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Santa Barbara

End-Functionalized Polymers as Next-Generation Building Blocks

A dissertation submitted in partial satisfaction of the
requirements for the degree Doctor of Philosophy
in Chemistry

by

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June 2024

End-Functionalized Polymers as Next-Generation Building Blocks

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by

Michael Czuczola

This thesis is dedicated to all aspiring scientists. Follow your passions, let curiosity guide you, and don't forget to drive with the windows down. Jakoś to będzie.

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Okayama Y.; Eom T.; **Czuczola, M.**; Abdilla A.; Blankenship J. R.; R. Albanese K. R.; Javier Read de Alaniz J.; Bates C. M.; Hawker, C. J. Heterotelechelic silicones: Facile synthesis and functionalization using silane-based initiators. *Macromolecules* **2023**, 56, 21, 8806–8812.

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ABSTRACT

End-Functionalized Polymers as Next-Generation Building Blocks

by

Michael Czuczola

Polymers have revolutionized modern life, finding countless applications due to their low production cost, tunable material properties, and long-term stability. However, this ubiquity and durability present global sustainability challenges necessitating the development of next-generation polymers capable of closed-loop recycling. Currently, sorting and recycling most consumer plastic products is not economically feasible due to the complexity of plastic types, resulting in only 5% of plastics in the United States being recycled. Promising strategies to enhance our recycling capabilities and transform plastics into a sustainable commodity include improving the blending of different polymers, incorporating degradable comonomers, and upcycling unwanted plastic products.

To further explore polymer blending, **Chapter 2** and **Appendix A** discussed improving polymer blending by developing polymers end-functionalized with complementary quadruple hydrogen-bonding end groups for improved miscibility. 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (Napy) functionalized polymers reduced macrophase separation through the formation of the UPy-Napy heterocomplex in solution and thin film

studies. This approach enables the creation of challenging silicone-based blends, benefiting both industrial applications and fundamental research.

To expand upon the utility of degradable comonomers, **Chapter 3** and **Appendix B** presented a platform to access vinyl-based α,ω -dithiol oligomers by degradation of copolymers derived from α -lipoic acid or ethyl lipoate with various vinyl comonomers. Structurally diverse polymeric α,ω -dithiols are synthesized by incorporating and then reducing disulfide bonds within the vinyl polymer backbone, demonstrating controllable molecular weights and tunable glass-transition temperatures (T_g). The utility of these α,ω -dithiol oligomers is highlighted for use as building blocks or crosslinkers in efficiently photocrosslinked networks.

Further expansion of these α,ω -dithiol polymers for facile access to customizable random multiblock copolymers (MBC) was discussed in **Chapter 4** and **Appendix C**. By oxidizing the thiols of low and high T_g dithiol polymers, a diverse range of random MBCs with high molecular weights and modulated mechanical properties were synthesized. This approach enabled precise control over MBC block molecular weight, tunable composition, and added chemical degradability. The versatility and scalability of this approach paves the way for future studies on telechelic thiol vinyl-based polymers and random MBCs.

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Chapter 1. Introduction

1.1 Ubiquity of Polymers

Plastics in everyday life have massive benefits on the quality of life for many people and touch upon every aspect in modern life.¹⁻³ Plastics have many important benefits including being cost-effective, lightweight, mechanically robust, versatile design space, and quick manufacturing.⁴⁻⁶ This has led to many applications where plastics are the best choice compared to other materials ranging from sterilized medical equipment, car tires, shoe soles, contact lenses, coatings, and countless more.⁷ Plastics are mainly comprised of polymers, long chains of repeating similar chemical units. In the pursuit of interesting and useful polymers, polymer chemists leverage synthetic organic chemistry techniques to functionalize polymers allowing access to more complex, next-generation, functionalized polymers with novel properties which are already commonly used in many products. For example, amine functionalized silicones combine the polarity of amines with the occlusive advantages of silicones in hair cosmetic products.^{8,9} Functionalized polymers are already important materials in today's society and have opened the doors to many advancements and applications.

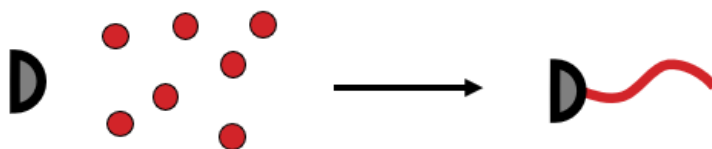
1.2 Functionalization Strategies of Polymers

To access functionalized polymers, polymer chemists have developed two main strategies: (1) incorporating functionalized monomers, initiators, or terminators directly during polymerization, and (2) post-polymerization functionalization of polymers (**Figure 1.1**).^{10,11} With the first strategy, the desired functional groups must be tolerant to the given polymerization conditions. If it is not tolerated, it will require protecting groups and an additional deprotection step which is undesired for many applications.¹² Functionalized monomers can be polymerized directly or copolymerized with unfunctionalized monomers to

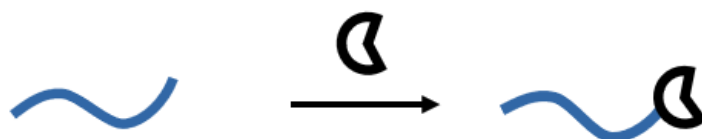
modulate the amount of incorporation.¹³ With the indirect approach, post-polymerization functionalization involves installation of the functional group after polymerization.¹⁴ This can have advantages as functional groups not tolerant to polymerization conditions can be attached directly to the polymer chain.¹⁵ Also, beginning with the same polymer batch starting material but selectively only changing the functional group can allow better control over structure-property-relationships by observing the effects of the functional group on polymer chain or network properties exclusively.¹⁶

(a) Direct polymerization

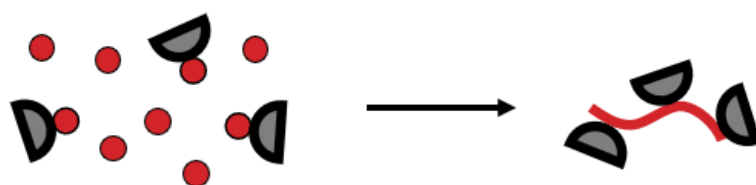
Functional initiator



Functional terminator



Functional comonomer



(b) Post-polymerization modification



Figure 1.1. Strategies for functional polymers through (a) incorporation during polymerization or (b) post-polymerization modification.

Many strategies to modify polymers post-polymerization exist. Click chemistry is a popular method for simple, atom-economic, and high-yielding reactions, including thiol-ene click reactions.^{17,18} With this approach, modifying polymer properties and accessing complex architectures like diblock, triblock, multiblock copolymers, comb, bottlebrush, star polymers are easy to achieve.¹⁹ These complex polymer architectures have been used in many applications such as nanoparticles, bioconjugation, polymer-drug conjugation, biocompatible surfaces, scaffolds, hydrogels, and thermoplastic elastomers.^{20–24}

1.3 Polymer Sustainability: Blending and Degradation

With the abundant use of polymers, we must be aware of current and future issues our society will face as a consequence of polymers in everyday life²⁵. Plastic pollution is a multifaceted problem. Despite state-of-the-art materials recovery facilities, recycling rates are very low, 5% for consumer plastics.^{26–28} Polymer chemists are actively exploring strategies to achieve sustainable polymers: polymer blending (block copolymer compatibilizers, end-functionalized), polymer depolymerization back to monomer, and degradable bonds along the polymer backbone (**Figure 1.2**).

Polymer blending involves the mixing of two chemically distinct polymer species. Most polymers blends are thermodynamically immiscible which indicates a high Flory-Huggins interaction parameter (χ). To overcome this enthalpic barrier to blending, the chain repulsion between dissimilar polymers needs to be reduced.²⁹ Without proper blending,

heterogeneous polymer mixtures tend to result in undesirable, brittle material.³⁰ One avenue to achieve robust materials from otherwise brittle polymer blends, is to add a block copolymer additive to the homopolymer mixture.³¹ This block copolymer additive localizes along the interface of the two different polymer domains and reduces the domain droplet size. Multiblock copolymers have particularly been successful in this regard, being able to stitch homopolymer domains together multiple times.^{32,33} Another strategy involves polymer functionalization, installing functional groups on polymers can overcome the segregation strength through reactive blending or strong attractive forces.^{34–37} In situ blend compatibilizers are produced when forming covalent bonds,³⁸ ionic bonds,^{39,40} or hydrogen bonds in the system.^{41,42} Polymer blending strategies can utilize existing homopolymers for useful material without the difficult requirement of sorting for chemically identical polymers.

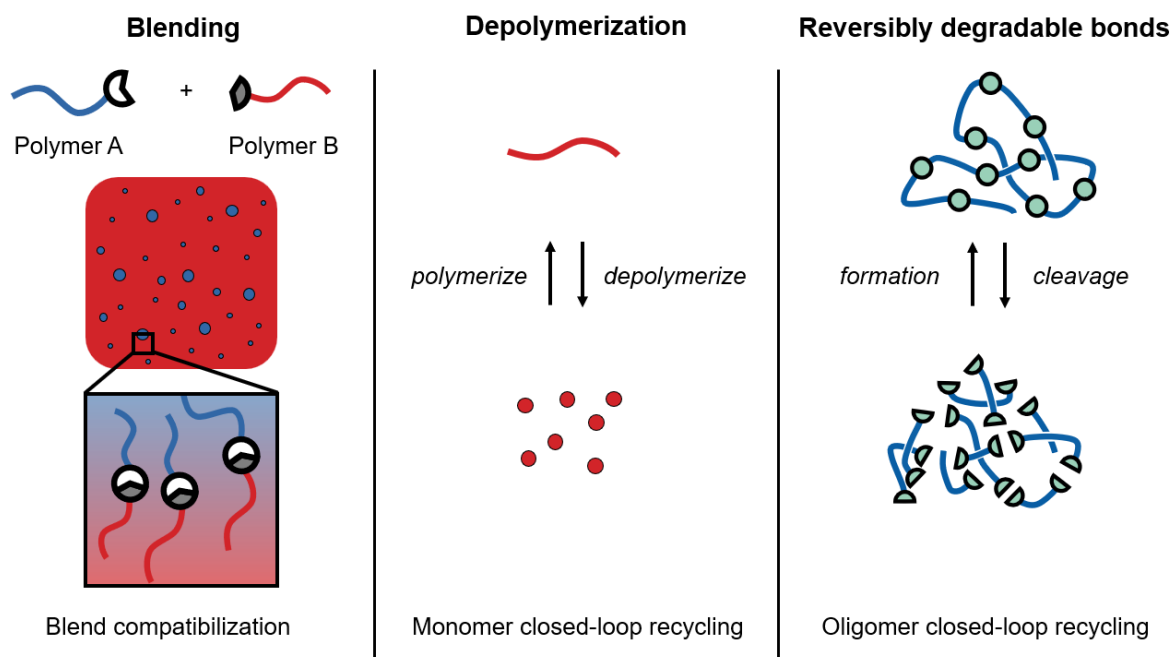


Figure 1.2. Polymer sustainability strategies: blending, depolymerization, and degradable bonds.

A grand goal for plastic sustainability is closed-loop-recycling, where the polymer can be converted back into the starting material.⁴³ Additionally, upcycling, where value is added to the polymers through some beneficial transformation, extends the life use of these materials.⁴⁴⁻⁴⁶ With careful selection of monomer, depolymerization back to the monomers is possible.⁴⁷ However, this limits the substrate scope and material properties as only select monomers allow practical depolymerization back to original monomers. Additionally, depolymerization may require high temperatures and further distillation for purification of monomers, both of which can be highly energy intensive.

Degradable or labile bonds in the polymer backbone are beneficial for creating materials with inherent degradability. Polyesters have demonstrated chemical or biological degradability through the ester bond by backbone cleavage using acids and bases, or enzymes.^{48,49} However, challenges remain as the amorphous regions are quickly degradable while the crystalline regions of these polymers are slow to degrade. These biodegradable polymers are typically hard to modify their properties as their monomer scope is limited and does not include commodity plastics such as vinyl-based polymers.⁵⁰

A degradable comonomer approach can be a drop-in additive to the existing polymer manufacturing infrastructure to synthesize materials with similar mechanical properties but with added degradability to the polymer backbone.^{51,52} Polymer degradation to oligomers can be less energy intensive while still making the processing and purification of oligomers easier compared to the starting parent polymers.⁵³ If the degradation reaction of the polymer is chemically reversible, closed-loop recycling can be achieved through repolymerization.⁵⁴ Chemical degradation processes can result in oligomers with reactive end groups, these can

be used as handles to transform unwanted degradation products into higher-value materials, thereby upcycling.⁵⁵

1.4 Importance of Silicones

Polysiloxanes or silicones are crucial in a multitude of industrial and academic uses due to their unique properties of thermal stability, low glass-transition temperature (T_g), electric insulation, biocompatibility, hydrophobicity, and durability.^{8,56–60} Many of these beneficial properties derive from the inorganic backbone consisting of repeating Si–O bonds. The simplest polysiloxane contains methyl groups, polydimethylsiloxane. Moreover, a versatile reactive moiety in silicones is the Si–H bond, or silyl hydride (**Figure 1.3**).⁶¹ This industrially relevant functional group can be used for hydrosilylation in an addition reaction with vinyl group, catalyst by a platinum catalyst.^{62,63} Many platinum catalysts are available, but Karstedt's catalyst is favored due to the high activity and selectivity which allows it to be used in low concentrations (10 ppm) with minimal side products, even being able to catalyze the reaction at room temperature.^{64–66} Although silicones are used for a variety of applications, challenges remain with respect to immiscibility with organic polymers, showcasing a very high χ value.^{67,68} Expanding the capabilities to blend silicones would benefit many relevant current uses of silicones.^{69,70}

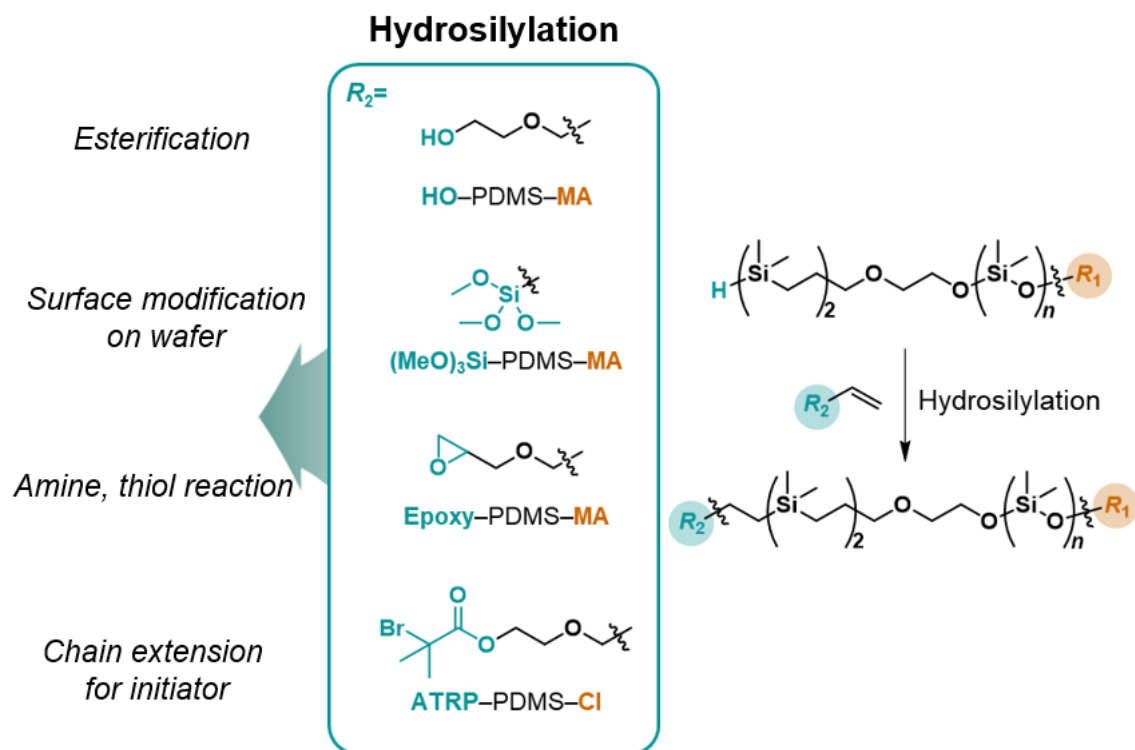


Figure 1.3. Hydrosilylation using silyl hydride moiety for functional silicones.⁷¹

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Chapter 2. Quadruple Hydrogen Bonded Silicone- based Polymer Blends

2.1 Abstract

Blending polymers is a versatile and cost-effective method to control material properties but blends typically exhibit poor mechanical properties due to macrophase separation of their constituents. Compatibilizing polymer blends by reducing the interfacial tension between polymer domains can improve the resulting material properties. One strategy to compatibilize immiscible polymer blends is functionalizing the two polymers with complementary hydrogen bond pairs, thereby reducing the enthalpic penalty of mixing. Here, we present a compatibilization strategy for blends of PDMS and PMMA using 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (Napy) end-functionalized polymers capable of quadruple hydrogen bonding heterocomplexation. Reversible quadruple hydrogen bonding is observed by variable temperature ^1H -NMR where the UPy dimer dissociates at 85 °C and UPy-Napy heterocomplex dissociates at 65 °C. Optical photothermal infrared spectroscopy (O-PTIR) and optical microscopy verified blend compatibilization by IR chemical mapping and a lack of macrophase droplets, respectively. Stoichiometry of H-bonding end groups were found to play a crucial role in proper blend compatibilization.

2.2 Introduction

Plastics offer great utility in modern society, but the staggering amount of environmental plastic accumulation globally has manifested a plastic pollution crisis.¹⁻³ Despite all efforts to mitigate this crisis by recycling plastics, more plastics are incinerated or landfilled than are reused.⁴ Less than 5% of plastics are recycled into secondary material.⁵ Current state-of-the-art materials recycling facilities must physically sort plastic waste by polymer composition to produce chemically pure polymer feedstocks for reuse.^{6,7} Any contamination of chemically different polymers will lead to thermodynamically favored

macrophase separation, which imparts poor mechanical properties. A promising strategy to eliminate the need to physically sort plastic waste is the compatibilization of traditionally immiscible polymer blends. A necessity exists to investigate strategies which make plastics more sustainable through blend compatibilization by exploring a model polymer system which has a high Flory–Huggins interaction parameter (χ) with most polymers.

An excellent model system to study blend compatibilization involves polysiloxanes since they are ubiquitous in daily life with applications in cosmetics,⁸ food products,⁹ construction,¹⁰ upholstery,¹¹ and medical devices.¹² The unique nature of the Si–O bond affords polysiloxanes exceptional properties including excellent thermal stability, low toxicity, biocompatibility, low surface energy, and high electrical resistivity.^{13–15} However, polydimethylsiloxane (PDMS) exhibits a high Flory–Huggins interaction parameter (χ) with most other polymers, resulting in immiscibility and, therefore, poor recyclability.¹⁶ To address this issue, researchers have explored methods of stabilizing immiscible silicone polymer blends through block copolymer compatibilizers,¹⁷ reactive blending,¹⁸ interpenetrating networks,¹⁹ and end-group interactions.^{20,21}

Hydrogen bonding end-group interactions show potential for polymer blend compatibilization. When attached to two chemically distinct polymers, functional groups containing complementary pairs of multiple hydrogen bond donors and acceptors can reduce the free energy of a polymer blend, resulting in a strong and stable interface that limits coalescence.^{22–29} Due to the quadruple hydrogen bonding motif, the high equilibrium constant for heterodimerization between 2-ureido-4[1H]-pyrimidinone (UPy) and 2,7-diamido-1,8-naphthyridine (Napy) provides a strong attractive force between polymer chains and has been shown to limit macrophase separation.^{30–39} Only small amounts of end groups are needed for

blend compatibilization, as shown by successful compatibilization with polymer molecular weights up to 115 kg/mol.³³ Polymer blends have been investigated with a range of techniques such as optical microscopy, small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM) but each have limitations in identifying the distinct polymer domains as it is difficult to rigorously characterize the macrophase separated polymer domains.^{40,41} Optical photothermal infrared spectroscopy (O-PTIR) is a recently developed technique that rapidly produces a IR chemical map of a surface with submicron resolution that can better characterize the individual polymer domains.⁴² Compatibilization of polymer blends can be confirmed by O-PTIR by monitoring changes in the IR chemical map when using hydrogen bonding end groups.

Inspired by this success, we sought to understand the synergistic effects of UPy and Napy on the performance of silicone polymer blends. Modular synthesis of end-functionalized polymers provides a facile synthetic platform using industrially relevant hydrosilylation on readily available polysiloxanes and atom-transfer radical polymerization (ATRP), which provides control over chain ends and molecular weight. Herein, we blended Napy functionalized PDMS and UPy functionalized PMMA (**Figure 2.1**). Initial experiments confirmed the formation and reversibility of the UPy-Napy (UN) heterocomplex between UPy-PMMA and Napy-PDMS using ¹H-NMR. To investigate macrophase separation, polymer thin films were prepared, and optical microscopy and O-PTIR were used to characterize blend compatibilization. To further confirm that the UN heterocomplex is responsible for blend compatibilization, small-molecule Napy was doped into the compatibilized blends to disrupt hydrogen bonding, leading to macrophase separation.

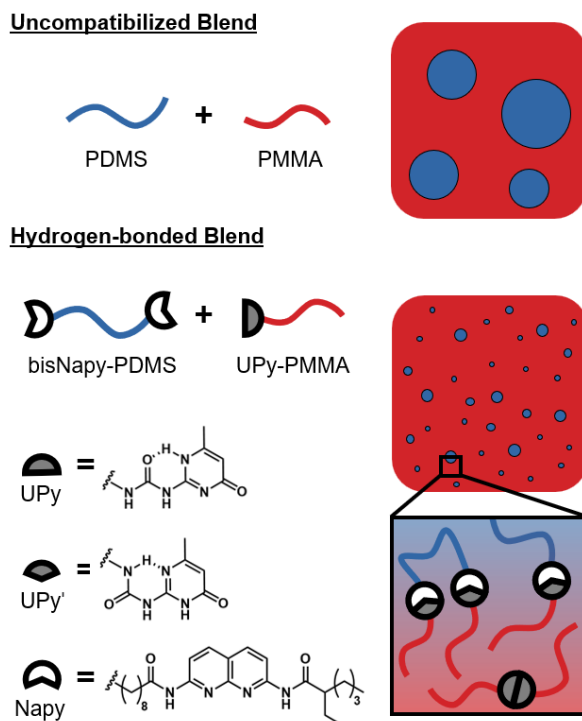


Figure 2.1. Overview of blend compatibilization enabled by UPy-PMMA and bisNapy-PDMS.

2.3 Results and Discussion

To probe whether the UN heterocomplex could be used in blend compatibilization of a high χ system, Napy-functionalized PDMS and Upy-functionalized PMMA were synthesized. To take advantage of the variety of silyl hydride functionalized PDMS derivatives that are commercially available, we synthesized an alkene-containing Napy using previously reported procedures.^{31,32} Hydrosilylation was employed to produce 9.4 kDa Napy-PDMS and 30 kDa bisNapy-PDMS from commercially available monofunctional and telechelic silyl hydride PDMS, respectively (**Figure 2.2**). Monofunctional Napy-PDMS was used to study the blends in solution by ¹H-NMR spectroscopy, while the bisNapy-PDMS was used in spin-coating experiments to study the blending in the solid state. UPy-functionalized PMMA (6.3 and 20 kg/mol) was synthesized via thermal ATRP catalyzed by CuBr with a nitrobenzyl-protected

UPy ATRP initiator. The nitrobenzyl protecting group was necessary to prevent the dimerization of UPy during the polymerization and to facilitate characterization of the polymer.^{43,44} Quantitative deprotection of the nitrobenzyl moiety was achieved with UV light, enabling the UPy group to participate in hydrogen bonding (**Figure 2.3**). With the nitrobenzyl protecting group, the molecular weights of the UPy-PMMA measured by size-exclusion chromatography (SEC) closely matched ¹H-NMR values. Upon deprotection, the molecular weights measured by SEC shifted to lower values due to the UPy group interacting with the SEC column (**Figure A1**). Molecular weights of the nitrobenzyl UPy polymer were used for this reason to allow accurate stoichiometry of the polymer end groups in the blends.

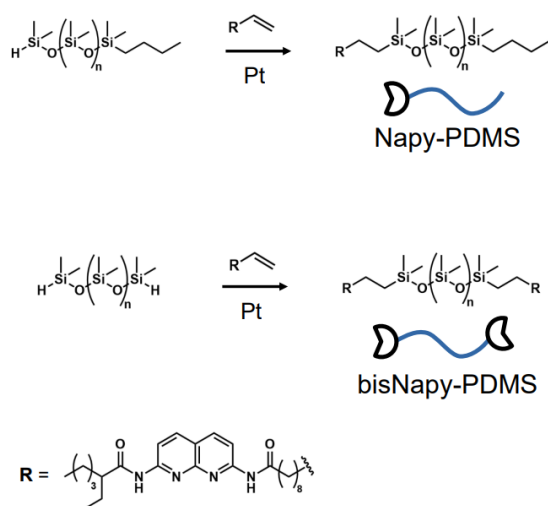


Figure 2.2. Synthetic strategy to generate functionalized polysiloxanes bisNapy-PDMS and Napy-PDMS using hydrosilylation.

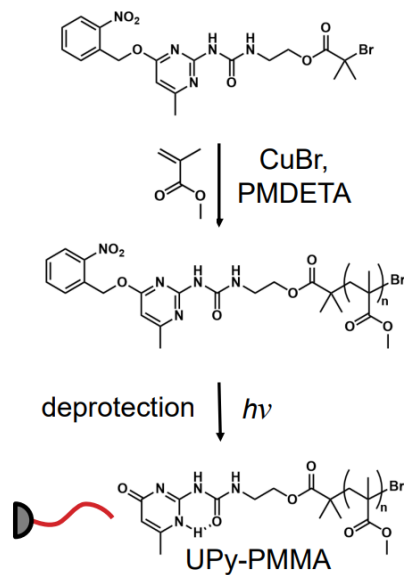


Figure 2.3. Synthetic strategy to obtain UPy-PMMA with a range of molecular weights and narrow dispersity.

