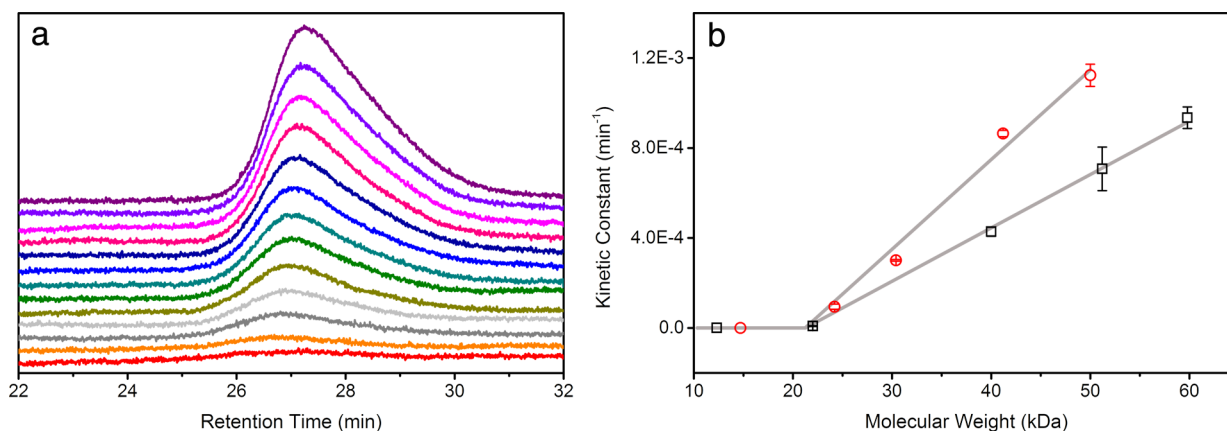


Figure 2. (a) GPC trace of SiO₂NPs-MA-PMA-50k, 2 mg/mL in THF, at 3, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120 min ultrasonication. (b) Molecular weight dependence of first-order kinetic coefficient for reactions conducted at 5 °C in the SiO₂NPs-MA-PMA series (black square, slope = 2.38×10^{-5} , $r^2 = 0.96$) and the PMA-MA-PMA series (red circle, slope = 4.51×10^{-5} , $r^2 = 0.99$). The error bars were obtained with three parallel experiments.