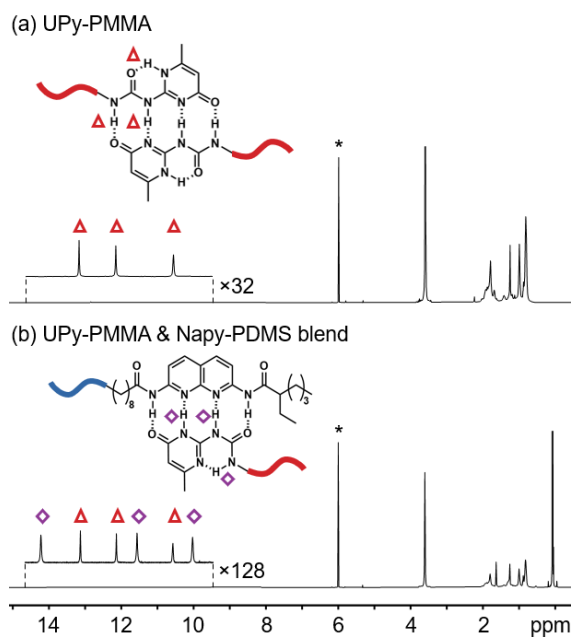


Figure 2.4. 500 MHz ^1H -NMR of (a) UPy-PMMA and (b) stoichiometric blend of UPy-PMMA & Napy-PDMS in 1,1,2,2-tetrachloroethane- d_2 at 20 mg/mL. Both quadruple hydrogen bonding groups were observed in the polymer blend.

To determine if UN heterocomplexation occurs between the quadruple hydrogen bonding functionalized polymers, ^1H -NMR was used to observe diagnostic peaks which agreed with previous literature using small molecule UPy-Napy derivatives.³⁶ The ^1H -NMR of UPy-PMMA (**Figure 2.4a**) showed dimerization of the UPy groups at 10.4, 11.9, and 12.9 ppm. When UPy-PMMA and Napy-PDMS were added together at a 1:1 ratio of the UPy:Napy groups (**Figure 2.4b**), UN heterocomplex protons were observed at 9.9, 11.4, and 13.9 ppm. A mixture of the UPy dimer and UN heterocomplex were observed in the polymer blend due to the equilibrium between UPy dimers and UN heterocomplex. In contrast, small molecule UN heterocomplexes have been shown to exclusively form the UN heterocomplex with no significant UPy dimer formation.³⁶ The observed mixture of UPy dimer and UN heterocomplex in the polymer system can be attributed to polymer immiscibility leading to some UPy dimer formation in addition to the UN heterocomplex. To further probe the formation of UPy dimer, increasing amounts of Napy-PDMS were added, which decreased the integration of UPy dimer peaks while increasing the integration of UN heterocomplex peaks (**Figure A2**). Even with a 3-fold excess of Napy-PDMS, however, UPy-PMMA dimers were still observed. Additionally, blending UPy-PMMA with small-molecule Napy at a 1:1 ratio of UPy:Napy resulted in a mixture of UPy dimer and UN heterocomplex, although at a higher integration of UN heterocomplex compared to the polymer blend system (**Figure A3**).

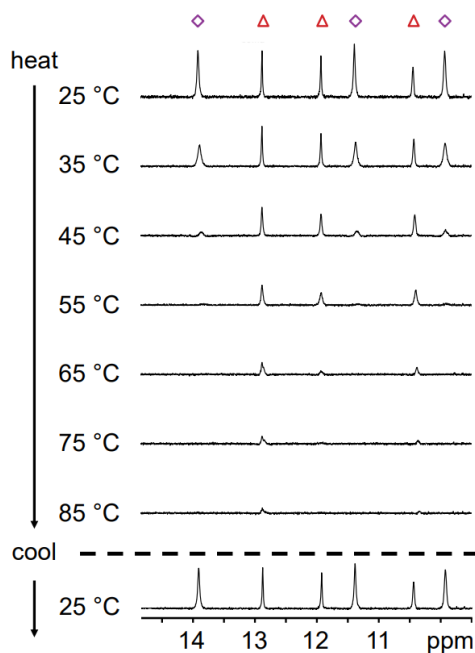


Figure 2.5. 500 MHz ^1H -NMR of UPy-PMMA and Napy-PDMS stoichiometric blend in 1,1,2,2-tetrachloroethane- d_2 ; temperature increased to 85 °C then decreased to 25 °C. Dissociation and reassociation of H-bonding protons shows the dynamic nature of these complexes.

Variable temperature ^1H -NMR of the UPy-PMMA and Napy-PDMS stoichiometric blend found the quadruple hydrogen bonding groups to be reversible with temperature (**Figure 2.5**). The temperature was increased from 25 °C to 85 °C in 10 °C increments then decreased back to 25 °C. The UN heterocomplex dissociated at 55 °C, shown by the disappearance of the heterocomplex resonances. Meanwhile, the UPy dimer interaction needed higher temperatures for dissociation (up to 85 °C). Upon cooling the sample back to 25 °C, all proton peaks returned, and the integration values returned to previous amounts, showing these hydrogen bonding interactions are reversible.

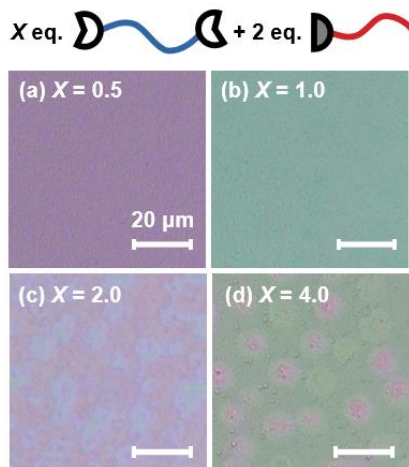


Figure 2.6. Optical microscope images of UPy-PMMA and bisNapy-PDMS spin coated blends at different UPy:Napy equivalents showing blend compatibilization where $X =$ (a) 0.5 (b) 1.0 (c) 2.0 (d) 4.0.

Having demonstrated heterocomplex formation between UPy-PMMA and Napy-PDMS in solution, thin film studies with higher molecular weight polymers were performed to investigate solid-state blend compatibilization. As expected, stoichiometric blending of UPy and Napy groups led to the best blend compatibilization. No surface droplets were observed with the bisNapy-PDMS & UPy-PMMA blends at equivalent UPy:Napy amounts or when the Napy content was decreased (**Figure 2.6a,b**). At higher Napy content, however, surface droplets emerged. (**Figure 2.6c,d**). For further evidence that the surface droplets corresponded to macrophase separated PDMS, increasing surface droplets amount was observed with unfunctionalized PMMA and PDMS blends as the wt% of PDMS increased (**Figure A4**). Differential scanning calorimetry (DSC) of the bisNapy-PDMS and UPy-PMMA blend showed two distinct T_g at $-120\text{ }^{\circ}\text{C}$ and $100\text{ }^{\circ}\text{C}$, which coincide with homopolymer PDMS and PMMA, respectively, suggesting that the two polymers remain macrophase separated with domains unobservable with the performed techniques. (**Figure A6**)

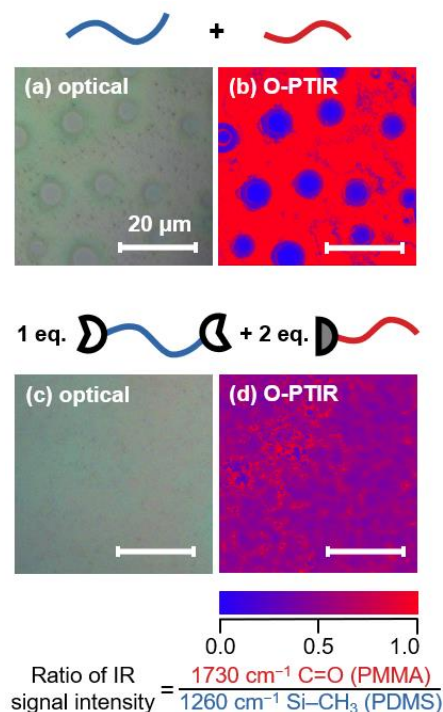


Figure 2.7. Blend compatibilization verified by O-PTIR. (a) PMMA and PDMS blend optical image. (b) IR chemical map of PMMA and PDMS blend where the color scale refers to the ratio of IR signal intensity at 1730 cm⁻¹ to 1260 cm⁻¹. Blue regions are rich in PDMS and red regions are rich in PMMA. (c) UPy-PMMA & bisNapy-PDMS blend optical image. (d) IR chemical map of UPy-PMMA and bisNapy-PDMS blend where the color scale refers to polymer-rich regions plotted as the ratio of IR signal intensity at 1730 cm⁻¹ to 1260 cm⁻¹. Blue regions are rich in PDMS, and red regions are rich in PMMA.

To rigorously characterize the surfaces of the compatibilized blend, optical photothermal infrared (O-PTIR) spectroscopy was used to confirm blending of UPy-PMMA and bisNapy-PDMS with submicron resolution. This technique uses visible light (532 nm) for contactless, non-destructive, and highly sensitive IR analysis of the polymer blend surface (**Figure A5**). This approach allows for much smaller spatial resolution and IR chemical

mapping of surfaces. For unfunctionalized PDMS and PMMA, droplets on the film surface were observed by optical microscopy (**Figure 2.7a**). These droplets were found to match the IR spectrum of PDMS while the surrounding matrix matched PMMA. By normalizing the IR spectra and taking the ratio of peak intensity at 1730 cm^{-1} (C=O stretch from PMMA) to 1260 cm^{-1} (CH_3 symmetric bending in Si- CH_3 from PDMS), an IR chemical map (**Figure 2.7b**) exhibited distinct polymer-rich regions of PDMS (blue) and PMMA (red), confirming macrophase separation. In the case of the hydrogen bonding blend, no surface droplets were observed (**Figure 2.7c**). In contrast to the control, the IR chemical map of the functionalized system (**Figure 2.7b**) showed mixing of the two polymer phases on a submicron level when the same normalization process was applied. O-PTIR clearly shows blend compatibilization by the overlap of the IR spectra on the surface of the polymer blends when using complementary H-bonding end groups.

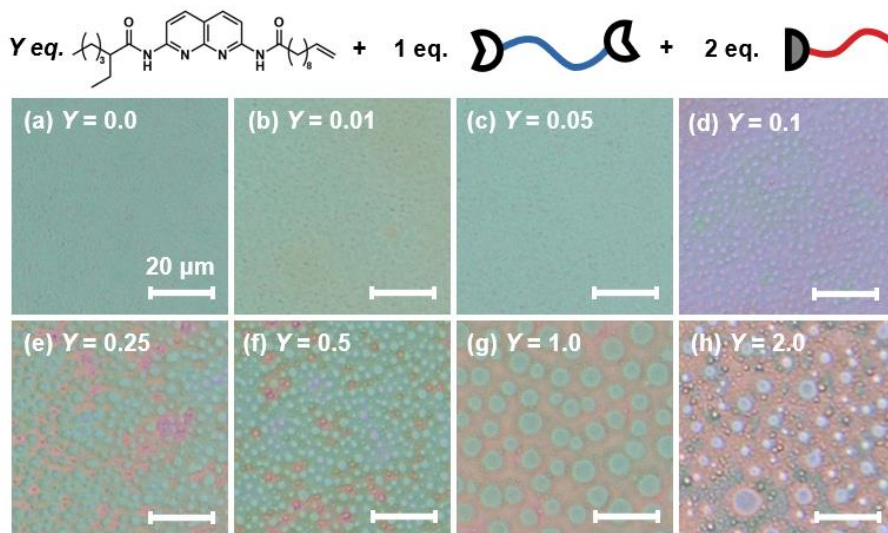


Figure 2.8. UN heterocomplex important for blend compatibilization. Optical microscope images of UPy-PMMA and bisNapy-PDMS spin coated blends showing macrophase separation with different added small-molecule Napy equivalents.

To verify the UN heterocomplex is critical for blend compatibilization in the films, small-molecule Napy was added to disrupt the hydrogen bonding. This small molecule competed with the Napy groups on the PDMS and resulted in less mixing of the two polymers. At low equivalents of small-molecule Napy (**Figure 2.8a-c**), no surface droplets were observed. However, surface features started to develop at 0.1 equivalents of the small-molecule Napy (**Figure 2.8d**). Increases in the equivalents of Napy resulted in an increase of droplet size from less than 1 μm to 10 μm in size (**Figure 2.8e-h**). This small-molecule additive study further demonstrated that hydrogen bonding between the polymer chains is needed for polymer blending and can be disrupted by small-molecule Napy. Overall, the incorporation of hydrogen bonding groups into silicone polymer blends presents a promising avenue for enhancing their properties by overcoming macrophase separation, expanding the applicability of such blends.

2.4 Conclusion

In summary, we present a compatibilization strategy for silicone-organic blends using complementary quadruple hydrogen bonding end groups capable of heterodimerization. Surface droplet reduction can be achieved using hydrogen bonding end groups which form the UN heterocomplex. O-PTIR proved critical in confirming blend compatibilization between the functionalized PDMS and PMMA. Since this strategy works with a high χ value system such as PMMA and PDMS, presumably it can be applied to achieve blend compatibilization in other lower χ value polymer blends. Development of polymer blend technology is vital to improve recyclability of plastics as this will eliminate the need to physically separate plastics before recycling.

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**Chapter 3: Synthesis of Structurally Diverse
Dithiols: Telechelic Oligomers from α -Lipoic Acid
and Vinyl Copolymerization**

3.1 Abstract

Dithiol compounds are an essential class of materials currently utilized as building blocks or cross-linkers in various applications. However, readily available dithiols are exceedingly simple and lack dangling side chain residue or functionality, which can significantly influence their physical and chemical properties. Here, we present structurally diverse dithiol oligomers with customizable side chain residues (esters, amides etc.) derived from copolymers of α -lipoic acid (LA) derivatives and various vinyl comonomers. Importantly, the molecular weight of the polymeric dithiols can be varied (ranging from 1–24 kg mol⁻¹) by adjusting the feed ratio (mol%) of LA or LA-derivative. Remarkably, dithiols with different side chain residue display a wide range of glass transition temperatures (T_g) varying from –62 °C to 11 °C a rarity among commercially available dithiols. Additionally, tailor-made structurally diverse telechelic thiols were employed in thiol-Michael click chemistry, resulting in UV cross-linked networks with tunable modulus and T_g . Finally, dithiols also demonstrated efficacy as cross-linkers to cross-link commercial polybutadiene (PB) through thiol-ene reactions, thus expanding the scope of these dithiol oligomers across different fields of material science.

3.2 Introduction

Dithiols have garnered considerable attention in materials chemistry for their role as building blocks and cross-linkers in creating soft and smart materials.^{1–4} Highly reactive thiols are favored for their applicability in click reactions^{5–7} such as thiol-Michael addition reaction,⁵ radical-mediated thiol-ene reactions,⁸ thiol-yne reactions,⁹ thiol-isocyanate reactions,¹⁰ and thiol-epoxy reactions.¹¹ Because of their broad utility, commercially available dithiols have

been leveraged to form chemically cross-linked materials^{12–14} for surface modification and coatings^{15–18}, engineering adhesives¹⁹, 3D printing^{20–22}, smart liquid crystal elastomers (LCE)^{1,3,4}, nanoparticles^{29–31}, etc. Recent reports highlighted the utility of polymeric dithiols in segmented or multiblock thermoplastic polymers where short-chain dithiols acted as chain extenders, facilitating chain growth and improving material properties.^{23–28}

Despite their widespread utility, commercially available dithiols are inherently fixed length with distinct low molecular weights, thus limiting their applicability. Furthermore, low molecular weight dithiols often have a foul odor, making them unpleasant to use.¹⁶ Widely used dithiol terminated polymers, such as PEG-based dithiol and PDMS-based dithiol, are limited in structural diversity and innate functionality.^{23,24} Methods to impart functionality into commercial dithiols include C–H functionalization, which often involves metal catalysts that could chelate to thiols.³² Polymeric dithiols can be synthesized using trithiocarbonate containing RAFT (reversible addition–fragmentation chain transfer) agents, followed by deprotection of end group via aminolysis³³. However, this strategy relies on expensive difunctional chain transfer agents. Thus, structurally diverse vinyl dithiols with tunable material properties are rare.

Recognizing their limited availability but widespread utility, we aimed to explore methods for generating structurally diverse, functional dithiol materials. Incorporating disulfides or thioesters, cleavable functional groups, along the backbone of vinyl-based copolymers could provide a potential source of thiol chain-ends. To this end, the thionolactone-containing monomer, dibenzo-[*c,e*]-oxepane-5-thione (DOT), has been investigated by Gutekunst, Roth, Guillaneuf and Johnson.^{34–38} Thionolactones efficiently copolymerize with various vinyl functionalities, thereby installing thioester moieties along the backbone.

Appropriate selection of cleavage agents can yield dithiol polymers. Despite the potential of DOT, the multistep synthesis involved in the production of cyclic comonomer restrict its further utilization.

Conversely, our group, amongst others, has recently demonstrated that α -lipoic acid (LA), readily available at the kilogram scale, can serve as a comonomer to produce degradable, self-healing polymers.^{39–60} The small molecule building block, containing a 1,2-dithiolane ring, undergoes radical ring-opening polymerization (ROP) with vinyl monomers through RAFT process³⁹, conventional free-radical process^{40,47}, or in the presence of cation⁵⁴ or anions^{55, 56} to yield vinyl copolymers with disulfide bonds along the polymer backbone^{57,58}. Reduction of the cleavable disulfide bond in the presence of a mild reducing agent led to degradation of the copolymer into low molecular weight oligomers.⁴⁰

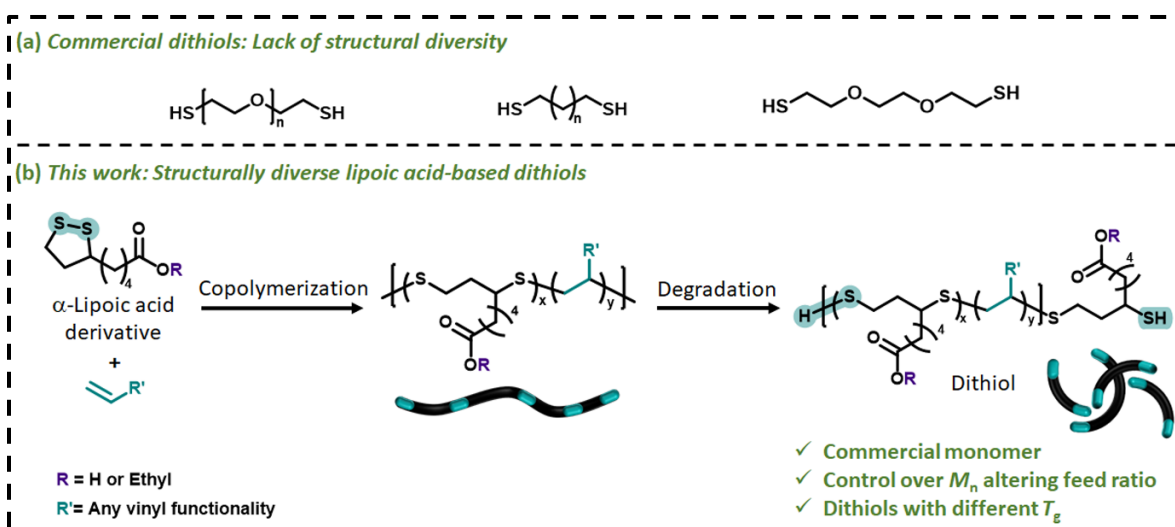


Figure 3.1. 1,2-Dithiolanes as degradable comonomer for the synthesis of structurally diverse dithiols. (a) Commercially available dithiols lacking structural diversity. (b) Degradable copolymer of α -lipoic acid derivative and vinyl functionality: a potential source of structurally diverse dithiols.

By leveraging this concept, we demonstrated the synthesis of dithiol oligomers by cleaving disulfide bonds within copolymers consisting of α -lipoic acid (LA) or ethyl lipate (ELp) with various vinyl comonomers. Conventional free radical polymerization of ELp with different vinyl comonomers, such as acrylates (*n*-butyl acrylate, isobornyl acrylate, and 2-cyanoethyl acrylate), acrylamides (*N,N*-dimethylacrylamide, 4-acryloylmorpholine, and *N*-dodecylacrylamide), or styrene, results in materials containing various side chain functionalities. Thus, we present a platform of structurally diverse telechelic thiols upon degradation using reducing agent. Importantly, the molecular weight of the dithiol oligomers is well controlled simply by adjusting the LA or ELp feed ratio. The dithiol oligomers synthesized by this strategy exhibit a wide range of glass-transition temperatures (T_g , $-62\text{ }^{\circ}\text{C}$ to $11\text{ }^{\circ}\text{C}$) owing to the presence of different functionalities pendant to the backbone. We envision that this new class of material with different thermal properties has the potential to expand the physical properties of functional materials. Therefore, photocrosslinking of acrylate- and acrylamide-based telechelic thiol building blocks was investigated as representative examples to produce networks with high stiffness. Furthermore, efficient cross-linking using dithiol oligomers was demonstrated with commercial polybutadiene (PB), highlighting the broad utility of these dithiols in various aspects of materials chemistry to generate scalable commodities with varied properties.

3.3 Results and Discussion

Structurally diverse polymeric α,ω -dithiol are synthesized through the incorporation and subsequent reduction of disulfide bonds in the vinyl polymer backbone (**Figure 3.1**). Our group previously demonstrated that the number of disulfide bonds in the resultant copolymer

increases with reaction conditions at low temperature and high concentration. Furthermore, the molar fraction of incorporation for such bonds entirely depends on the relative feed ratio and reactivity of the monomers ⁴⁰.

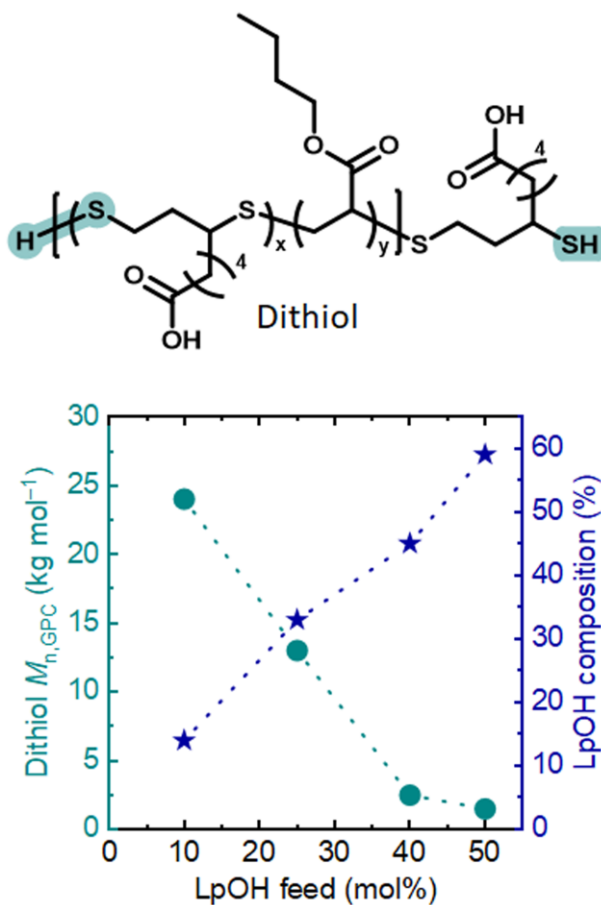


Figure 3.2. α -Lipoic acid feed ratio (mol%) as a synthetic handle tuned molecular weight of dithiol polymers while keeping other polymerization conditions (concentration, temperature, and duration of the reaction) constant. Polymer composition was akin to feed ratio.

To establish the relation between the feed ratio of comonomers and molecular weight of dithiols, initially, α -lipoic acid (LA) was copolymerized with *n*-butyl acrylate (nBA) at various feed ratio (LA feed 10 mol%, 25 mol%, 40 mol%, and 50 mol%) keeping total monomer concentration 2 M and temperature at 30 °C during conventional free-radical

polymerization (**Scheme B1**). In general, the disulfide bonds incorporated in the polymer backbone increased with an increase in LA feed ratio.⁴⁰ As expected, such copolymerization led to incorporation of disulfide bonds via LA-LA diad and the composition of LA in the resulting polymer was found to be similar to the feed (14 mol%, 33 mol%, 45 mol%, and 59 mol%), keeping LA conversion around 60–80% (**Table B1, Figure B1**). Reduction of these parent copolymers with tris(2-carboxyethyl) phosphine hydrochloride (TCEP) produced oligomeric dithiols with tunable molecular weights (24 kg mol⁻¹, 13 kg mol⁻¹, 2.5 kg mol⁻¹, and 1.5 kg mol⁻¹ respectively) (**Table B1, Figure B2, Figure 3.2**).

To focus on thiol chain-ends and avoid carboxylic acid reactivity, ethyl lipoate (ELp) is widely favored as a degradable monomer due to its straightforward synthesis (**Scheme B2, Figure B3**).^{40,46,47} To explore structurally diverse copolymers and degraded products (dithiol oligomers), in this study we copolymerized ELp with several different vinyl functionalities such as acrylates, acrylamides, and styrenics under similar free-radical polymerization while maintaining monomer feed ratio 50:50 (ELp:vinyl) and concentration 2 M constant (**Scheme B3-B5, Figure B4-B20**). Akin to LA, vinyl comonomers having different side-chains impart structurally diverse copolymers and eventually α,ω -polymeric dithiols (**1–7**) with different molecular weights ranging from 1–7.2 kg mol⁻¹ upon reduction (**Figure B21**). High-molecular weight (22 kg mol⁻¹) α,ω -polymeric dithiol (**8**) was also synthesized by decreasing ELp feed to 20 mol%, this shows the versatility of this process to procure a wide scope of dithiols (**Figure 3.3**). Interestingly, the newly formed class of dithiols exhibited a range of glass-transition temperature (T_g) varying from –62 °C to 11 °C, rendering them unique in terms of both structure and property (**Figure B22, Figure 3.3**).

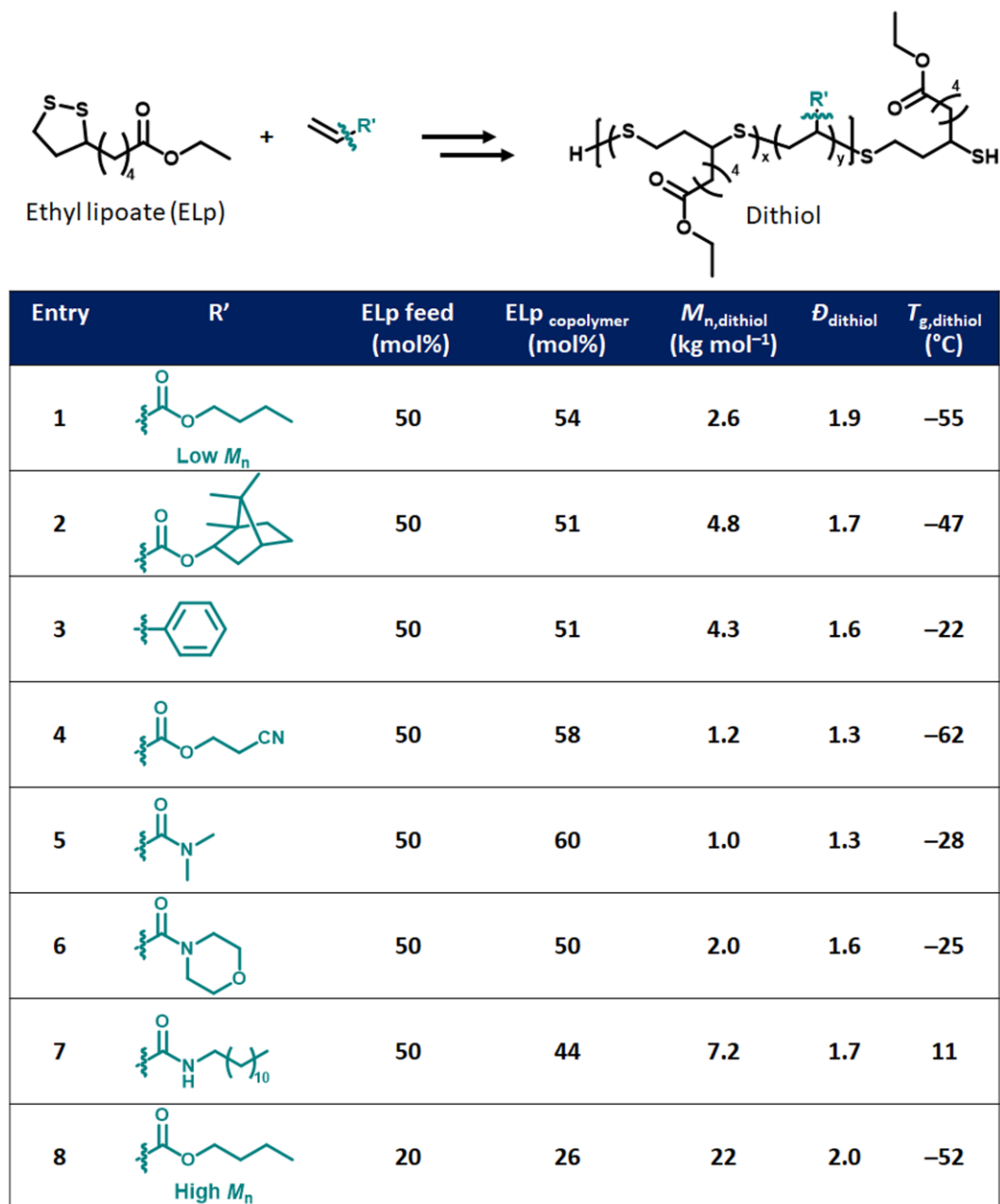


Figure 3.3. Structurally diverse dithiols by copolymerization of α -lipoic acid derivative with a variety of vinyl comonomers while keeping total monomer concentration at 2 M using conventional free-radical polymerization at 30 °C with V-70 as a thermal azoinitiator. Degradation of copolymer (Conditions: TCEP, THF/H₂O, 60 °C) produced dithiols with different side chain residues resulting in varying distinct glass-transition temperatures (T_g).

With a broad range of novel dithiols synthesized, it was imperative to characterize the chain-end fidelity. Primarily, the reactivity of the as-synthesized dithiol was investigated through thiol-Michael reaction with maleimide. For instance, dithiol oligomer **1** was end-capped with *N*-benzyl maleimide in the presence of photoinitiator (2,2-Dimethoxy-2-phenylacetophenone) and 365 nm UV light (**Scheme B6**). As expected, ¹H NMR of the purified product displays clear signals at 4.6 and 7.3 ppm attributed to the benzylic moiety which confirms reactivity of the thiol chain-ends (**Figure B23**).

Having confirmed the presence of reactive thiol chain ends of the synthesized dithiol oligomer, we employed our dithiols as building blocks for the formation of crosslinked networks to showcase their potential in functional materials. Therefore, telechelic thiol oligomer building blocks consisting of either *n*-butyl acrylate (**1**), isobornyl acrylate (**2**), or acrylamide (**5**) were investigated as representative examples (**Figure 3.4**). For cross-linking, a tri-functional cross-linker, 1,1',1''-(nitrilotris(ethane-2,1-diyl))tris(1H-pyrrole-2,5-dione) (**Tri-M**), was synthesized following a previous report (**Scheme B7, Figure B24-B25**).

Importantly, a precise stoichiometric mixture of the telechelic thiol and **Tri-M** was necessary to obtain highly crosslinked networks. Surprisingly, it was observed that dithiol oligomer **1** was unable to produce a highly cross-linked network as indicated by a molecular weight of $M_n=2600 \text{ g mol}^{-1}$ via size-exclusion chromatography (SEC) and the gel fraction was zero (**Figure B26**). This implies that the stoichiometric balance between dithiol oligomers and **Tri-M** was not appropriate, leading to incomplete network formation. Therefore, determining the actual molecular weight of dithiol for the network formation becomes essential.

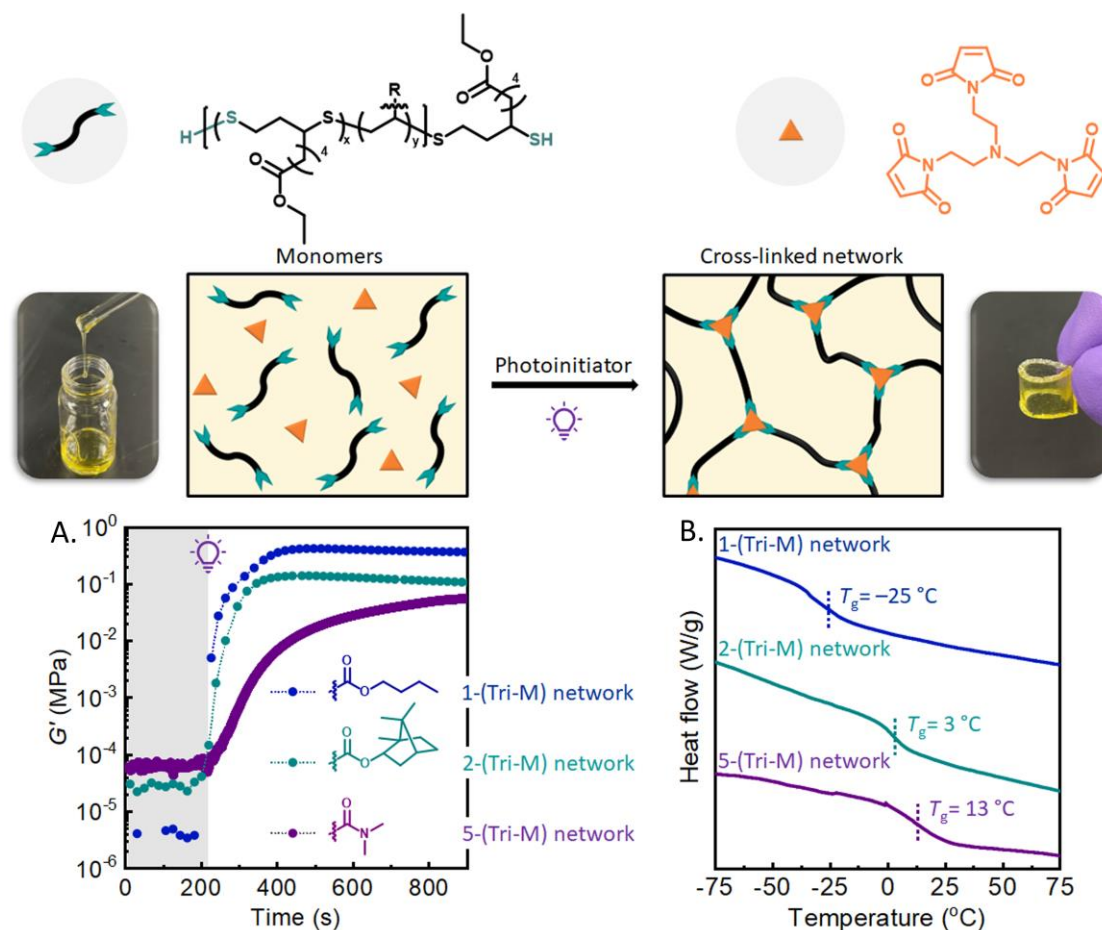


Figure 3.4. Ethyl lipoate (ELp) derived dithiols as building blocks for network formation. (A) Kinetics of network cross-linking between tris (2-maleimidoethyl) amine (**Tri-M**) and different dithiol oligomers in the presence of photoinitiator (2,2-Dimethoxy-2-phenylacetophenone) and UV light. Evolution of the storage moduli in the presence of dithiol oligomers **1**, **2**, and **5** are shown here. (B) Glass-transition temperature (T_g) of the formed networks can be tuned employing different dithiol building blocks.

Hence, we conducted several titration experiments where the amount of dithiol varied based on our perceived molecular weight while keeping the amount of **Tri-M** constant. For dithiol oligomer **1**, several solvent-free thiol-Maleimide networks were made with the **Tri-M** cross-linker, varying the perceived molecular weight (2600 g mol⁻¹ to 700 g mol⁻¹), and subsequently determined the gel fraction of each sample (**Figure B26**). Interestingly, gel fraction was highest (above 80%) when considering the molecular weight around 1000 g mol⁻¹ (**Figure B26**). Similarly, the effective molecular weight for network formation of the dithiol oligomer **2** was 1500 g mol⁻¹ (**Figure B27**), while dithiol oligomer **5** was 1000 g mol⁻¹, which is akin to M_n obtained from SEC (**Figure B28**).

After establishing ideal stoichiometry for network formation, network properties were investigated. UV crosslinking of the resins (dithiol oligomer and maleimide) was quantitatively studied using oscillatory shear rheology as presented in **Figure 3.4A**. In this experiment, the in situ change in shear modulus was monitored over time, keeping the light intensity at 400 mWcm⁻². Upon irradiation for dithiol oligomer **1**, storage modulus (G') increased over time and reached a plateau within 400 s, displaying clear gel point at 220 s. Comparable results were observed for telechelic thiols **2** and **5** exhibiting gel point at ~ 300 s and ~ 400 s respectively. This demonstrated the excellent efficacy of the novel dithiol oligomer to form highly cross-linked networks with varying storage moduli (**Figure B29, Figure 3.4A**).

To probe the modulated thermal properties of the networks, differential scanning calorimetry (DSC) revealed varying T_g s among the networks (**Figure 3.4B**). The T_g of telechelic thiol **1** is -55 °C, which increased to -25 °C for **1-network** upon cross-linking with **Tri-M**, primarily due to high network rigidity. Similarly, as expected, for **2-network** and **5-network**, T_g were, 3 °C and 13 °C which are significantly higher than their constituent dithiols

which are $-47\text{ }^{\circ}\text{C}$ and $-28\text{ }^{\circ}\text{C}$, respectively. This observation further underscores the significance of the structurally diverse dithiol oligomer in tuning the thermal property of the materials (**Figure 3.4B**).

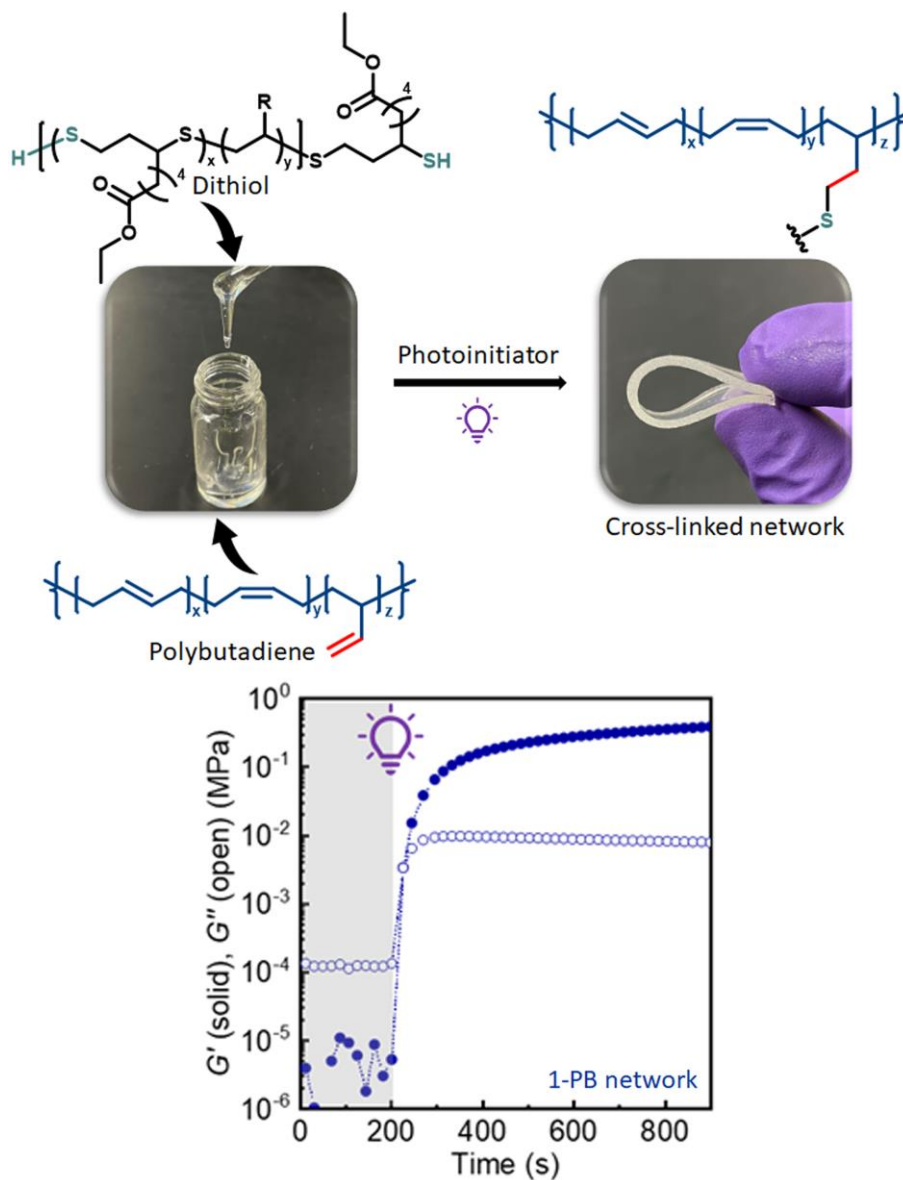


Figure 3.5. Polybutadiene (PB) efficiently crosslinked using dithiol polymers. Dithiols can cross-link in the presence of photoinitiator and UV light. Here, only 1 mol% of dithiol was required for gelation.

To show the versatility of the novel dithiols, their use as additives for crosslinking was also investigated. For this, commercially available non-polar polybutadiene (PB, $M_n = 28 \text{ kg mol}^{-1}$) was employed. Polybutadiene contains a significant amount of reactive pendant olefins resulting from the 1,2-addition during polymerization.⁶¹ Taking advantage of these reactive olefinic units, polybutadiene was cross-linked via addition of 1 mol% of dithiol oligomer in the presence of photoinitiator (DMPA, 20 mol% with respect to thiol), and the kinetics were monitored via rheology experiments (**Figure B30-B31** and **Figure 3.5**). Gelation was observed for telechelic thiol **1** upon shining UV light where storage modulus (G') increased over time exhibiting gel point at 230 s (**Figure 3.5**). The gel fraction of the cured system was high, above 90% (Figure S30). Similar phenomena were also observed with telechelic thiol **2** and **3**, demonstrating the cross-linking ability of the novel system (**Figure B31**). This expands the availability of structurally diverse dithiols for network formation.

3.4 Conclusion

In summary, we demonstrated the synthesis of a class of novel, structurally diverse dithiol oligomers derived from degradable copolymers. These polymeric dithiols exhibit distinct thermal properties (T_g), imparted by the various vinyl functionalities and tunable molecular weights. Benefitting from this structural diversity, reactive telechelic thiols also enabled tunable thermal properties in the formed cross-linked networks. These novel dithiols showed potential not only as a building block but also as cross-linkers to obtain highly cross-linked networks. This straightforward and versatile strategy to access dithiol oligomers will widen the scope of designing various tailor-made thiol-functionalized polymers and improve the prospects of dithiols in material chemistry.

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Chapter 4: Dithiol Copolymers as Building Blocks for Random Multiblock Copolymers

4.1 Abstract

α,ω -Dithiol polymer building blocks provide a versatile strategy for the preparation of random multiblock copolymers (MBCs) with controllable segment molecular weight, tunable composition, and added chemical degradability. This facile synthetic strategy affords access to dithiol chain-ends through an initial copolymerization of vinyl or styrenic monomers with ethyl lipoate followed by disulfide bond reduction, producing dithiol terminated polymer products. This two-step strategy allows for preparation of thiol terminated polymers over a wide range of molecular weights (2 – 32 kDa) by simply controlling the feed ratio of vinyl monomer to ethyl lipoate. Linear thiol terminated segments are repolymerized via oxidative coupling to prepare designer random multiblock copolymers with high molecular weights (68 – 95 kDa) and controlled degradability at disulfide bond sites. This approach for preparation and recombination of dithiol terminated segments allows for blending of chemically distinct dithiol polymer building blocks with tunable composition and segment length. Thus, by leveraging this approach, we demonstrate the ability to tune multiblock copolymer mechanical properties over a wide range through facile modulation of block incorporation ratio.

4.2 Introduction

Multiblock copolymers (MBCs) represent an evolving frontier in polymer science and offer a flexible platform for preparing block architected polymers where each block typically exhibits different physical or chemical characteristics, allowing a combination of diverse properties within a single material.^{1–3} These unique materials find themselves improving

properties in thermoplastic elastomers,^{4–6} actuators⁷, membranes^{8–10}, medical applications^{11–17}, and as polymer blend compatibilizers^{18–22}.

However, the diversity of tailorable MBCs has been restricted by synthetic challenges. The earliest instances of random MBCs were primarily synthesized through step-growth polymerizations, combining various polymer segments to produce high molecular weight polycondensation products.^{23–26} Traditional step-growth polymerizations for MBC formation require precise stoichiometric balance between complementary polymerizable groups to achieve high-molecular weight polymers and subtle variations in prepolymer chain-end stoichiometry can appreciably impact final product properties²⁷. To overcome the limitations of classical, precise stoichiometry, novel strategies that employ identical prepolymer chain-ends allow for greater tunability and flexibility in the prepolymer's molecular weight and feed ratio, enabling the creation of diverse, high-molecular weight MBCs^{28–31}. Critically, positioning reversible bonds at the chain-ends of the segments allows chemically recyclable MBCs by degradation to high and low glass-transition temperature (T_g) telechelic polyolefin-like oligomeric units³².

Telechelic thiol functionalized vinyl oligomers are being explored as a reversible system for chemical recycling through the formation and cleavage of disulfide bonds^{33,34}. Directly accessing telechelic thiol vinyl polymers, however, requires custom reversible addition–fragmentation chain-transfer (RAFT) agents followed by aminolysis,^{35–38} bifunctional atom transfer radical polymerization (ATRP) initiator with subsequent nucleophilic substitution of the halide,³⁹ or an end-capping strategy using anionic polymerization⁴⁰. More recently, degradable comonomers such as thionolactone dibenzo[c,e]oxepine-5(7H)-thione (DOT) can produce α,ω -dithiol polystyrene (PS)³⁴ with

careful selection of cleavage reagent, while ethyl lipoate (EtLp) has been used to produce α,ω -dithiol poly(*n*-butyl acrylate) (PnBA)³³ oligomers after disulfide bond cleavage. In both of these cases, oxidization of α,ω -dithiol polymer species has shown high-molecular weight recovery.

Here we report a straightforward method for α,ω -dithiol polymer synthesis and subsequent creation of random MBCs with customizable mechanical properties. This versatile approach provides a comprehensive toolkit for tailoring MBC composition and properties for a range of potential applications. Key synthetic advantages of this approach lie in the ability to tailor segment molecular weight, control MBC composition, and install targeted chemical degradability. By preparing parent copolymers of vinyl or styrenic monomers with EtLp and cleaving disulfide bonds, a range of daughter dithiol polymers can be prepared. Blending and repolymerization of dithiol terminated polymers allows MBCs with adjustable composition and mechanical properties and opens doors to facile preparation of new MBC copolymer chemistries.

4.3 Results and Discussion

To develop a synthetic toolkit for MBCs, we first expanded the methodology for linear α,ω -dithiol polymers with various side chain residues. Building upon previous reports, copolymers of acrylic or styrenic monomers with EtLp present a range of incorporated monomer sequences, but crucially contain disulfide bonds along the chain backbone at EtLp diads³³. These disulfide bonds can be reduced to produce low molecular weight, α,ω -dithiol terminated polymer species (**Figure 4.1**).

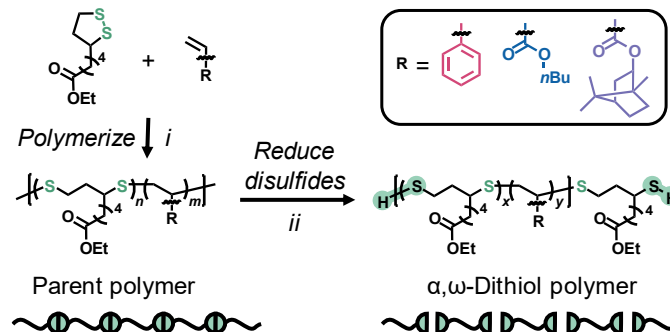


Figure 4.1. Synthetic scheme for α,ω -dithiol polymers using facile free radical polymerization of EtLp and comonomer where i) V-65, 40 °C and ii) TCEP•HCl, THF/H₂O, 60 °C.

A library of targeted α,ω -dithiol copolymers with varied molecular weights were produced simply by adjusting the feed ratio of EtLp to comonomer. By tuning this feed ratio, the number of EtLp repeat units—and consequently, the number of degradable EtLp diads—in the parent copolymers was controlled. Parent copolymers with higher disulfide contents produced lower molecular weight dithiol species. Thus, daughter materials of varying molecular weights were targeted. As a representative example, the copolymerization of EtLp with *n*-butyl acrylate (*n*BA) at various feed ratios (50 mol% – 20 mol% of EtLp) produced parent copolymers ranging from 100 kDa – 260 kDa (**Table C1**). These parent copolymers were subsequently degraded with TCEP to produce daughter dithiol polymers with molecular weights spanning 1.9 kDa – 24 kDa (**Figure 4.2**). In a similar manner, daughter copolymers of PS (9 kDa – 33 kDa) and poly(isobornyl acrylate) (8 kDa) were synthesized. The EtLp to comonomer composition in the dithiol polymers matched the starting feed ratio, confirming the utility of the feed ratio as a reliable handle for tuning the molecular weight of the daughter copolymers (**Table C2**).

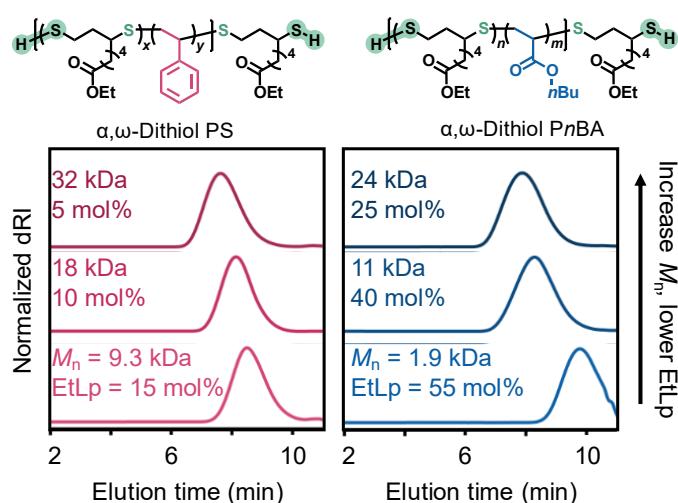


Figure 4.2. THF SEC results for representative PS and PnBA α,ω -dithiol copolymers showcasing the variety of molecular weights achieved by tuning the feed ratio of EtLp.

To demonstrate disulfide and thiol reversibility on polymer chain-ends, repeated oxidation and reduction of thiol and disulfide linkages was conducted. We recognized the repolymerization followed a step-growth mechanism, where high conversion was critical to attain high-molecular weight species. Additionally, the materials are inherently disperse, which may affect stoichiometry for repolymerization. As such, we followed previously established protocols to verify optimized oxidation conditions leading to high molecular weight recovery by SEC (**Tables C3, C4**). Comparison of parent, daughter dithiol, and repolymerized polymers by $^1\text{H-NMR}$ revealed no changes, confirming the absence of deleterious alterations (**Figure C1**). Moreover, this approach is extensible to other non-vinyl dithiol polymers such as α,ω -dithiol PDMS (**Table C5**).