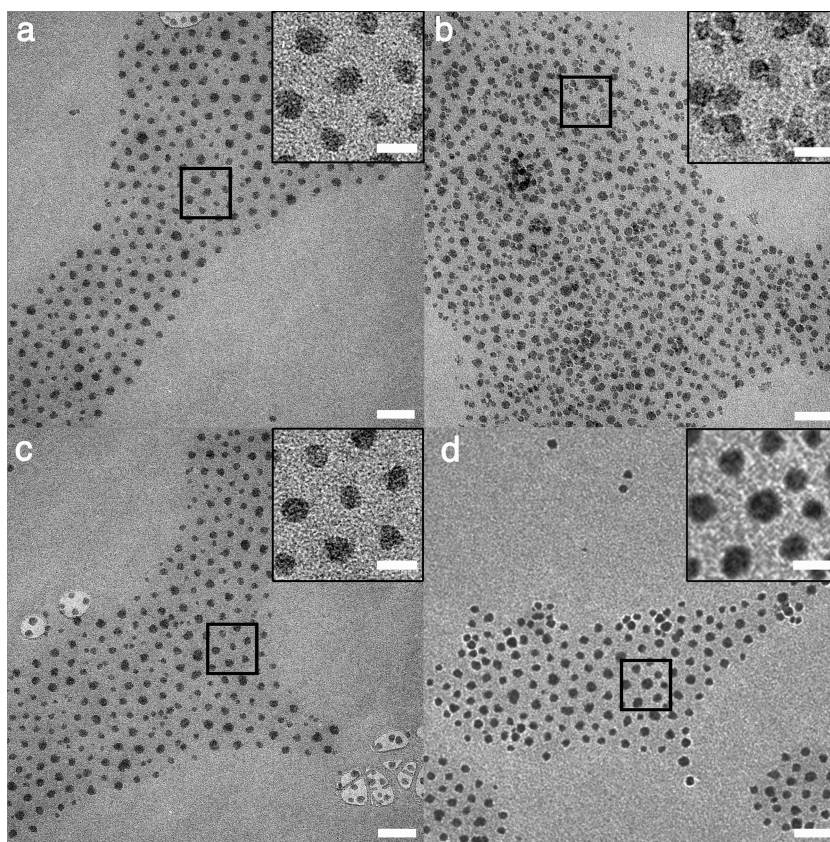


Figure 3. TEM micrographs of SiO₂NPs-MA-PMA-40k after 3 min (a) and 480 min (b) ultrasonication. Insets are sections of the TEM micrographs as marked. TEM micrographs of SiO₂NPs-EE-PMA-40k after 3 min (c) and 480 min (d) ultrasonication. Scale bars are 100 nm and inset scale bars are 30 nm.

activation is observed.^{6,10} We tested similar behavior for the interface-anchored mechanophore by synthesizing a series of SiO₂NPs-MA-PMA with grafted PMA chains of various molecular weights. The weight percent of polymer content in the grafted nanoparticles was determined using thermogravimetric analysis (TGA) and ranged from 48.2% to 79.6% for grafted PMA of various molecular weights (Figure S1). The molecular weight (M_n) of grafted PMA was quantified by calibrating the mechanochemically cleaved PMA to polystyrene standards. Thus, as shown in Figure 2a, the amount of PMA cleaved after sonication was quantified to give the first-order kinetic coefficient for the retro-cycloaddition reaction (see Figures S6–S8, Supporting Information for detailed calculations). These kinetic coefficients were then plotted (Figure 2b, black squares) and compared to a MA-centered linear PMA (PMA-MA-PMA) (Figure 2b, red circles). A linear response of the kinetic coefficient to the molecular weight increase of the grafted PMA was observed, whereas the threshold molecular weight is similar to that of PMA-MA-PMA. These results reveal that when present at interfaces, the activation of polymer bound mechanophores still follows the usual molecular weight dependence and the threshold molecular weight similar to their homopolymer counterparts. It is concluded that the empirical threshold molecular weight and reaction kinetics obtained in a homopolymer system, which is relatively simple to design and examine, will help guide the design of mechanophore-functionalized composite interphases.

Selective mechanophore activation is evident from studies of morphological change of PMA-grafted nanoparticles before and after sonicating mechanophore-anchored nanoparticles com-

pared to the appropriate controls (i.e., grafted polymers lacking the mechanophore). Transmission electron microscope (TEM) micrographs, shown in Figure 3, indicate that the interface of polymer and nanoparticle was altered after mechanophore activation; before activation, the grafted nanoparticles appear to self-assemble into a hexagonal pattern where each nanoparticle is separated by domains of PMA polymer (Figure 3a). After sonication, however, the pattern of nanoparticles was irregular, with the appearance of aggregates of several nanoparticles, and the average distance between neighboring SiO₂NPs significantly decreases from 46.9 ± 8.2 nm to 28.3 ± 10.9 nm, the latter of which were largely contributed to by emerging interstitial spaces below 15 nm (Figure 3b, Figure S9, Supporting Information). This intriguing phenomenon was attributed to cleavage of PMA chains and was supported by ester group anchored SiO₂NPs-PMA control, which did not exhibit any significant change in interparticle distances after sonication (Figure 3c,d). The size of the SiO₂ remained similar regardless of sonication (Figures S9 and S10, Supporting Information).

To conclude, the interfacially selective mechanochemical activation of a maleimide–anthracene mechanophore anchored PMA grafted SiO₂NPs system was observed in sonication-generated elongational flow. Comparison of the mechanophore-featured heterointerface system with a series of controls confirms the mechanophore's unique mechanochemical response to the mechanical stimulus. Quantification of PMA cleavage reveals that interface-anchored mechanophores exhibit behavior seen in chain-centered mechanophores. We demonstrate that first-order kinetics, threshold molecular weight, and linear response to polymer chain size are applicable as guiding

principles at interfacial regions, just as they are for chain-centered mechanophores. This discrete system, with its versatility of parameters—e.g. mechanophore species, polymer species, grafting density, tether length—is a promising model system for designing smart, mechanically sensitive and self-repairing composite materials.^{22,23}

■ ASSOCIATED CONTENT

📄 Supporting Information

1. Synthetic routes and characterizations of MA-mechanophore related compounds 2. Quantification methods and eq 3. Other miscellaneous information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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