Building upon the success of high molecular weight recovery of each linear polymeric species separately, random MBCs were synthesized by repolymerizing chemically distinct dithiol daughter copolymers concurrently. MBCs containing PnBA and PS blocks were

selected to mimic high-performance commercial materials with segments of both high and low glass-transition temperature (T_g) (**Figure 4.3**). The MBCs synthesized for this study had high molecular weights (69 – 95 kDa), varied compositions (30 – 90 wt% PS dithiol) and high dispersity ($\mathcal{D} = 1.6 - 1.8$), as expected for step-growth polymerization (**Table C6**). Encouragingly, MBCs containing repolymerized disulfides remained transparent, while those comprising dithiol blends or TCEP-degraded MBCs lacking covalent linkages appeared optically opaque when drop-cast, indicative of phase separation^{41,42}. (**Figure 4.4**).

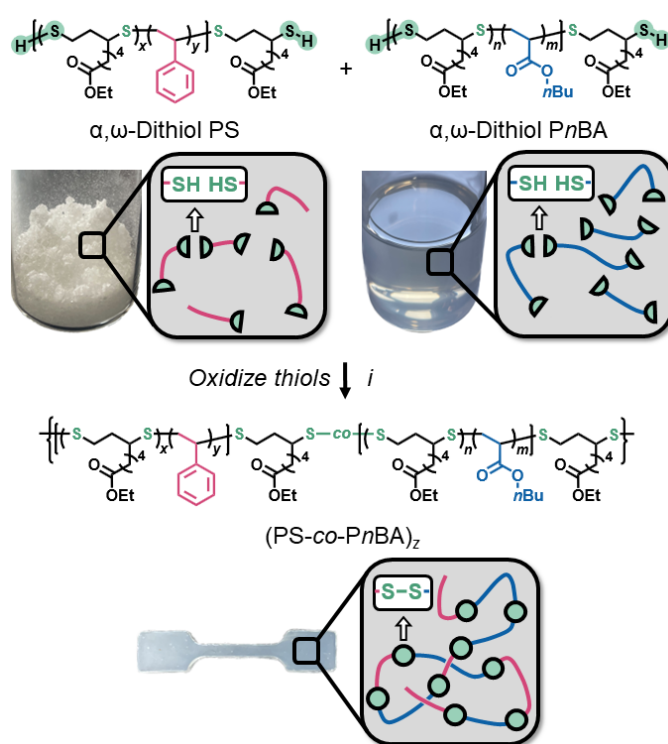


Figure 4.3. Synthetic scheme for random multiblock copolymers produced from dithiol polymer blends. Pictures of material show altered physical properties after thiol oxidation *i*) I_2 , pyridine, DCM.

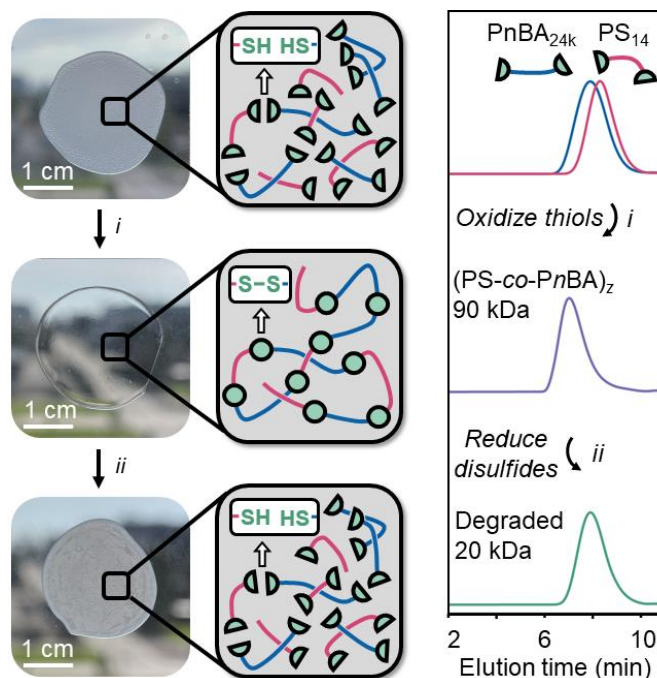


Figure 4.4. Optical images of opaque dithiol blend before thiol oxidization, optically transparent multiblock copolymer, and opaque degraded multiblock copolymer. THF SEC traces tracked molecular weight changes. *i*) TCEP•HCl, THF/H₂O, 60 °C and *ii*) I₂, pyridine, DCM.

To further investigate the miscibility of polymer domains in the MBCs, differential scanning calorimetry (DSC) and small angle X-ray scattering (SAXS) was used to verify the covalent bonds between distinct polymer blocks. As seen through DSC, the (PS-co-PnBA)_z series, samples exhibited only a single T_g (**Figure C2**). Furthermore, the SAXS data (**Figure C4**) revealed no indications of microphase separation. This suggests that the incorporation of EtLp in both blocks facilitated effective mixing of polymer domains, resulting in generally homogeneous compositions by reducing the Flory–Huggins interaction parameter (χ) compared to similar weakly segregating (PS-co-PnBA)_z systems without EtLp incorporation⁴³. Conversely, a higher χ system such as (PS-co-PDMS)_z would lead to microphase separation

(Figure 4.5). Indeed, disordered microphases were observed using SAXS (Figure C5 and C6), consistent with theoretical⁴⁴ expectations and previous experimental²⁹ findings in random multiblock copolymer literature. Additionally, these materials exhibited two distinct T_g values corresponding to the PS and PDMS blocks (Figure C3).

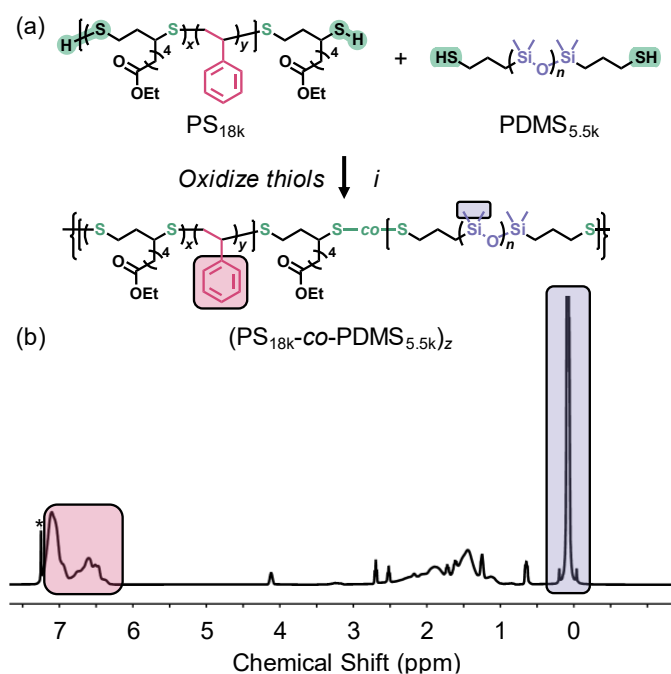
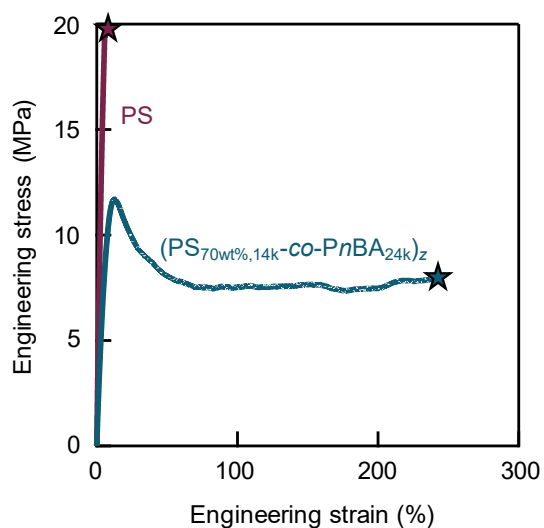


Figure 4.5. (a) Synthetic scheme for random multiblock copolymers using non-vinyl, commercially available dithiol PDMS for a higher χ analog *i*) I_2 , pyridine, DCM. (b) ¹H-NMR showing incorporation of both PS and PDMS into multiblock copolymer. Red box highlights PS benzyl protons and purple box highlights methyl group protons on PDMS

With precedent set for the synthesis of MBCs from dithiol daughter polymers, we sought to characterize the mechanical properties of the repolymerized materials. Mechanical testing in uniaxial tension elucidated the impact of segmental copolymer composition on materials properties, demonstrating that MBCs arising from dithiol polymers have greater degrees of tunability and toughness than classic polystyrene materials. Specifically, (PS-co-

$PnBA)_z$ exhibited enhanced toughness compared to commercial PS, as observed by the significant improvement in area below the stress-strain curve (**Figure 4.6a**). Moreover, by leveraging the ability to adjust the feed ratio of daughter dithiol copolymers, random MBCs with tunable properties were achieved (**Figure 4.6b**). For example, significant modulation of elongation at break was achieved for a series of $(PS-co-PnBA)_z$ that ranged from brittle to highly ductile materials. The present results illustrated the utility of this simple strategy for preparing random MBCs and demonstrated its potential for various applications owing to the tunable structure.

(a) Enhanced toughness



(b) Tunable properties

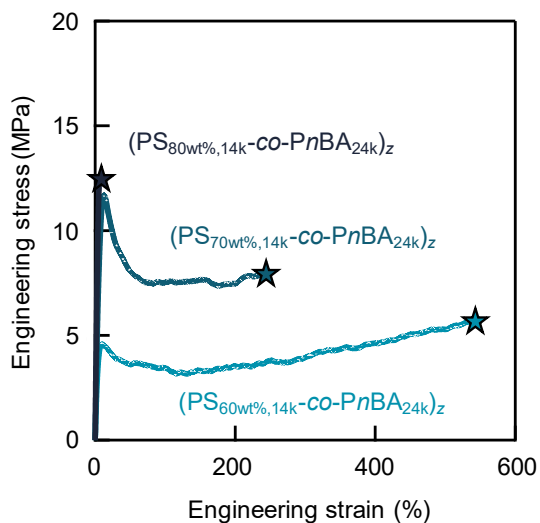


Figure 4.6. Mechanical tensile testing of multiblock copolymers showing (a) enhanced toughness compared to polystyrene (PS) and (b) tunable mechanical properties depending on dithiol composition.

4.4 Conclusion

In summary, we present a versatile strategy for synthesizing random MBCs using linear α,ω -dithiol polymers. Vinyl α,ω -Dithiol polymer building blocks with a range of molecular weights (2 – 32 kDa) were synthesized via free radical copolymerization with EtLp, followed by cleavage of disulfide bonds to yield telechelic thiol chain ends. These dithiol polymers can be combined at various feed ratios and repolymerized by reforming the disulfide bonds, resulting in a diverse range of random MBCs with high molecular weights (68 – 95 kDa). The mechanical properties of the random MBCs were found to depend on the feed ratio of high and low T_g dithiol polymers. This approach enables precise control over block molecular weight, tunable composition, and chemical degradability of the resulting MBCs. The versatility

and scalability of this approach paves the way for future studies on telechelic thiol vinyl-based polymers and random MBCs.

4.5 References

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Appendix A. Supporting Information for Chapter 2

Materials

1,1,2,2-tetrachloroethane-d₂ was dried over 4 Å molecular sieves for 24 h prior to use in variable temperature ¹H-NMR studies. Starting materials and reagents were used as received unless otherwise stated: 1,1,2,2-tetrachloroethane-d₂, chloroform-d, *N,N*-dimethylformamide-d₇ [Cambridge Isotope Laboratories], monohydride terminated polydimethylsiloxane asymmetric 80-120 cSt (MCR-H21), hydride terminated polydimethylsiloxane 1000 cSt (DMS-H31), platinum-divinyltetramethyldisiloxane complex; 2% Pt in xylene (Karstedt's catalyst) [Gelest], methyl methacrylate 99%, stabilized [Acros Organics], magnesium sulfate anhydrous (MgSO₄), sodium bicarbonate (NaHCO₃), potassium carbonate anhydrous (K₂CO₃), ethanol anhydrous [Fisher Chemical], copper (I) bromide (CuBr) [Strem Chemicals], poly(methyl methacrylate) (PMMA, 35 kDa), 10-undecenoic acid, *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA), palladium (II) acetate (Pd(OAc)₂), oxalyl chloride, 30% ammonium hydroxide solution, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos), 1,4-dioxane anhydrous, 2-nitrobenzyl bromide, triethylamine, α-bromoisobutyryl bromide [Sigma Aldrich]. Tetrahydrofuran (THF), acetonitrile (ACN), dimethylformamide (DMF), toluene, and dichloromethane (DCM) were obtained from a solvent purification system (PureSolv, Innovative Technology Inc); other solvents, including hexanes, ethyl acetate, acetone, and methanol, were used as received. All other chemicals were purchased from Sigma Aldrich and used as received. Chromatographic separation was conducted with normal phase silica gel (60 Å, 0.040–0.063 mm, Geduran) using a Biotage Isolera One.

Spin coating procedure

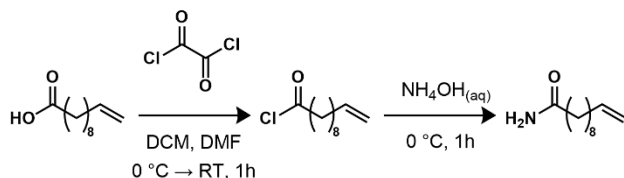
Wafer pieces were cut using a diamond tipped scribe into 1 cm × 1 cm squares, sonicated in acetone and isopropyl alcohol for 5 minutes each, dried under nitrogen, and UV/ozone cleaned for 30 minutes. Wafers were used within 12 hours after UV/ozone cleaning. PDMS and PMMA were dissolved separately in CHCl₃ (0.1 g/mL stock solutions). Solutions then were added together and mixed at the appropriate ratio and spin-coated (3000 rpm, 60 seconds) on a silicon wafer. After spin-coating, samples were annealed in a vacuum oven at 150 °C, well above the glass transition temperatures (T_g) of the polymers, for 24 hours.

Characterization methods

¹H-NMR spectra were collected on a Bruker Avance NEO 500 MHz using chloroform-d or 1,1,2,2-tetrachloroethane-d₂ as a deuterated solvent. Size exclusion chromatography (SEC) was measured using Waters e2695 separation module with a Waters 2414 differential refractive index detector equipped with two columns (PLgel, 5 μm MiniMIX-D, 250×4.6 mm columns + guard) with chloroform containing 0.25% TEA at 35 °C as the mobile phase. O-PTIR spectra and images were collected on spin coated thin filmed using a mIRage™ microscope from Photothermal Spectroscopy Corp. (Santa Barbara, CA). The microscope includes a 532 nm probe laser, the power of this source was adjusted to ~ 5 mW at the sample surface. A Quantum Cascade Laser (DRS Daylight Solutions, San Diego, CA) covering the mid-IR range of 950 – 1800 and 2700 – 3000 cm⁻¹. Differential Scanning Calorimetry (DSC) was performed on a TA Instruments Q2000 DSC with three repeated cycles between –150 and +150 °C at a constant rate of 10 °C/min. Only the second heating scan is shown. High

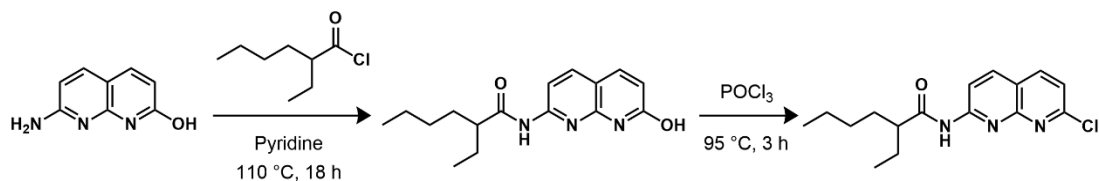
resolution mass spectrometry (HRMS) data was collected on a Waters Xevo G2-Xs QToF in ESI+ mode. Samples were run via column bypass in acetonitrile.

Undec-10-enamide was prepared adapted from Pirkle et al.¹

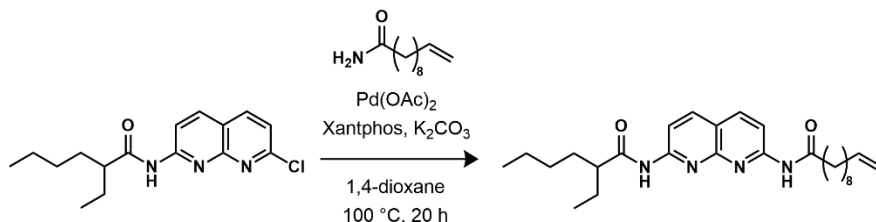


Dissolved 10-undecenoic acid (3.0 g, 16.3 mmol, 1.0 equiv.) and dry DMF (120 μ L, 1.54 mmol) in 50 mL dry DCM into a flame dried 100 mL round bottom flask equipped with stir bar. Reaction mixture was cooled to 0 $^{\circ}$ C. Added oxalyl chloride (4.13 g, 32.5 mmol, 2.0 equiv.) dropwise and let stir for 1 hour, letting it slowly warm to room temperature. Solvent removed under reduced pressure to give a crude oil. Cooled reaction flask to 0 $^{\circ}$ C using ice bath then added 50 mL of 0 $^{\circ}$ C (pre-cooled) 30% ammonium hydroxide solution into flask. Capped and stirred flask on ice for 1 hour. White solid product collected after filtration and dried under vacuum (2.81 g, 94%). ^1H NMR (400 MHz, CDCl_3) δ 5.80 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.56 (d, J = 59.1 Hz, 2H), 5.09 – 4.82 (m, 2H), 2.21 (t, 2H), 2.03 (q, J = 1.5 Hz, 2H), 1.62 (p, J = 7.5 Hz, 2H), 1.44 – 1.21 (m, 10H). ^{13}C NMR (126 MHz, CDCl_3) δ 175.98, 139.28, 114.26, 36.08, 33.89, 29.41, 29.39, 29.32, 29.17, 29.00, 25.64. HRMS (ESI+) m/z calcd for $\text{C}_{11}\text{H}_{21}\text{NO}$ $[\text{M}+\text{Na}]^+$: 206.1521, observed: 206.1529.

7-(2-Ethylhexanoylamino)-2-chloro-1,8-naphthyridine (Napy-Cl) was prepared as reported by Ligthart et al.²



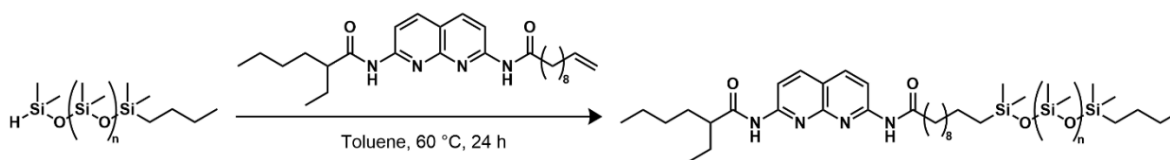
***N*-(7-(2-ethylhexanamido)-1,8-naphthyridin-2-yl)undec-10-enamide (Napy-alkene)** was prepared adapted from Ligthart et al.²



An oven dried two-neck 250 mL round bottom flask equipped with rubber septa, stir bar, and condenser then pump/purged with argon 3 times. 7-(2-Ethylhexanoylamino)-2-chloro-1,8-naphthyridine (3.48 g, 11.4 mmol, 1.0 equiv.), undec-10-enamide (2.50 g, 13.6 mmol, 1.2 equiv.), Pd(OAc)₂ (0.128 g, 0.57 mmol, 0.05 equiv.), Xantphos (0.82 g, 1.42 mmol, 0.125 equiv.), and potassium carbonate (2.20 g, 15.9 mmol, 1.4 equiv.) were quickly added to reaction flask under argon. Added 200 mL dry 1,4-dioxane then replaced rubber septa with glass stopper. Reaction mixture heated to reflux (100 °C) for 20 h. The mixture was cooled, filtered, and removed solvent by reduced pressure. The crude product was purified by silica gel column chromatography (eluent = EtOAc /Hex 20:80) resulting in product as a white powder (3.90 g, 76%). ¹H NMR (500 MHz, CDCl₃) δ 9.31 (s, 1H), 8.91 (s, 1H), 8.49 (dd, J = 8.9, 5.5 Hz, 2H), 8.10 (dd, J = 8.8, 4.4 Hz, 2H), 5.86 – 5.71 (m, 1H), 5.05 – 4.86 (m, 2H), 2.44 (t, J = 7.6 Hz, 2H), 2.30 – 2.19 (m, 1H), 2.05 – 1.96 (m, 2H), 1.80 – 1.44 (m, 6H), 1.40 – 1.15 (m, 14H), 0.93 (t, J = 7.4 Hz, 3H), 0.88 – 0.80 (m, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 175.74,

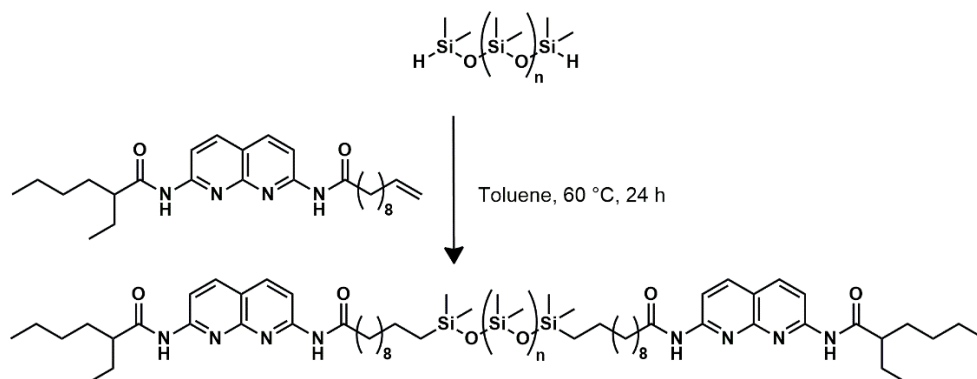
172.85, 154.38, 154.13, 153.68, 139.19, 139.10, 139.06, 118.32, 114.24, 113.82, 113.81, 50.62, 37.89, 33.83, 32.37, 29.79, 29.34, 29.30, 29.22, 29.11, 28.93, 25.98, 25.29, 22.80, 13.99, 12.05. HRMS (ESI+) m/z calcd for $C_{27}H_{40}N_4O_2$ $[M+H]^+$: 453.3229, observed: 453.3219.

Napy-PDMS synthesis



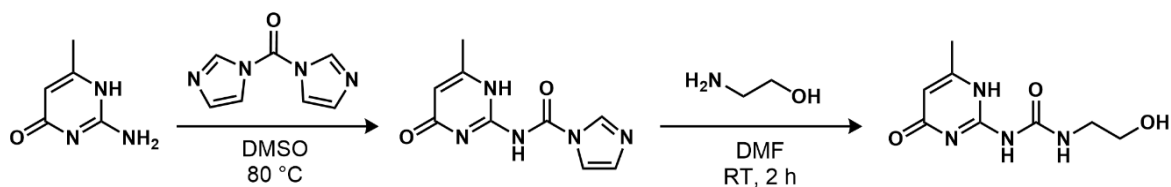
In a 5 mL vial, monohydride terminated polydimethylsiloxane (MCR-H21) (1 g, 0.2 mmol, 1 equiv.), N-(7-(2-ethylhexanamido)-1,8-naphthyridin-2-yl)undec-10-enamide (0.18 g, 0.4 mmol, 2 equiv.), 2 mL dry toluene, and stir bar was added and vial capped. Reaction mixture degassed with argon for 10 min while stirring. 10 ppm Karstedt's catalyst was added, and reaction mixture temperature was raised to 60 °C using an aluminum heating block for 24 h. Reaction mixture was cooled and diluted with 2 mL DCM then passed through silica plug using DCM as eluent. Solvent removed under reduced pressure. Crude mixture was dissolved in hexanes and washed with acetonitrile. Hexanes layer collected, solvent removed under vacuum, and product further dried in a vacuum oven at 50 °C overnight. Product isolated as a clear, colorless oil. (0.92 g, 84%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, $J = 25.1, 8.8$ Hz), 8.32 (s), 8.16 (d, $J = 8.8$ Hz), 2.44 (t, $J = 7.5$ Hz), 2.24 – 2.17 (m), 1.86 – 1.50 (m), 1.44 – 1.22 (m), 0.98 (t, $J = 7.4$ Hz), 0.94 – 0.85 (m), 0.60 – 0.49 (m), 0.29 – -0.10 (m). SEC: $M_n = 9.4$ kDa, $M_w = 11$ kDa, $\bar{D} = 1.2$.

bisNapy-PDMS synthesis

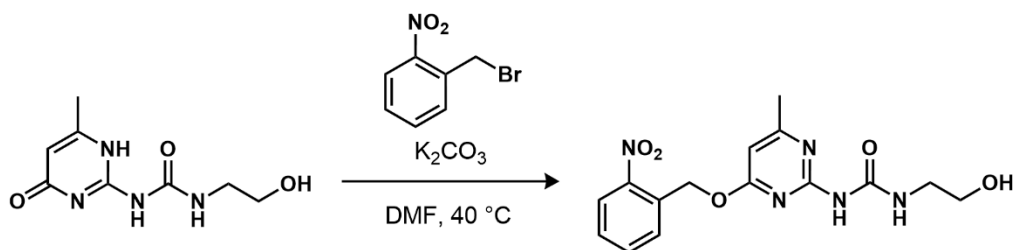


In a 5 mL vial, hydride terminated polydimethylsiloxane (DMS-H31) (1 g, 0.036 mmol, 1 equiv.), N-(7-(2-ethylhexanamido)-1,8-naphthyridin-2-yl)undec-10-enamide (0.065 g, 0.14 mmol, 4 equiv.), 2 mL dry toluene, and stir bar was added and vial capped. Reaction mixture degassed with argon for 10 min while stirring. 10 ppm Karstedt's catalyst was added, and reaction mixture temperature was raised to 60 °C using an aluminum heating block for 24 h. Reaction mixture was cooled and diluted with 2 mL DCM then passed through silica plug using DCM as eluent. Solvent removed under reduced pressure. Crude mixture was dissolved in hexanes and washed with acetonitrile. Hexanes layer collected, solvent removed under vacuum, and product further dried in a vacuum oven at 50 °C overnight. Product isolated as a clear, colorless oil. (0.89 g, 86%). ^1H NMR (500 MHz, CDCl_3) δ 8.46 (dd, $J = 17.6, 8.8$ Hz), 8.25 – 8.18 (m), 8.14 (dd, $J = 8.8, 1.8$ Hz), 2.46 (t, $J = 7.5$ Hz), 2.26 – 2.17 (m), 1.82 – 1.68 (m), 1.68 – 1.48 (m), 1.47 – 1.15 (m), 0.98 (t, $J = 7.4$ Hz), 0.93 – 0.82 (m), 0.57 – 0.48 (m), 0.25 – -0.10 (m). SEC: $M_n = 30$ kDa, $M_w = 51$ kDa, $D = 1.7$.

1-(2-Hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (UPy-OH) was prepared as reported by Feldman et al.³



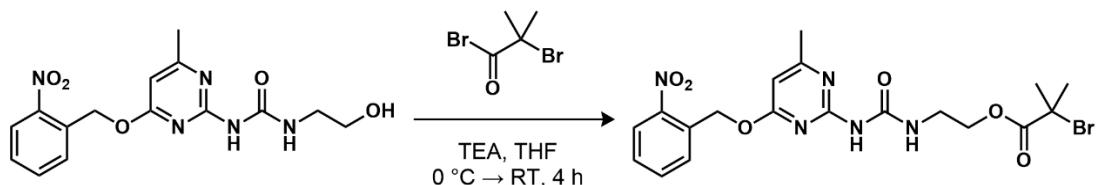
Synthesis of 1-(2-hydroxyethyl)-3-(6-methyl-4-((2-nitrobenzyl)oxy)-1,4-dihydropyrimidin-2-yl)urea (NO₂-UPy-OH)



Combine 1-(2-Hydroxyethyl)-3-(6-methyl-4-oxo-1,4-dihydropyrimidin-2-yl)urea (2 g, 9.4 mmol, 1 equiv.), nitrobenzyl bromide (2.6 g, 12.3 mmol, 1.3 equiv.), potassium carbonate (3.9 g, 28.3 mmol, 3 equiv.), and 50 mL dry DMF in a 100 mL flame dried round bottom flask equipped with stir bar and rubber septa. Reaction mixture degassed with argon for 10 min then heated at 70 °C for 24 h. Reaction mixture cooled to room temperature and added to 100 mL acetone then filtered out solid. Acetone collected and volume crude mixture reduced to about 20 mL under reduced pressure. Crude mixture precipitated into 600 mL DI water and put in fridge overnight. Solid precipitate collected and dried under vacuum for 2 days. Product isolated as a yellow solid (1.58 g, 48%). ¹H NMR (400 MHz, (CD₃)₂NCOD) δ 9.46 (s, 1H), 8.20 – 8.09 (m, 1H), 7.74 – 7.62 (m, 2H), 7.59 – 7.46 (m, 2H), 7.40 (s, 1H), 6.32 (s, 1H), 5.77 (s, 2H), 3.80 (t, 2H), 3.55 (t, 2H), 2.40 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 169.52, 168.15,

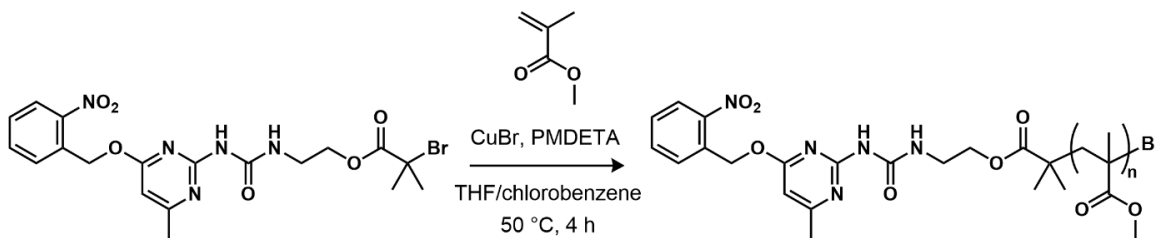
157.19, 155.59, 147.54, 133.82, 132.36, 128.97, 128.76, 125.03, 100.45, 64.80, 62.91, 42.89, 23.79. HRMS (ESI+) m/z calcd for $C_{15}H_{17}N_5O_5$ $[M+H]^+$: 348.1308, observed: 348.1319.

Synthesis of 2-(3-(6-methyl-4-((2-nitrobenzyl)oxy)-1,4-dihydropyrimidin-2-yl)ureido)ethyl 2-bromo-2-methylpropanoate (NO₂-UPy-Br)



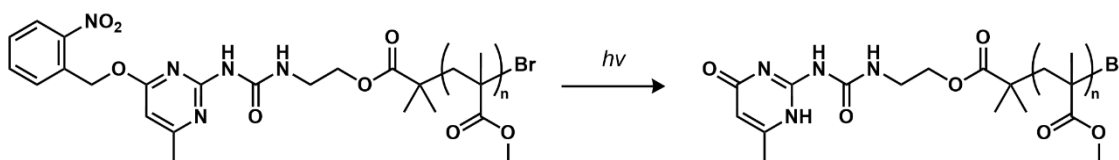
Combine 1-(2-hydroxyethyl)-3-(6-methyl-4-((2-nitrobenzyl)oxy)-1,4-dihydropyrimidin-2-yl)urea (1.5 g, 4.3 mmol, 1 equiv.), triethylamine (0.48 g, 4.7 mmol, 1.1 equiv.), 6 mL dry THF in a 20 mL vial equipped with stir bar and septa cap. Vial cooled to 0 °C and degassed with argon for 5 minutes. Added α -bromoisobutyryl bromide (0.99 g, 4.3 mmol, 1 equiv.) while stirring then let reaction solution warm to room temperature over 4 h. Added 150 mL DI water and extract into DCM (3 $\times$ 50 mL). Washed combined DCM layers with sat. $NaHCO_3$ (3 $\times$ 50 mL) and brine (50 mL). Dried DCM over $MgSO_4$, filtered, and solvent removed under vacuum. Product recrystallized from EtOH twice. Product isolated as a white solid (0.81 g, 23%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.16 – 8.05 (m, 1H), 7.69 – 7.60 (m, 2H), 7.55 – 7.45 (m, 1H), 7.27 (s, 1H), 6.28 (s, 1H), 5.74 (s, 2H), 4.34 (t, J = 5.3 Hz, 2H), 3.68 (q, J = 5.5 Hz, 2H), 2.38 (s, 3H), 1.92 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.55, 169.62, 167.85, 157.14, 154.38, 147.67, 133.74, 132.34, 129.05, 128.78, 125.02, 100.51, 64.99, 64.75, 55.72, 38.78, 30.74, 30.73, 23.88. HRMS (ESI+) m/z calcd for $C_{19}H_{22}BrN_5O_6$ $[M+H]^+$: 496.0832, observed: 496.0820.

Synthesis of NO₂-UPy-PMMA



In a 4 mL vial, dissolved 2-(3-(6-methyl-4-((2-nitrobenzyl)oxy)-1,4-dihydropyrimidin-2-yl)ureido)ethyl 2-bromo-2-methylpropanoate (0.1 g, 0.20 mmol, 1 equiv.) in 0.2 mL dry THF and 0.6 mL dry chlorobenzene then degassed reaction mixture with argon for 10 min. In a different 4 mL vial, Combine MMA (0.71 g, 7.1 mmol, 36 equiv.), CuBr (0.029 g, 0.2 mmol, 1 equiv.), and PMDETA (0.036 g, 0.2 mmol, 1 equiv.) then degassed reaction mixture with argon for 10 min. Combine both reaction mixtures and degassed with argon for 10 min. While stirring, heated combined reaction mixtures at 50 °C for 4 h. After 4 hours, reaction mixture cooled in an ice bath. Reaction mixture passed through neutral alumina plug using DCM as eluent, and precipitated into 0 °C, 100 mL MeOH. Precipitate collected by filtration and dried under vacuum. Product isolated as a white solid. SEC: M_n = 20 kDa, M_w = 26 kDa, D = 1.3.

Synthesis of UPy-PMMA



In a 4 mL vial, NO₂-UPy-PMMA (0.1 g) was dissolved in 2 mL DCM and irradiated with a UV lamp for 2 hours. Solution was precipitated into 0 °C MeOH. Precipitate collected and

dried under vacuum. Product isolated as a white solid. SEC DMF: $M_n = 20$ kDa, $M_w = 30$ kDa, $\bar{D} = 1.5$.

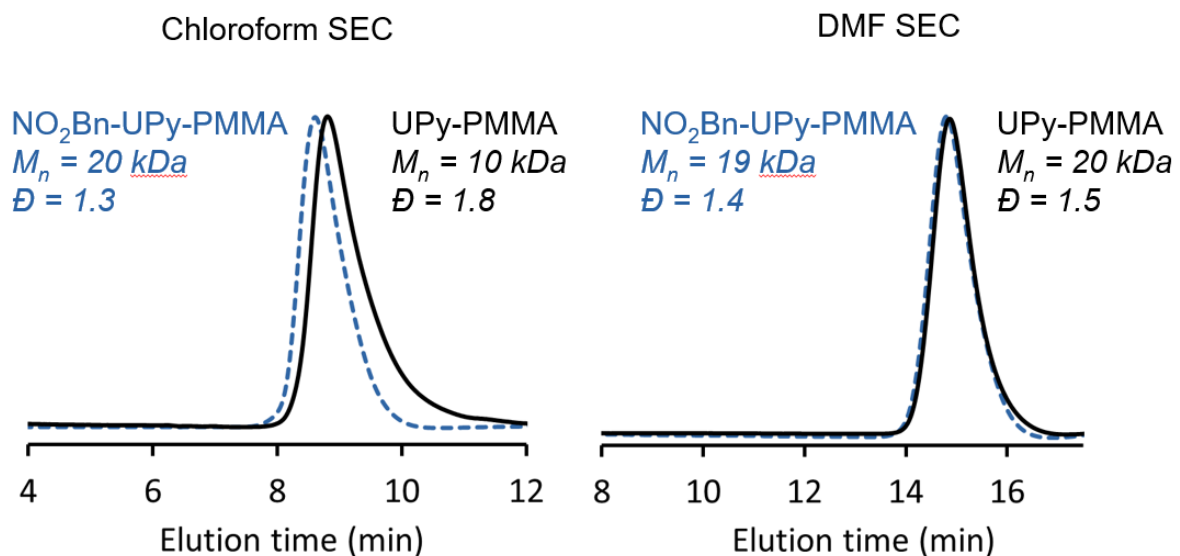


Figure A1. Protected NO₂Bn-UPy-PMMA (blue dotted line) and deprotected UPy-PMMA (solid black line) ran in different SEC solvents. Column interaction in chloroform solvent leads to a lower measured molecular weight and higher dispersity.

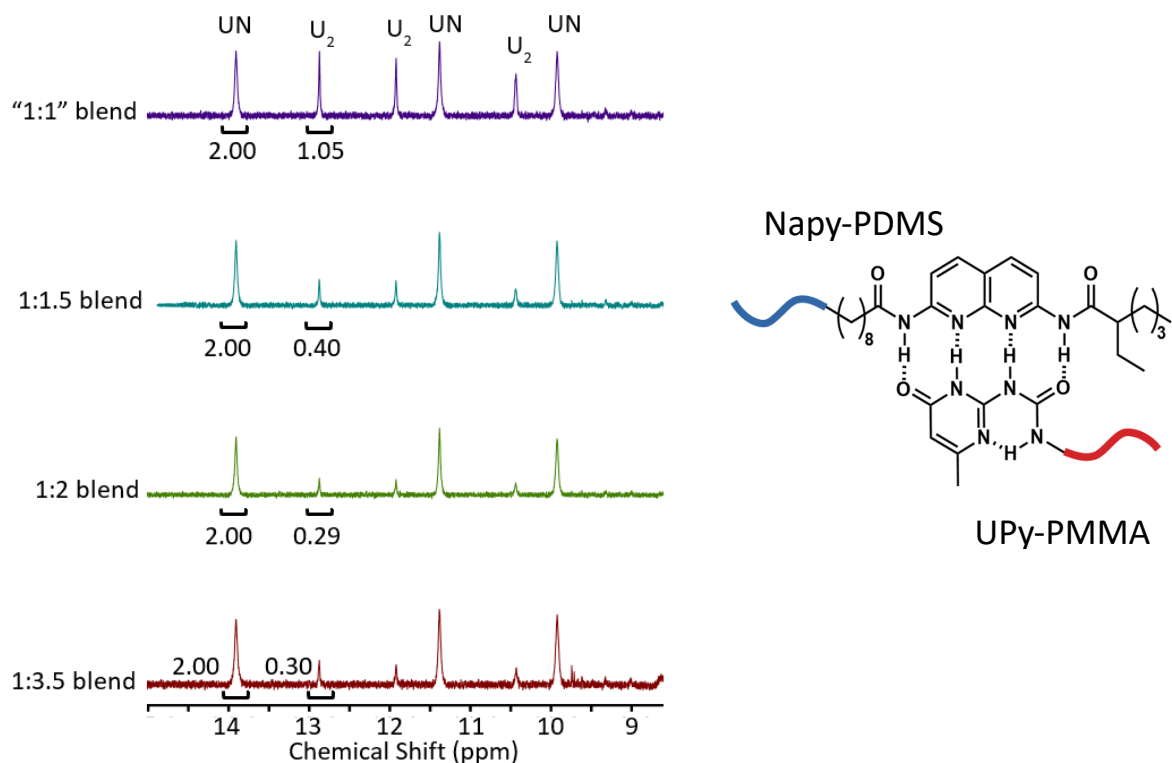


Figure A2. ^1H -NMR, increased ratio of Napy-PDMS to UPy-PMMA. Still observe UPy dimer at high Napy-PDMS loadings.

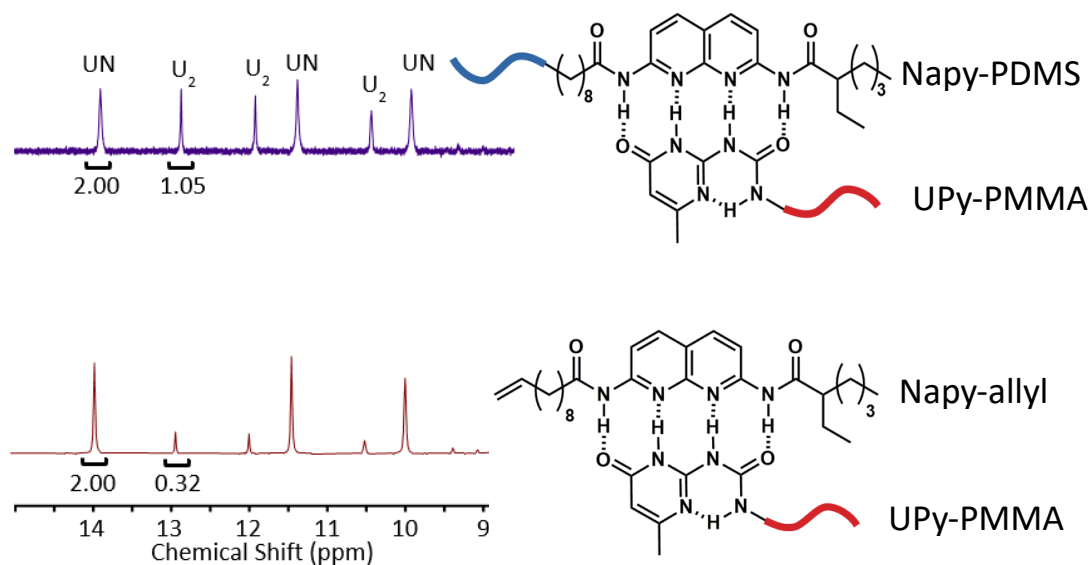


Figure A3. ^1H -NMR with small-molecule Napy. Observe UPy dimer but with lower integration when comparing to Napy-PDMS.

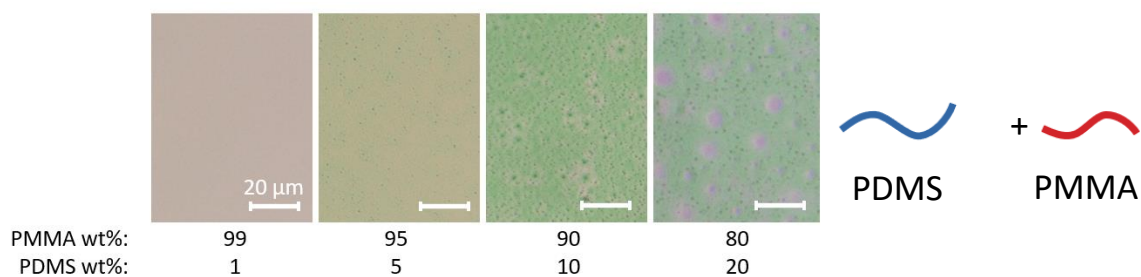


Figure A4. Spin-coated unfunctionalized 35 kDa PMMA and 28 kDa PDMS blends at different wt% ratios. Surface droplet size increases as wt% PDMS increases.

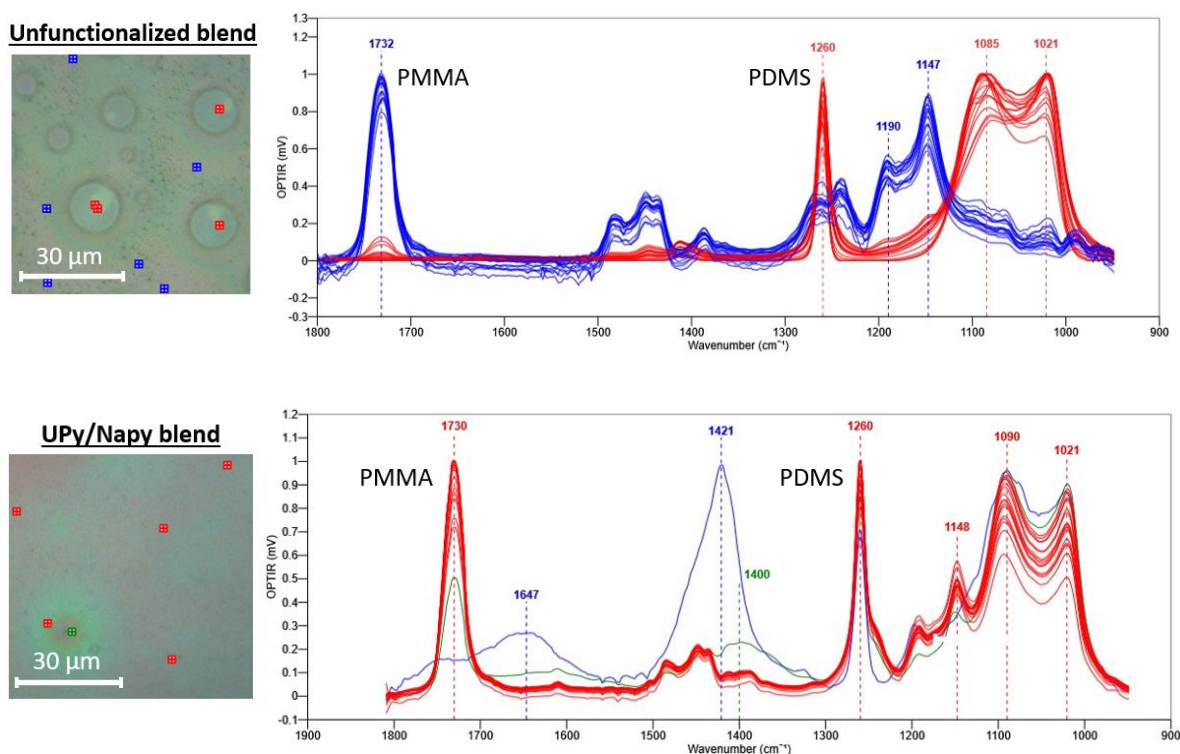


Figure A5. IR Spectra obtained from selected points in the control unfunctionalized blend and UPy/Napy blend using O-PTIR spectroscopy.

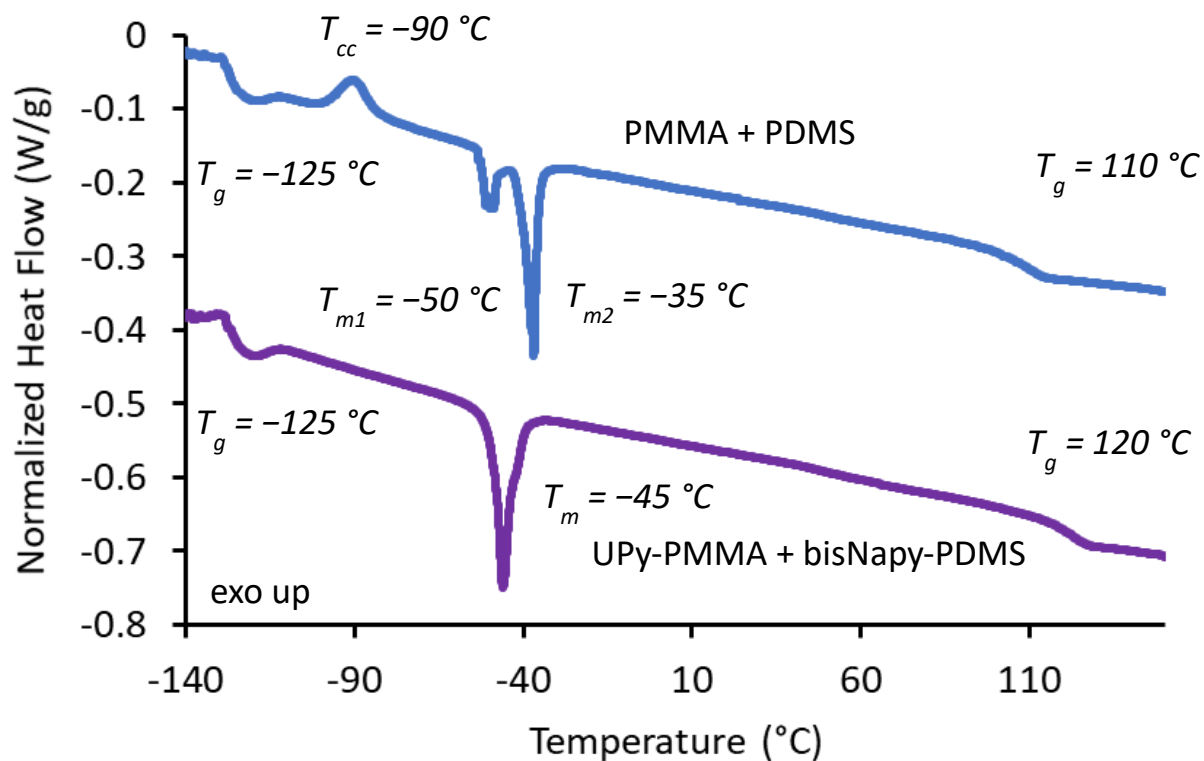


Figure A6. DSC of the unfunctionalized blend and UPy/Napy derivatives. Observe PDMS and PMMA T_g in both blends.

References

- (1) Pirkle, William H., and Yuelong Liu. "Design, synthesis, resolution, determination of absolute configuration, and evaluation of a chiral naproxen selector." *The Journal of Organic Chemistry* 59, no. 23 (1994): 6911-6916.
- (2) Ligthart, G. B. W. L.; Ohkawa, H.; Sijbesma, R. P.; Meijer, E. W. *J. Org. Chem.* **2006**, 71, 375–378.
- (3) Feldman, K. E.; Kade, M. J.; de Greef, T. F. A.; Meijer, E. W.; Kramer, E. J.; Hawker, C. J. *Macromolecules* **2008**, 41, 4694–4700.

Appendix B. Supporting Information for Chapter 3

Materials

All reagents were used as received unless otherwise stated. DL- α -lipoic acid (α LA) was purchased from Amazon (USA). Tris(2-carboxyethyl) phosphine hydrochloride (TCEP.HCl) was purchased from Ambeed, Inc. V-70 was purchased from FUJIFILM Wako Chemicals U.S.A. Corporation. All the monomers are purchased either from Sigma-Aldrich or Fisher Scientific. N,N'-Dicyclohexylcarbodiimide (DCC), methylene chloride (DCM), tetrahydrofuran (THF), hexanes, ethyl acetate, acetone, methanol, anhydrous ethanol and magnesium sulfate anhydrous (MgSO₄) were purchased from Fisher Scientific. All commercial monomers passed through basic alumina prior to use. Deuterated solvents were acquired from Cambridge Isotope Laboratories. Ethyl lipoate (ELp) was prepared as previously reported.¹

Characterization methods

¹H nuclear magnetic resonance spectroscopy:

Solution state ¹H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III HD 400 MHz or Bruker Avance NEO 500 MHz. Chemical shifts (δ) are reported in ppm relative to residual solvent in CDCl₃ (7.26 ppm).

Size-exclusion chromatography instrumentation:

Size-exclusion chromatography (SEC) was performed on a Waters instrument using a differential refractive index detector and two Tosoh columns (TSKgel SuperHZM-N, 3 μ m

polymer, 150 × 4.6 mm) with THF at 35 °C for the mobile phase. Molar masses and molar mass dispersities ($\mathcal{D}$) were determined against narrow PS standards (Agilent).

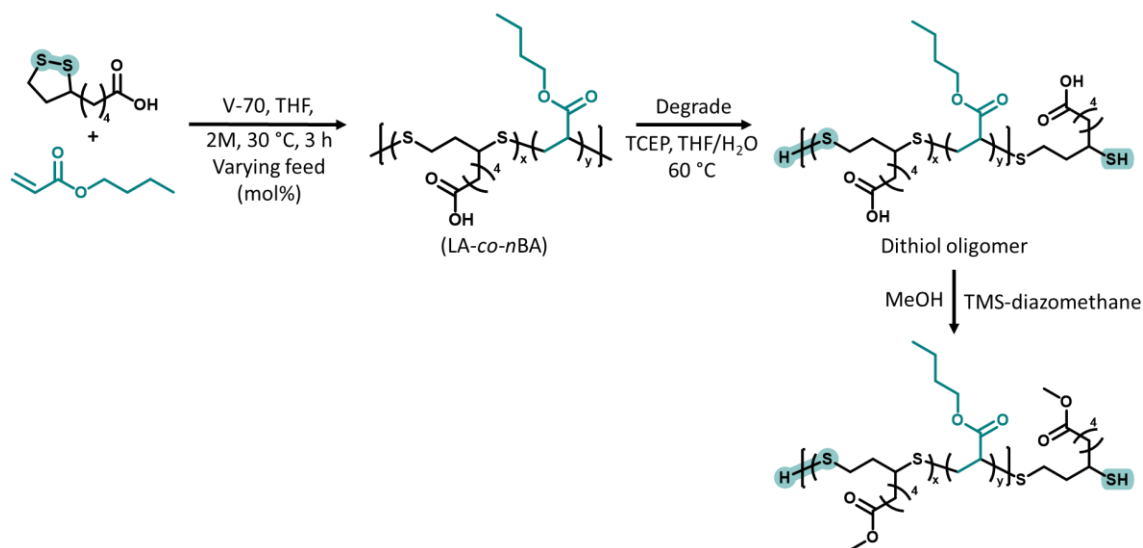
Differential scanning calorimetry (DSC):

DSC was performed on a TA Instruments Q2000 DSC with three repeated cycles between −100 and +150 °C at a constant rate of 10 °C/min using 3–5 mg of sample in a sealed aluminum pan. Brief annealing of the system followed by a second temperature ramp was conducted for each sample to investigate glass transition temperature (T_g).

Rheology experiment:

Frequency sweeps and isochronal time sweeps were obtained on a TA Instruments ARES G2 in oscillatory shear mode with an 8 mm parallel-plate geometry. In situ curing experiments were conducted with a TA UV accessory using an Omnicure S2000 light source with a wavelength range of 320–500 nm at 400 mWcm^{−2}. Changes in modulus were monitored at a frequency of 1 Hz and a strain of 1%. For all experiments, oscillatory shear was applied within the linear viscoelastic regime as verified from isochronal strain sweeps at a fixed temperature.

Scheme B1: Synthesis of lipoic acid (LA)-based dithiol oligomers with varying feed ratio



General synthesis of copolymer of lipoic acid (LA) and *n*-butyl acrylate (*n*BA)

[Poly(LA-co-*n*BA)] (LA:*n*BA= 50:50)

LA (1.65 g, 8.0 mmol, 400 equiv.), *n*BA (1.02 g, 8.0 mmol, 400 equiv.), V-70 (6.2 mg, 0.02 mmol, 1 equiv.), and THF (5 mL, 2 M) were added to a 20 mL vial equipped with stir bar and capped with septa. Reaction mixture was immediately cooled to 0 °C using an ice bath and degassed with Argon for 20 minutes. An aliquot was taken at time = 0 h to monitor conversion. Then the reaction mixture was placed in an oil bath at 30 °C and stirred for 3 h. The reaction was quenched by exposure to air and quickly precipitated into hexane. Precipitation was repeated thrice more by redissolving precipitate into THF (about 10 mL). Sample dried under reduced pressure on rotavapor followed by high vacuum. The product obtained was a clear, colorless, viscous oil. SEC (THF): $M_n = 50 \text{ kg mol}^{-1}$, $D = 1.7$.

Degradation of [Poly(LA-co-*n*BA)] (LA:*n*BA= 50:50) with TCEP

Poly(LA-*co*-*n*BA) (1 g, 0.02 mmol) parent polymer was added to a 50 mL round bottom flask equipped with magnetic stir bar and dissolved in minimal THF. A solution of TCEP (5 equiv. to thiol) in THF/water (4:1) was added and the reaction was stirred at 60 °C. Reaction was monitored by SEC until the molecular weight no longer decreased (typically 24 h). The solution was cooled to room temperature and THF was removed under reduced pressure. Then the reaction mixture was diluted with DCM and washed with saturated NaHCO₃ aq., and DI water. The organic layer was dried with anhydrous MgSO₄ and concentrated under vacuum to obtain the dithiol oligomer. SEC (THF): $M_n = 1.5 \text{ kg mol}^{-1}$, $D = 1.7$.

Methylation of LA-*co*-*n*BA dithiol oligomer (LA:*n*BA= 50:50) to determine composition

In a 20 mL dram vial, LA-*co*-*n*BA (500 mg, 0.33 mmol) was dissolved in 3 mL of THF. To the stirring solution, methanol (1.3 mL, 33 mmol) was added followed by a dropwise addition of TMS-diazomethane (~ 100 μ L, 0.2 M in ether) or until a light-yellow color remained in the stirring solution. The reaction mixture was left overnight to stir at room temperature and quenched with AcOH (10 drops) or until a colorless solution remained. The polymer was precipitated into cold methanol (50 mL $\times$ 5).

Similar procedure was followed for other three feed ratio (LA:*n*BA) 25:75, 40:60, and 50:50.

Table B1: Molecular characterization of LA-co-*n*BA

Entry	LA feed (mol%)	$M_{n,parent}$ (kg mol ⁻¹)	$\bar{D}_{Parent}$	$M_{n,deg}$ (kg mol ⁻¹)	LA _{polymer} (mol%)
1	10	30	1.8	24	14
2	25	53	1.8	13	33
3	40	55	1.8	2.5	45
4	50	50	1.7	1.5	59

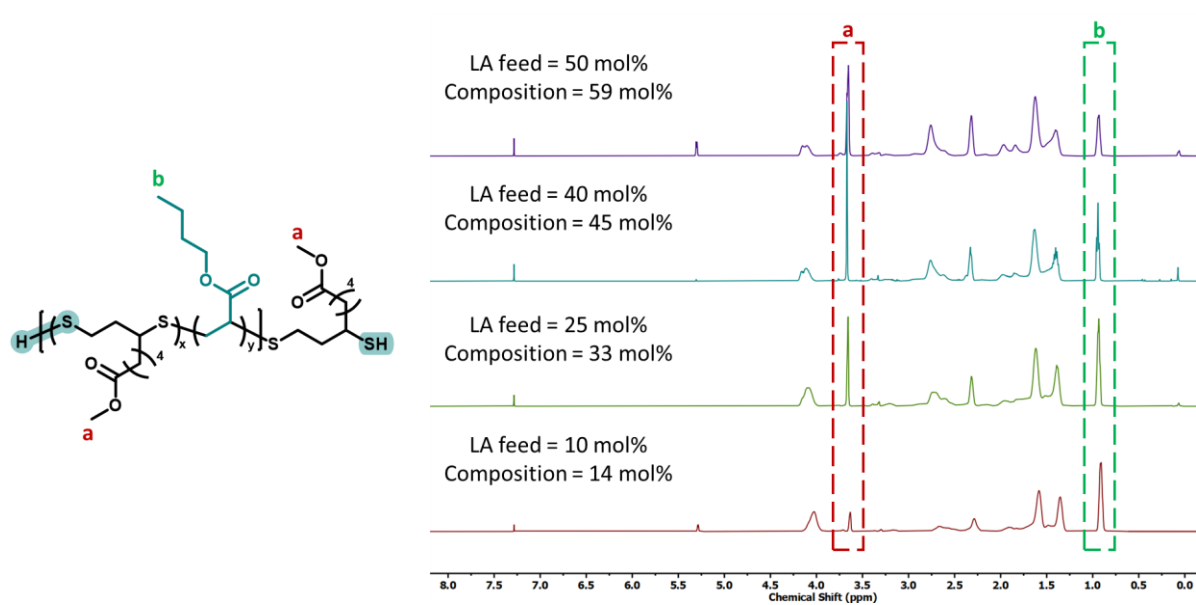


Figure B1. ¹H-NMR analysis of the methylated (LA-co-*n*BA) dithiol oligomers with different compositions and characteristic resonances denoted.

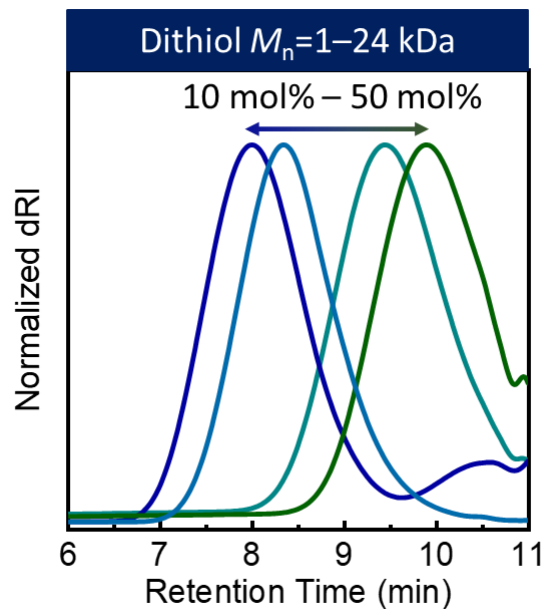
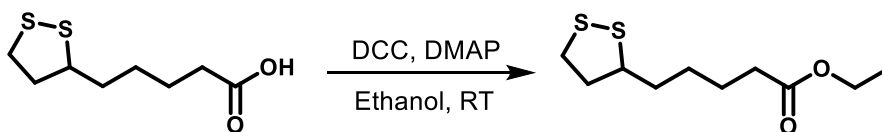


Figure B2. SEC traces of the methylated (LA-co-*n*BA) dithiol oligomers with different compositions. Molecular weight (M_n) of the dithiol increases (1 to 24 kDa) with decreasing the feed ratio of LA (50 mol% to 10 mol%).

Scheme B2: Synthesis of ethyl lipoate (ELp)



ELp was synthesized following the literature.¹

conversion. Then the reaction mixture was placed in an oil bath at 30 °C and stirred for 6 h to allow ELP conversion around 80%. The conversion was monitored via ^1H NMR. The reaction was quenched by exposure to air and quickly precipitated into cold methanol. Precipitation was repeated thrice more by redissolving the precipitate into THF (about 7–10 mL). Sample dried under reduced pressure on rotavapor followed by high vacuum. The product obtained was a clear, colorless, viscous oil.

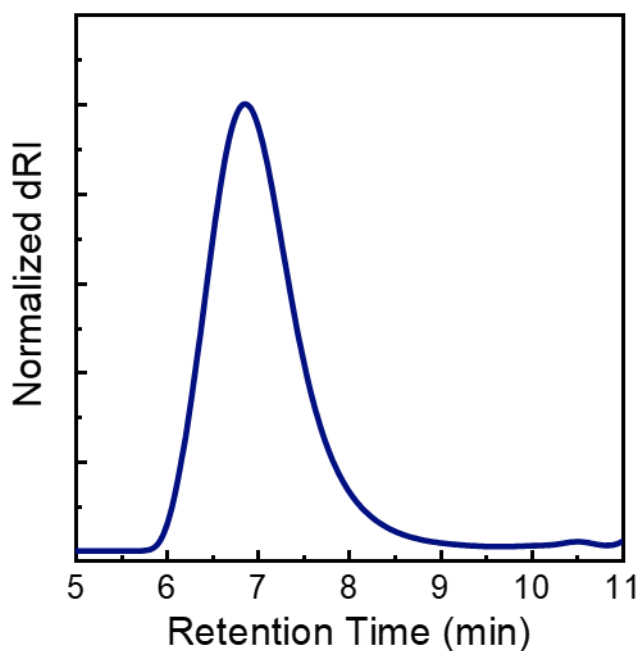


Figure B4. SEC trace with normalized differential refractive index (dRI) detection for ELP-*co-n*BA. SEC (THF): M_n : 98 kg mol $^{-1}$, $D = 1.7$.

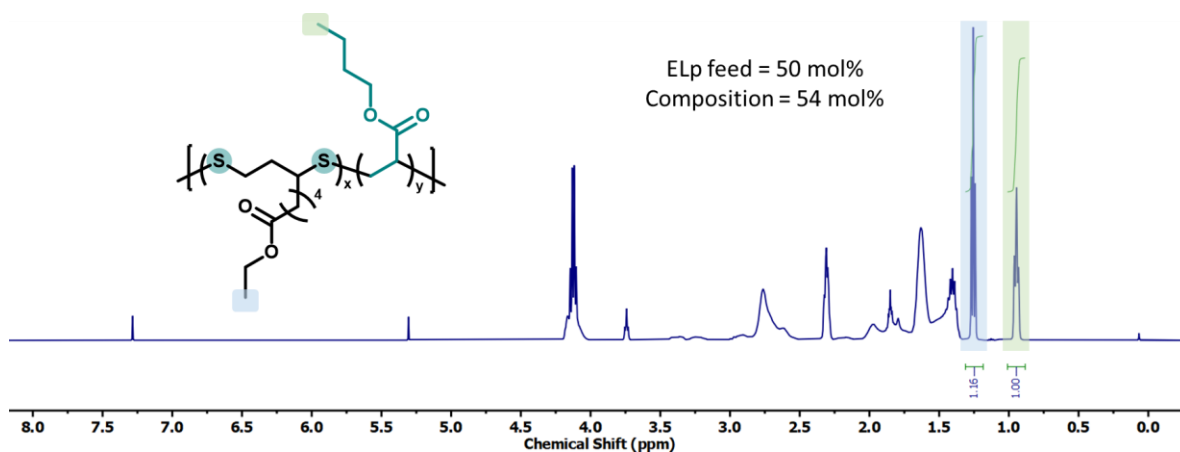
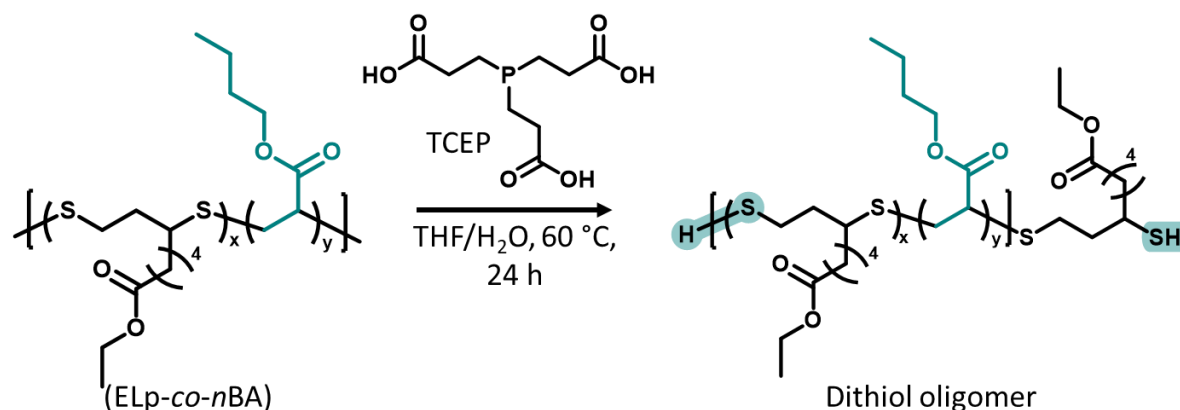


Figure B5. ^1H -NMR analysis of the ELp-co-nBA with characteristic resonances denoted.

Scheme S4: Degradation of [Poly(ELp-co-nBA)] (ELp:nBA=50:50) with TCEP



Poly(ELp-co-nBA) parent polymer (6 g, 0.061 mmol) was added to a 100 mL round bottom flask equipped with magnetic stir bar and dissolved in minimal THF. A solution of TCEP (5 equiv. to thiol) in THF/water (4:1) was added and the reaction was stirred at 60 °C. Reaction was monitored by SEC until the molecular weight no longer decreased (typically 24 h). The solution was cooled to room temperature and THF was removed under reduced pressure. Then the reaction mixture was diluted with DCM and washed with saturated NaHCO_3 aq., and DI

water. The organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the dithiol oligomer. SEC (THF): $M_n = 2.6 \text{ kg mol}^{-1}$, $D = 1.9$.

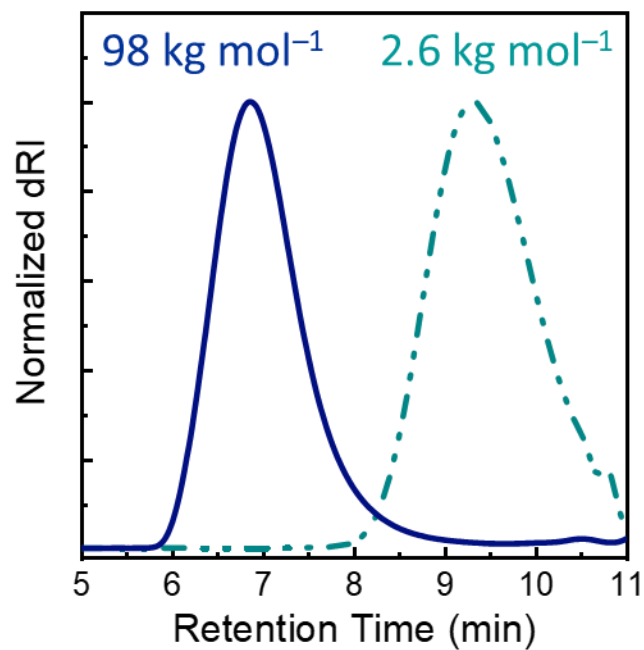
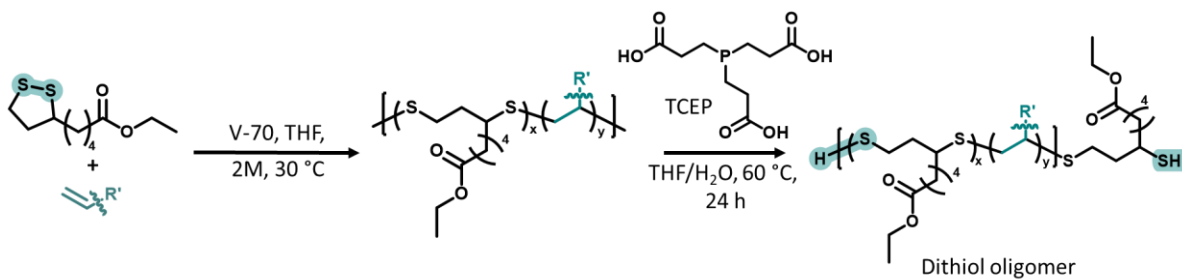


Figure B6. SEC traces comparing M_n before and after degradation of ELP-*co*-nBA.

Scheme B5: General scheme for the synthesis of various structurally diverse dithiol oligomers



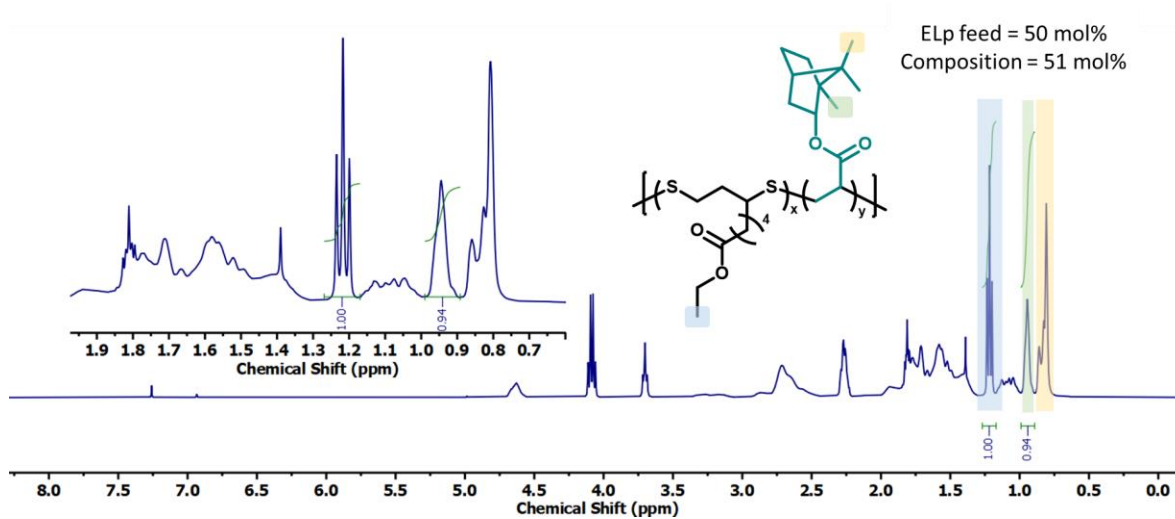


Figure B7. ^1H -NMR analysis of the ELp-co-IBA with characteristic resonances denoted.

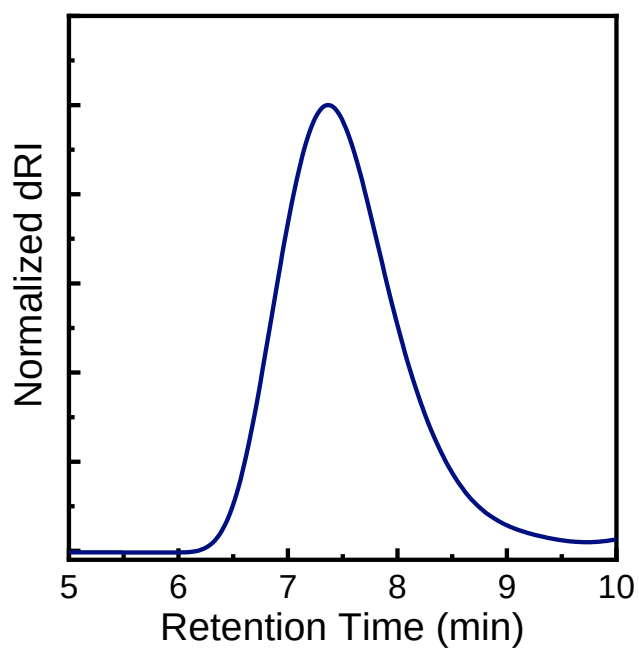


Figure B8. SEC trace with normalized differential refractive index (dRI) detection for ELp-co-IBA. SEC (THF): M_n : 51 kg mol $^{-1}$, $D = 1.7$.

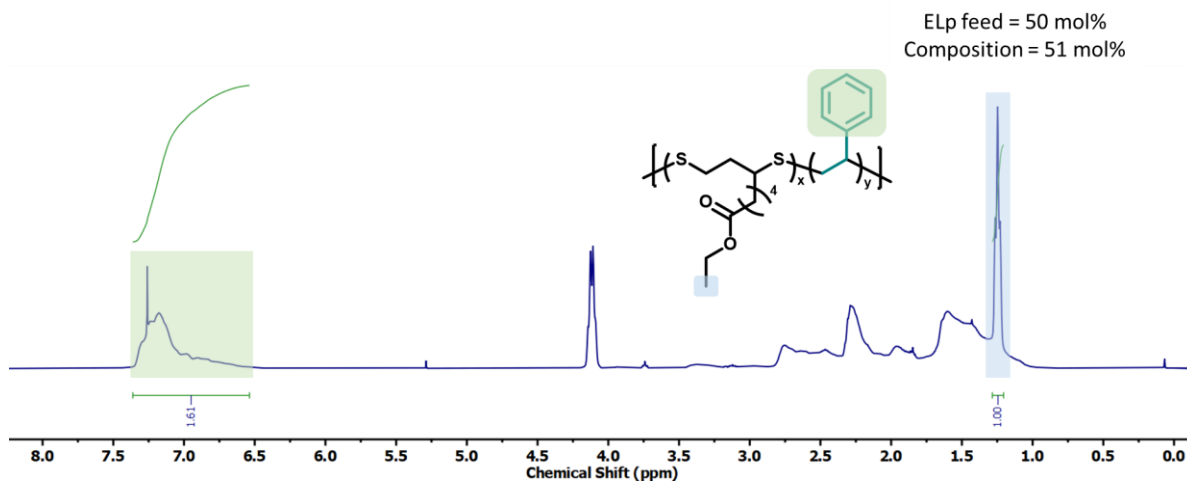


Figure B9. ^1H -NMR analysis of the ELp-*co*-St with characteristic resonances denoted.

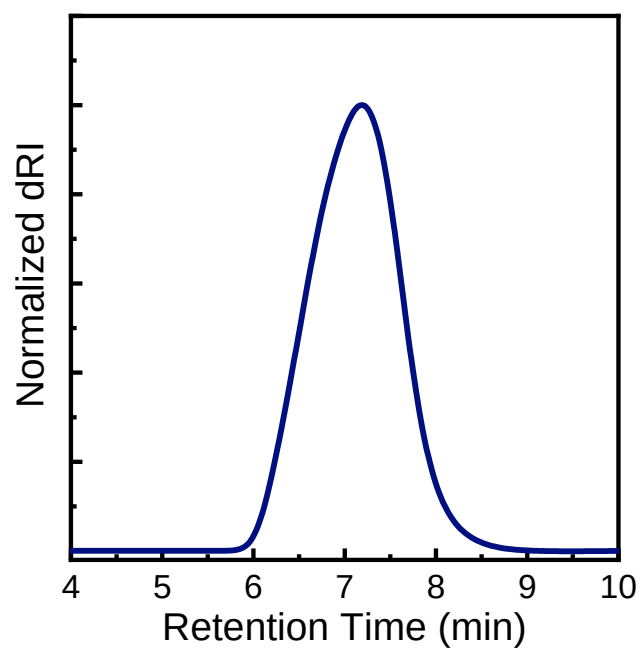


Figure B10. SEC trace with normalized differential refractive index (dRI) detection for ELp-*co*-St. SEC (THF): M_n : 90 kg mol $^{-1}$, $D = 1.8$.

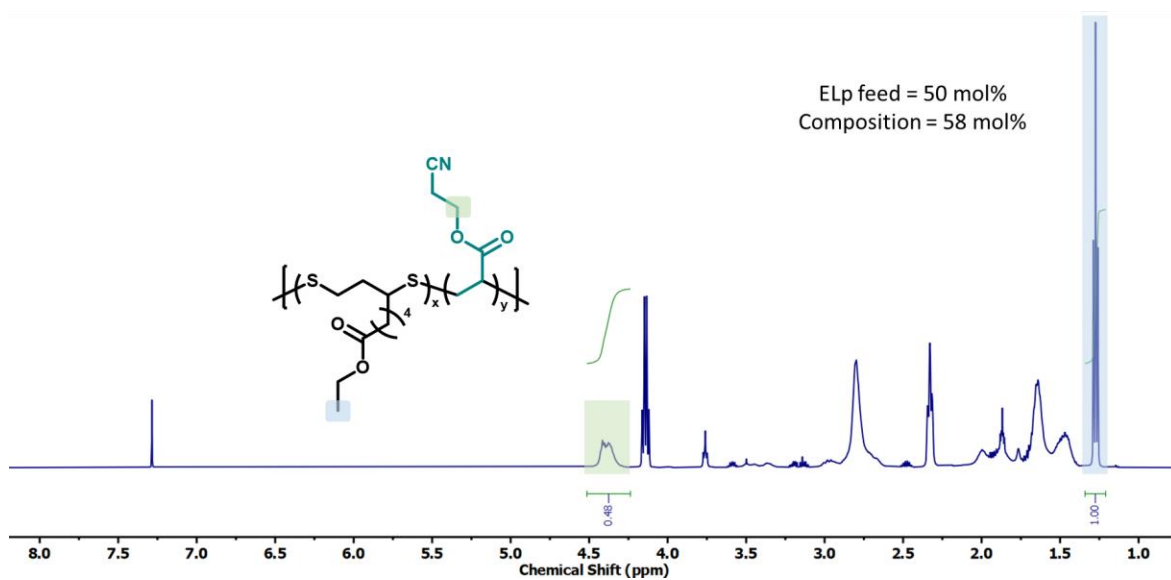


Figure B11. ^1H -NMR analysis of the ELP-co-CEA with characteristic resonances denoted.

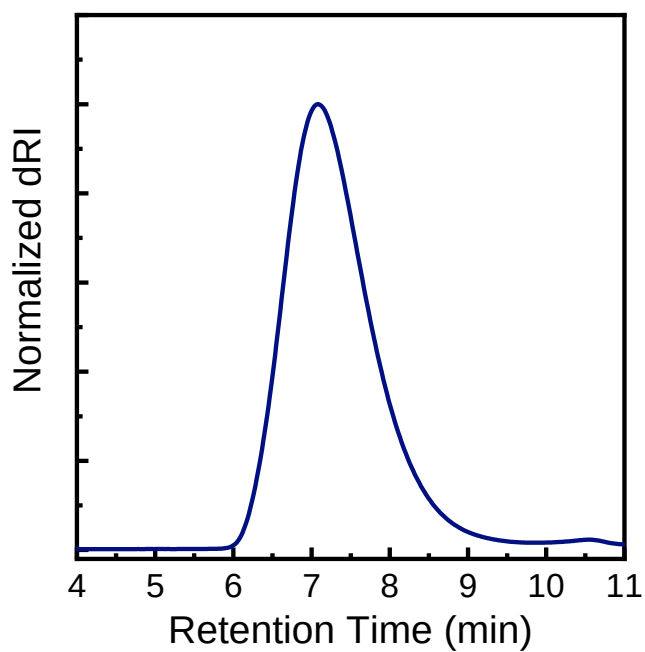


Figure B12. SEC trace with normalized differential refractive index (dRI) detection for ELP-co-CEA. SEC (THF): M_n : 67 kg mol $^{-1}$, $D = 2.1$.

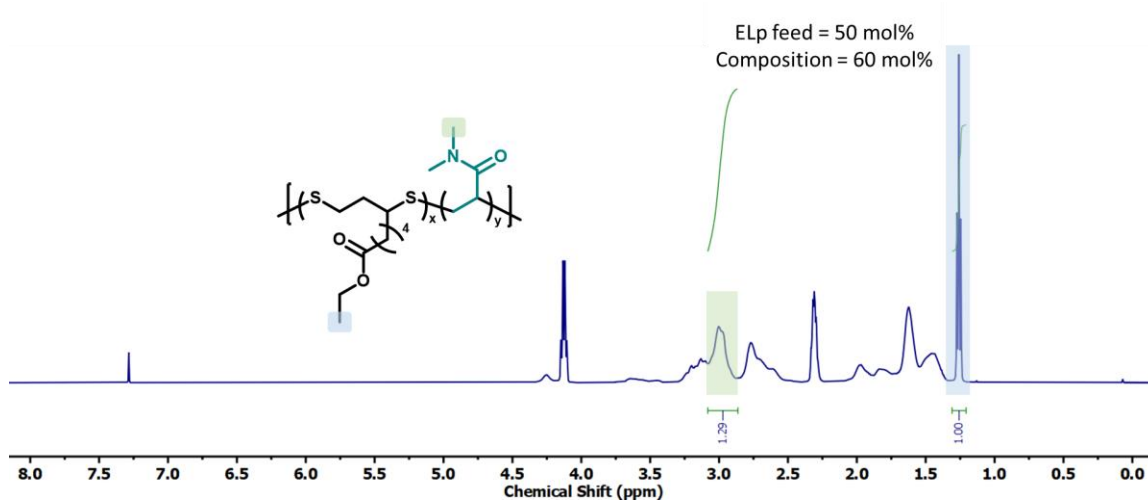


Figure B13. ^1H -NMR analysis of the ELP-co-DMAA with characteristic resonances denoted.

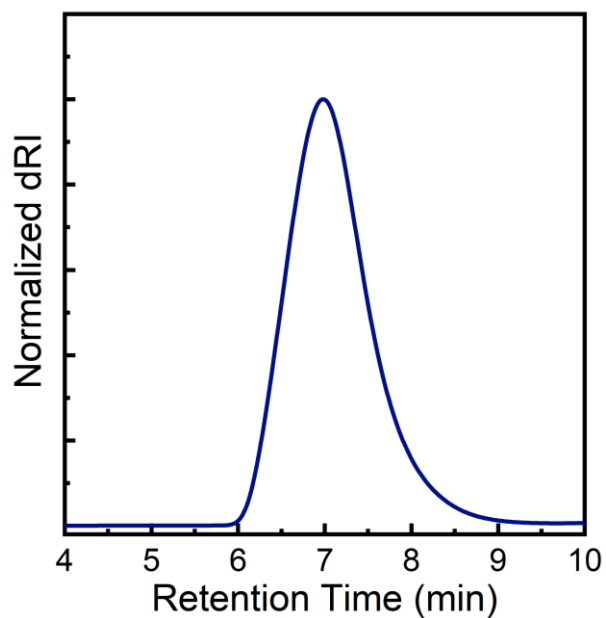


Figure B14. SEC trace with normalized differential refractive index (dRI) detection for ELP-co-DMAA. SEC (THF): M_n : 99 kg mol $^{-1}$, $D = 1.8$.

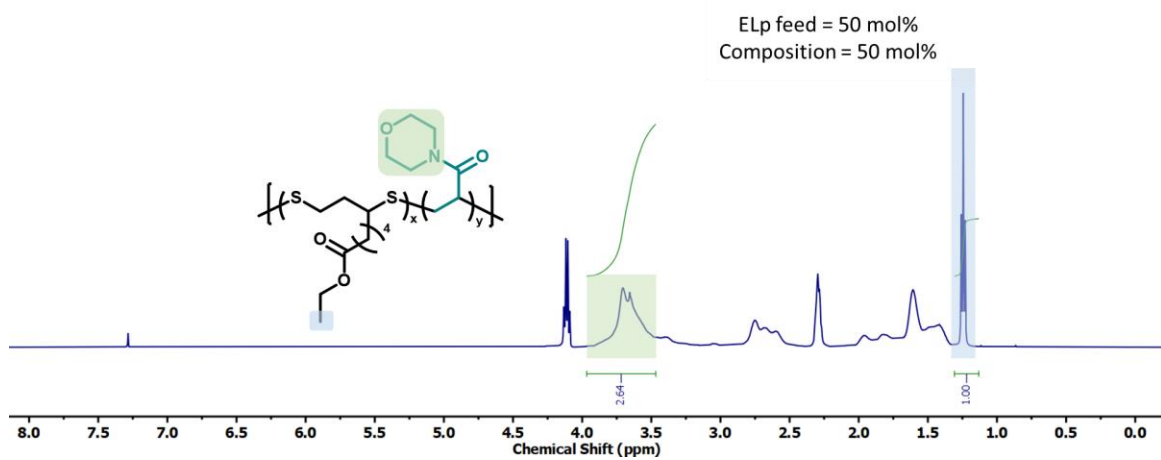


Figure B15. ^1H -NMR analysis of the ELp-*co*-AM with characteristic resonances denoted.

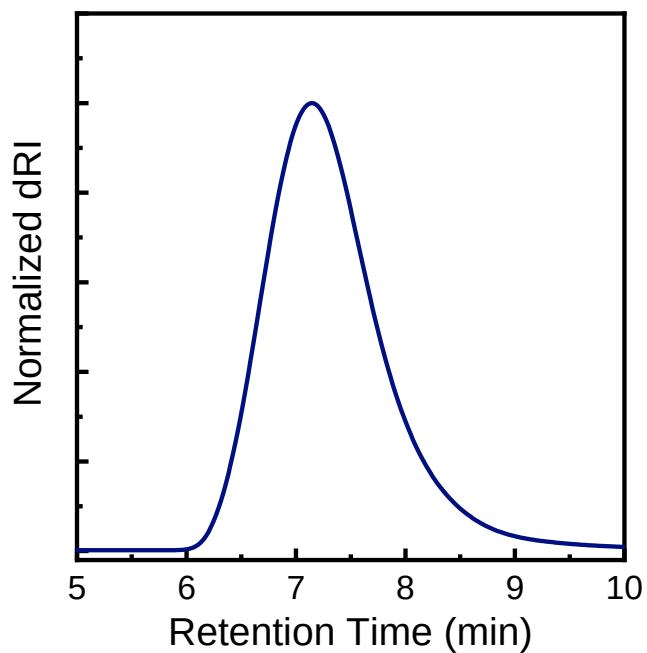


Figure B16. SEC trace with normalized differential refractive index (dRI) detection for ELp-*co*-AM. SEC (THF): M_n : 71 kg mol⁻¹, $\bar{D}$ = 1.9.

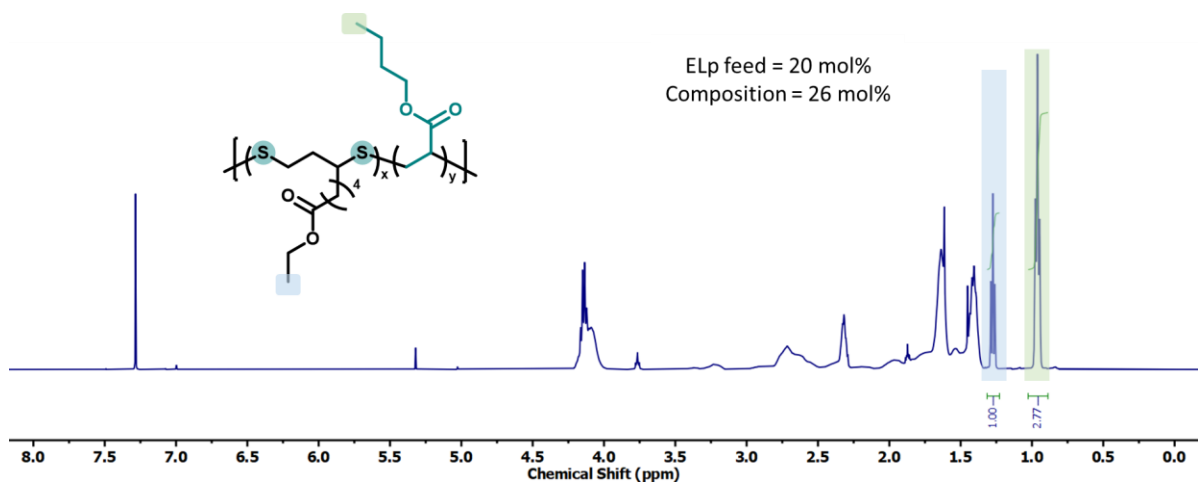


Figure B19. ^1H -NMR analysis of the ELP-*co*-nBA (ELp feed 20 mol%) with characteristic resonances denoted.

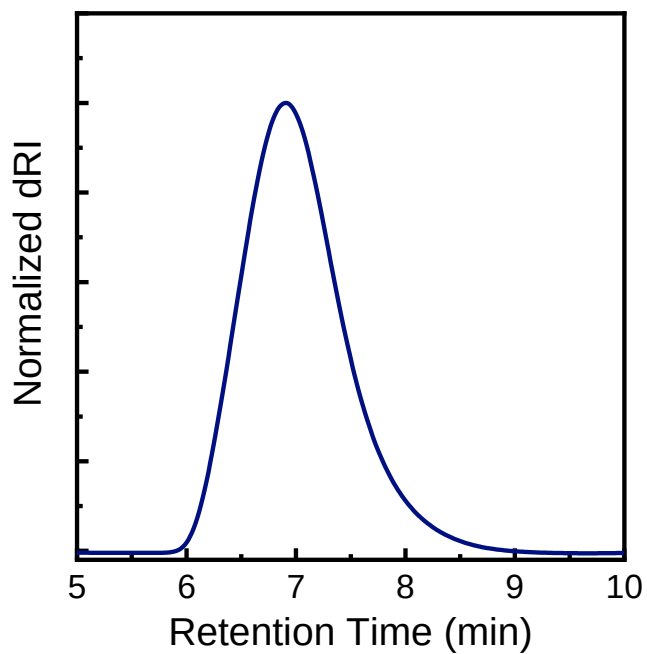


Figure B20. SEC trace with normalized differential refractive index (dRI) detection for ELP-*co*-nBA. SEC (THF): M_n : 111 kg mol $^{-1}$, $\bar{D}$ = 1.7.

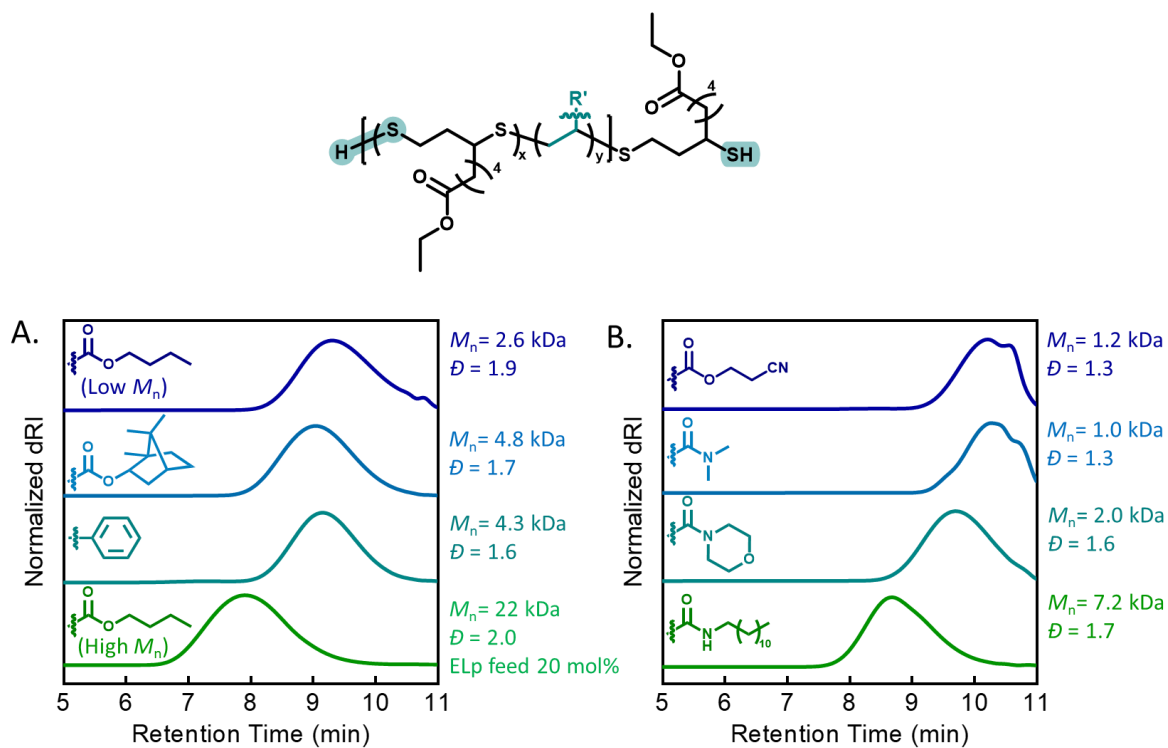


Figure B21. SEC traces with normalized differential refractive index (dRI) detection for the structurally diverse dithiol oligomers.

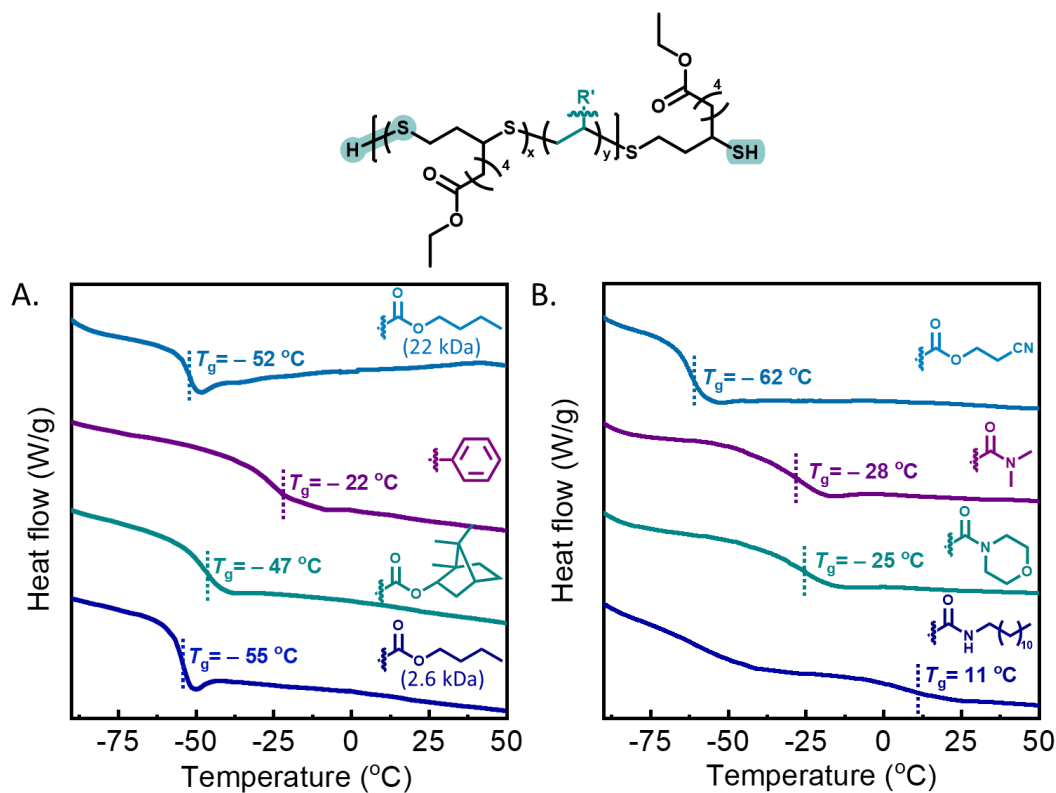
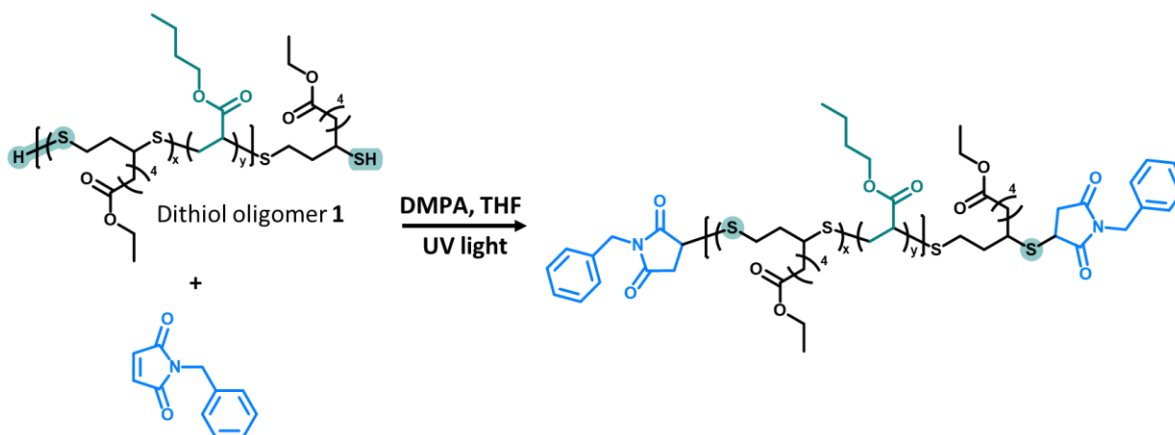


Figure B22. DSC thermograms of the structurally diverse dithiol oligomers. Brief annealing followed by a second temperature ramp was conducted for each sample to investigate glass transition temperature (T_g). The second heat, with a ramp rate of $10\text{ }^{\circ}\text{C min}^{-1}$, is plotted for clarity and plotted with exotherm up.

Scheme B6: Chain-end fidelity of the dithiol oligomer



To the stirred solution of dithiol oligomer **1** (300 mg, 0.115 mmol) in THF (0.5 mL), *N*-benzyl maleimide (108 mg, 0.576 mmol) was added. Then the reaction mixture was stirred in the presence of photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) and UV light for 4 h at room temperature. After that reaction mixture was precipitated in cold methanol (thrice) to obtain light yellow colored maleimide-functionalized oligomer.

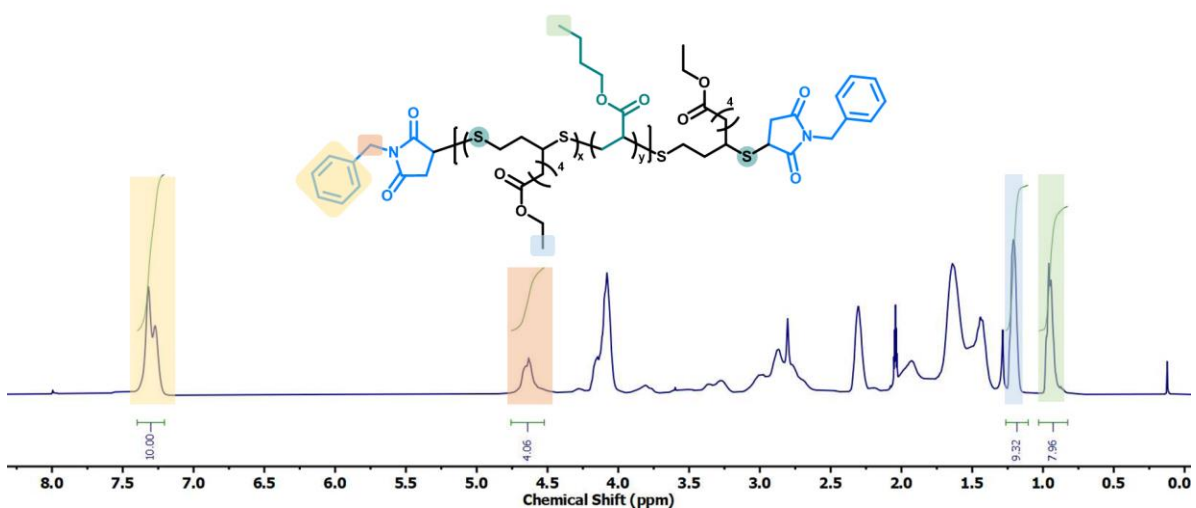


Figure B23. ^1H -NMR analysis of the maleimide-functionalized dithiol oligomer **1** with characteristic resonances denoted.

Scheme S7: Synthesis of cross-linker [tris(2-maleimidoethyl)amine] (Tri-M)

Tris(2-maleimidoethyl)amine (Tri-M) was synthesized following the literature report.²

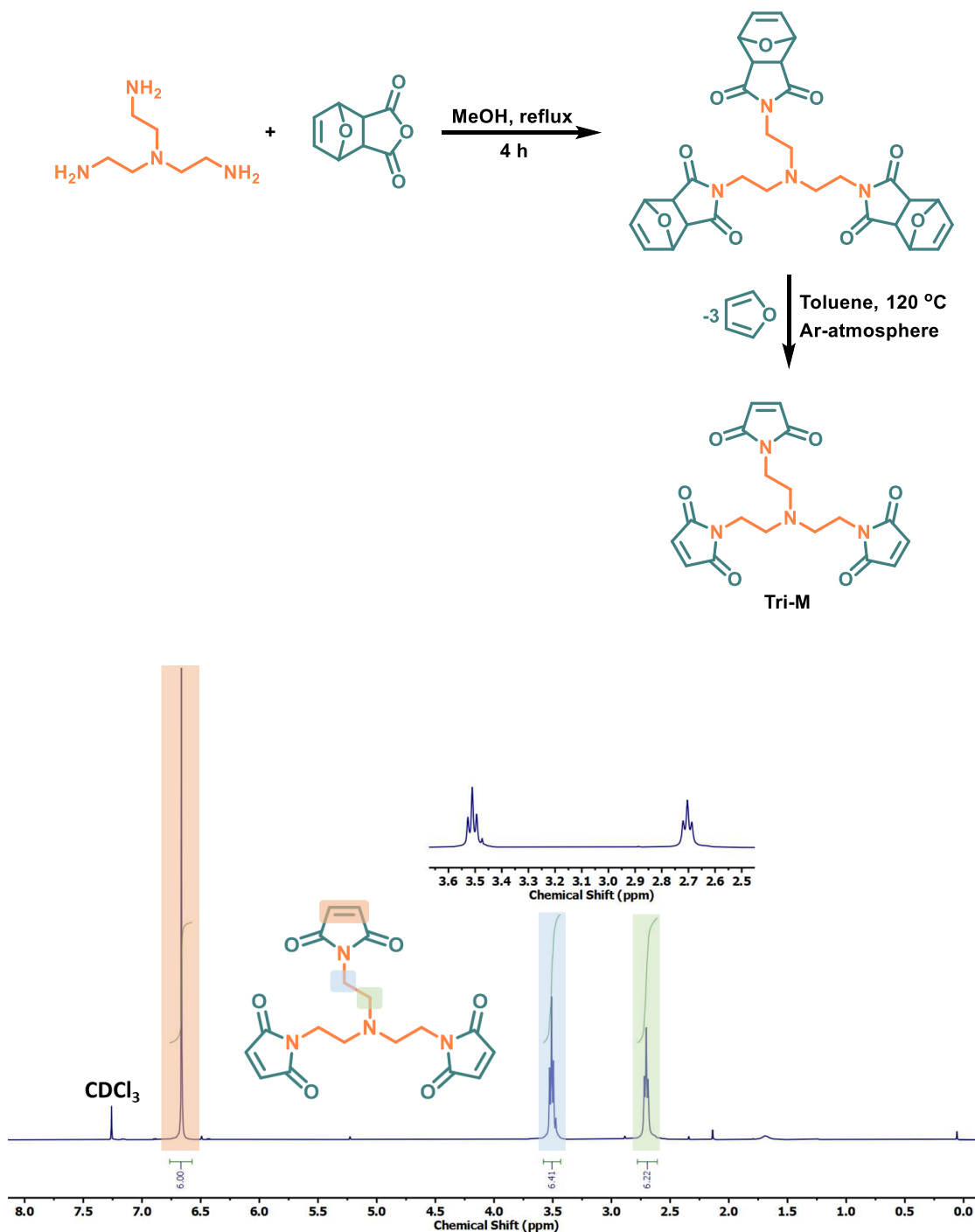


Figure B24. ¹H-NMR analysis of the **Tri-M** with characteristic resonances denoted.

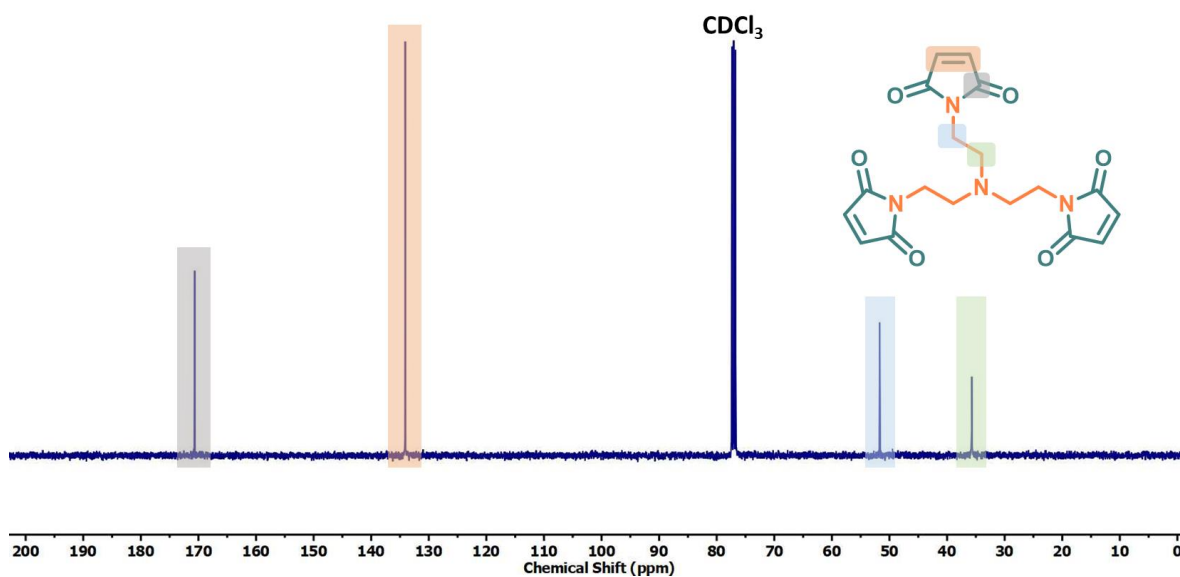
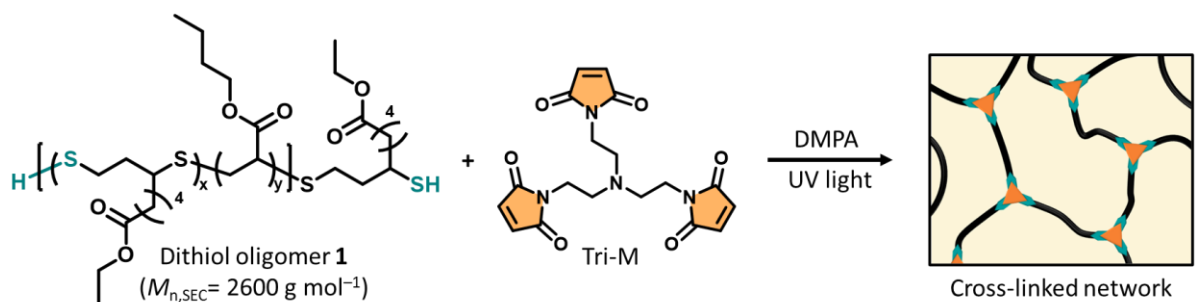


Figure B25. ^{13}C -NMR analysis of the **Tri-M** with characteristic resonances denoted.

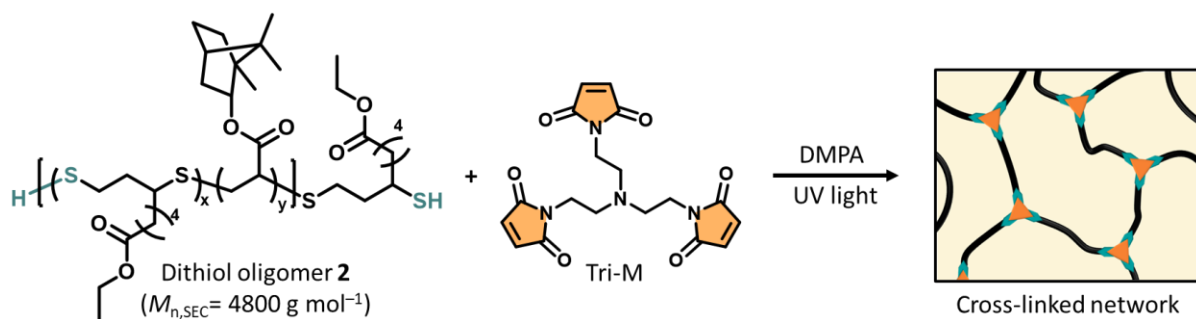
Determination of exact molecular weight of the dithiol oligomers for the network formation:

Titration experiments were carried out where the amount of dithiol varied based on our perceived molecular weight.



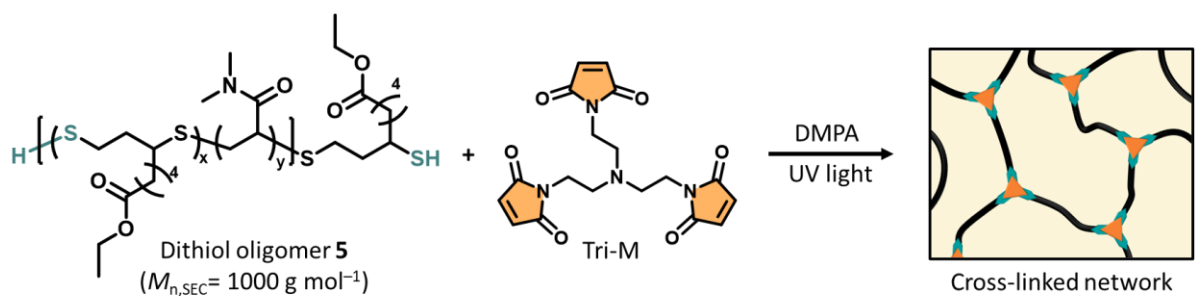
Entry	Tri-M (mg)	Dithiol (mg)	Assumed M_n of dithiol (g mol^{-1})	DMPA (mol%)	Solubility of Tri-M in dithiol	Gel fraction (%)
1	15	150	2600 (SEC)	20	Soluble	0
2	15	87	1500	20	Soluble	70
3	15	75	1300	20	Soluble	76
4	15	65	1100	20	Soluble	82
5	15	52	900	20	Soluble	85
6	15	40	700	20	Not soluble	–

Figure B26: Determination of exact molecular weight of the dithiol oligomer **1** for network formation



Entry	Tri-M (mg)	Dithiol (mg)	Assumed M_n of dithiol (g mol^{-1})	DMPA (mol%)	Solubility of Tri-M in dithiol	Gel fraction (%)
1	20	256	3300	20	Soluble	0
2	20	233	3000	20	Soluble	0
3	20	202	2600	20	Soluble	3
4	20	178	2300	20	Soluble	24
5	20	155	2000	20	Soluble	40
6	20	132	1700	20	Soluble	46
7	20	116	1500	20	Soluble	60
8	20	100	1300	20	Not soluble	–
9	20	77	1000	20	Not soluble	–

Figure B27: Determination of exact molecular weight of the dithiol oligomer 2 for network formation



Entry	Tri-M (mg)	Dithiol (mg)	Assumed M_n of dithiol (g mol^{-1})	DMPA (mol%)	Solubility of Tri-M in dithiol	Gel fraction (%)
1	20	93	1200	20	Soluble	85
2	20	77	1000	20	Soluble	87
3	20	62	800	20	Not soluble	–
4	20	46	600	20	Not soluble	–
5	20	31	400	20	Not soluble	–

Figure B28: Determination of exact molecular weight of the dithiol oligomer 5 for network formation

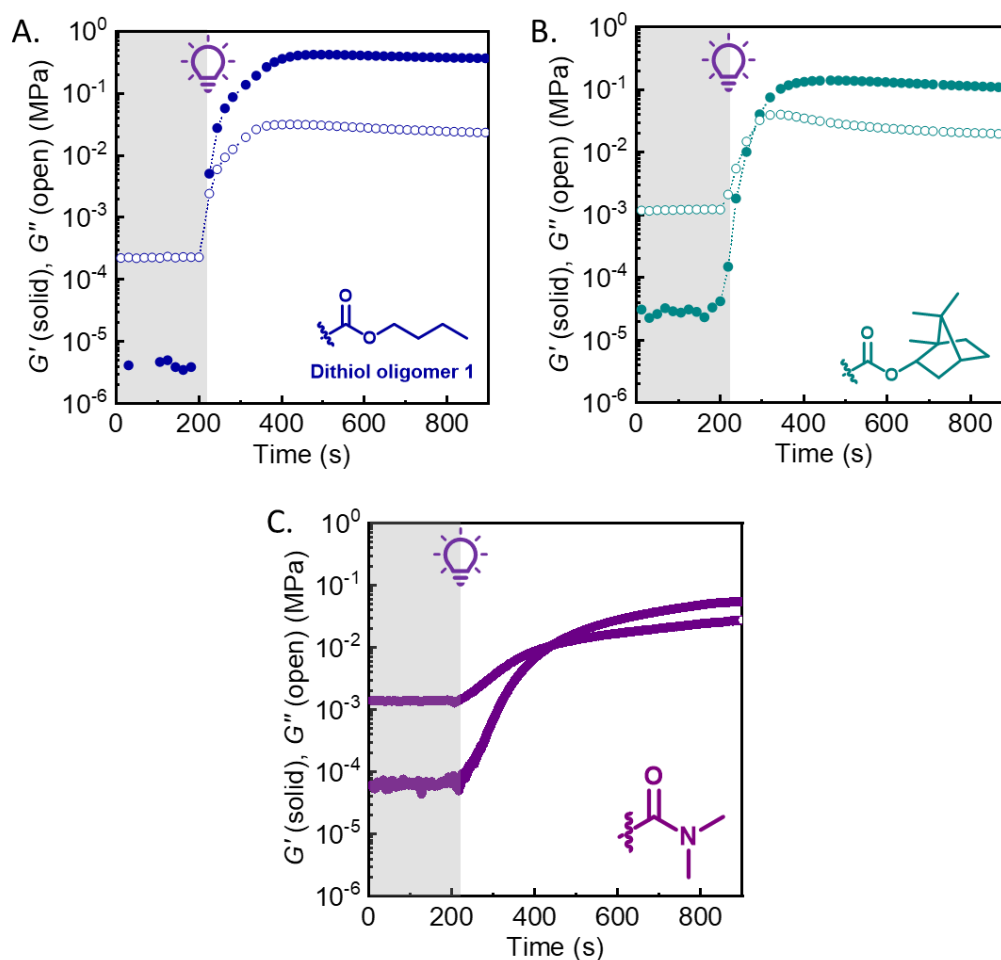


Figure B29. Kinetics of forming cross-linking networks between tris (2-maleimidoethyl) amine (**Tri-M**) and different dithiol oligomers. Evolution of the storage and loss moduli in the presence of building blocks (A) dithiol oligomer **1** (nBA containing dithiol) and (B) dithiol oligomer **2** (IBA containing dithiol) and (C) dithiol oligomer **5** (acrylamide containing dithiol) under UV light at intensity of 400 mW/cm^2 . Here dithiol oligomers act as a building block.

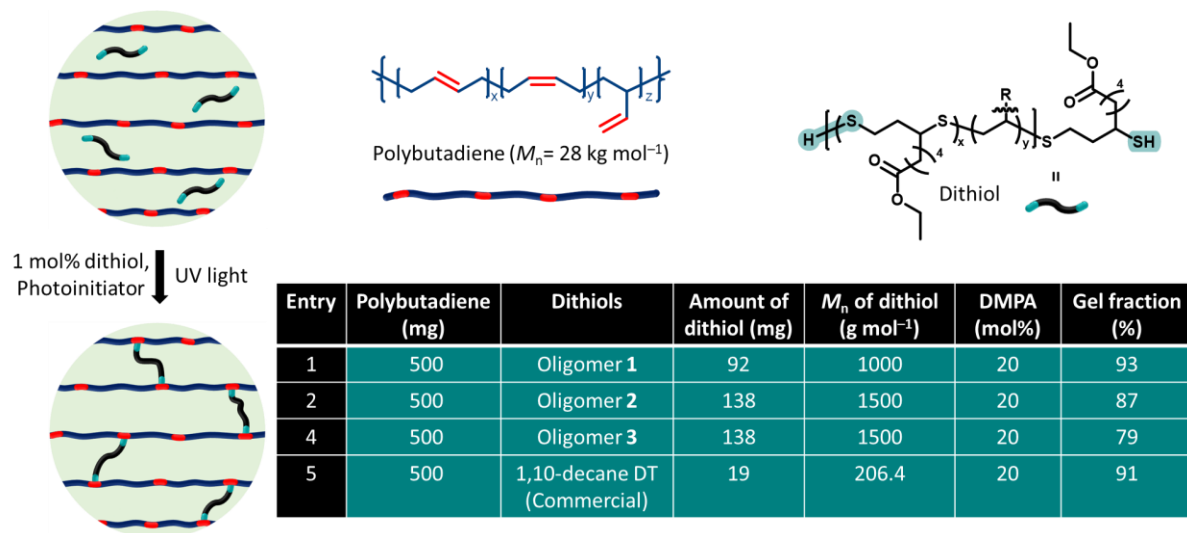


Figure B30. Cross-linking of polybutadiene (PB) with dithiol oligomers and commercial 1,10-decane dithiol (as a reference). Here we added only 1 mol% each dithiol to cross-link the PB. Gel fraction was also determined which is comparable to commercial dithiol.

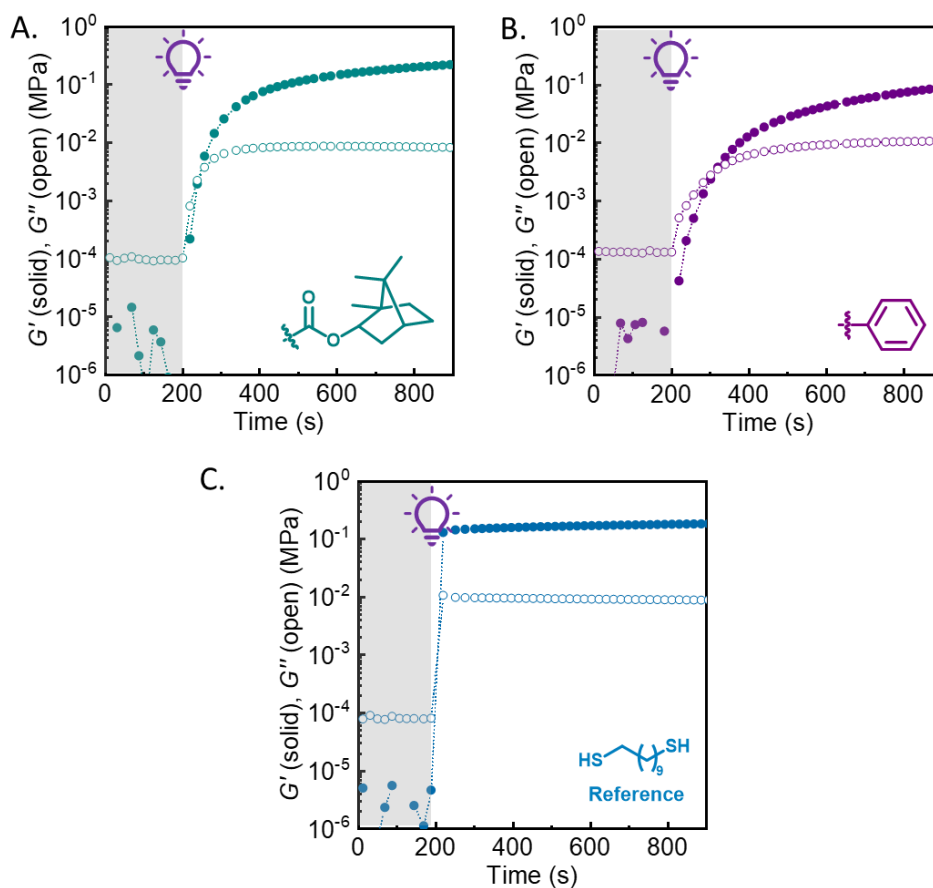


Figure B31. Kinetics of forming cross-linking networks of polybutadiene (PB) with different dithiol oligomers. Evolution of the storage and loss moduli in the presence of cross-linker (A) dithiol oligomer **2** (IBA containing dithiol) and (B) dithiol oligomer **3** (St containing dithiol) under UV light at intensity of 400 mW/cm². Here dithiol oligomers act as a cross-linker.

References:

- 1) Raeisi, M.; Tsarevsky, N. V. Radical Ring-opening Polymerization of Lipoates: Kinetic and Thermodynamic Aspects. *J. Polym. Sci.* **2021**, 59 (8), 675–684.
- 2) Hildebrandt, K., Kaupp, M., Molle, E., Menzel, J.P., Blinco, J.P., Barner-Kowollik, C. Star polymer synthesis via λ -orthogonal photochemistry. *Chem. Commun.* **2016**, 52(60), 9426-9429.

Appendix C. Supporting Information for Chapter 4

Materials

All commercial monomers passed through basic alumina prior to use. Starting materials and reagents were used as received unless otherwise stated: chloroform-d, [Cambridge Isotope Laboratories], mercaptopropyl terminated polydimethylsiloxane $M_n = 10$ kDa (DMS-SM21) [Gelest], magnesium sulfate anhydrous ($MgSO_4$), sodium bicarbonate ($NaHCO_3$), ethanol anhydrous [Fisher Chemical]. Tris(2-carboxyethyl)phosphine hydrochloride (TCEP) [AmBeed]. 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70) [FUJIFILM]. Butyl acrylate (*n*BA), pyridine, iodine, styrene (St), isobornyl acrylate (IBA) [Sigma Aldrich]. Tetrahydrofuran (THF), toluene, dichloromethane (DCM) were obtained from a solvent purification system (PureSolv, Innovative Technology Inc); other solvents, including hexanes, ethyl acetate, acetone, and methanol, were used as received. All other chemicals were purchased from Sigma Aldrich and used as received. Ethyl lipoate (EtLp) was prepared as previously reported.¹

Characterization methods

¹H nuclear magnetic resonance (NMR) spectroscopy

¹H-NMR spectra were collected on a Bruker Avance NEO 500 MHz using chloroform-d as a deuterated solvent.

Size-exclusion chromatography (SEC) instrumentation

Size-exclusion chromatography (SEC) was performed on a Waters instrument using a differential refractive index detector and two Tosoh columns (TSKgel SuperHBM-N, 3 μ m

polymer, 150 × 4.6 mm) with THF at 35 °C or chloroform containing 0.25% TEA at 35 °C for the mobile phase. Molar masses and molar mass dispersities ($\bar{M}_w/\bar{M}_n$) were determined against narrow PS standards (Agilent).

Differential scanning calorimetry (DSC)

DSC was performed on a TA Instruments Q2000 DSC with three repeated cycles between −150 and +150 °C at a constant rate of 10 °C/min. Only the second heating scan is shown.

Small-angle X-ray scattering (SAXS)

SAXS measurements were performed on a custom-built SAXS diffractometer housed at the University of California, Santa Barbara. The sample-to-detector distance was 1.7 m with a fixed wavelength of 1.54 Å. For all SAXS experiments, a silver behenate standard was used to calibrate the scattering angles. Two-dimensional (2D) data were reduced by azimuthal averaging to give $I(q)$, where I is the intensity in arbitrary units, $q = |\mathbf{q}| = 4\pi\lambda^{-1} \sin(\theta/2)$ is the magnitude of the scattering wave vector, λ is the wavelength of the incident beam, and θ is the scattering angle. Two data points (at $q = 0.15438 \text{ Å}^{-1}$ and $q = 0.16026 \text{ Å}^{-1}$), which correspond to two known dead pixels on the detector, were excised from the resulting data set for clarity.

Mechanical tensile testing

For uniaxial extension tensile tests, a Teflon dog bone mold was used to shape samples on a Carver press (Wabash, IN) 10 kPA at 160 °C for 10 min and then cooled (gauge depth = 0.5 mm, gauge width = 1.5 mm, gauge length = 10 mm, transition zone radius = 2.5 mm). Uniaxial tensile testing was performed on a TA. XT Plus Connect Texture Analyzer with a 50N load

cell using the Miniature Tensile grips (TA-96B) from the manufacturer. Grip surfaces were covered with adhesive backed foam padding to avoid damage to tensile bars and slip of samples from the grips. Samples were deformed at 0.1 mm/s until failure. Mechanical testing of polymer samples was performed in triplicate and representative data is included in the main text.

Data tables on parent, dithiol, and repolymerized samples

Table C1. PnBA parent, dithiol, repolymerized data

Sample	LpOEt feed (mol%)	LpOEt comp. (mol%)	Parent M_n (kDa)	Parent $\bar{D}$	Dithiol M_n (kDa)	Dithiol $\bar{D}$	Repoly. M_n (kDa)	Repoly. $\bar{D}$
PnBA _{24k}	20	26	111	1.7	24	1.9	91	1.7
PnBA _{20k}	20	25	190	1.9	20	2.0	181	1.6
PnBA _{14k}	20	26	261	1.8	14	2.0	245	1.8
PnBA _{11k}	30	40	152	1.8	11	1.8	75	2.4
PnBA _{9k}	30	31	173	1.9	9.0	1.9	167	1.9
PnBA _{5.1k}	50	55	98	1.7	5.1	1.4	bimodal	-
PnBA _{1.9k}	50	55	98	1.7	1.9*	1.6	bimodal	-

*Obtained by fractional precipitation of PnBA_{5.1k}

Table C2. PS and PIBA parent, dithiol, repolymerized data

Sample	LpOEt feed (mol%)	LpOEt comp. (mol%)	Parent M_n (kDa)	Parent $\bar{D}$	Dithiol M_n (kDa)	Dithiol $\bar{D}$	Repoly. M_n (kDa)	Repoly. $\bar{D}$
PS _{32k}	5	4	88	2.2	32	1.9	87	1.7
PS _{18k}	10	9	85	2.2	18	1.7	78	1.7
PS _{14k}	10	11	86	2.3	14	1.7	71	1.7
PS _{9.3k}	15	14	80	2	9.3	1.8	56	1.6
PIBA _{8k}	30	36	50	1.7	7.9	1.9	40	1.6

Table C3. PnBA_{11k} oxidization, iodine/pyridine equivalents optimization. 1.0 eq. I₂ to polymer chain was optimal.

Entry	Eq. I ₂ added	Eq. pyridine added	Dithiol M_n (kDa)	Dithiol $\bar{D}$	Repoly. M_n (kDa)	Repoly. $\bar{D}$
1	1.0	2.0	11	1.8	75	2.4
2	1.05	2.1	11	1.8	63	2.4
3	1.1	2.2	11	1.8	68	2.4
4	1.2	2.4	11	1.8	73	2.4
5	1.4	2.8	11	1.8	43	2.4

Table C4. PS_{9.3k} oxidization, iodine/pyridine equivalents optimization. 1.3 eq. I₂ to polymer chain was optimal.

Entry	Eq. I ₂ added	Eq. pyridine added	Dithiol <i>M_n</i> (kDa)	Dithiol <i>Đ</i>	Repoly. <i>M_n</i> (kDa)	Repoly. <i>Đ</i>
1	0.8	1.6	9.3	1.8	17	1.6
2	1.0	2.0	9.3	1.8	26	1.6
3	1.2	2.4	9.3	1.8	52	1.6
4	1.3	2.6	9.3	1.8	56	1.6
5	1.4	2.8	9.3	1.8	54	1.7

Table C5. PDMS_{5.5k} oxidization, iodine/pyridine equivalents optimization. 2.0 eq. I₂ to polymer chain was optimal.

Entry	Eq. I ₂ added	Eq. pyridine added	Dithiol <i>M_n</i> (kDa)	Dithiol <i>Đ</i>	Repoly. <i>M_n</i> (kDa)	Repoly. <i>Đ</i>
1	1.5	2.0	5.5	2.1	11	14
2	2.0	4.0	5.5	2.1	13	13
3	2.1	4.2	5.5	2.1	12	13
4	2.5	5.0	5.5	2.1	13	13

Table C6. Random multiblock copolymer samples data

Sample	PS feed (wt%)	PS dithiol M_n (kDa)	PDMS or PnBA block M_n (kDa)	Multibloc k M_n (kDa)	Multib lock $\bar{D}$
(PS _{50wt%} , 18k-co-PDMS _{5.5k}) _z	50	18	5.5	68	3.0
(PS _{25wt%} , 18k-co-PDMS _{5.5k}) _z	25	18	5.5	69	2.8
(PS _{30wt%} , 9.3k-co-PnBA _{20k}) _z	30	9.3	20	74	1.7
(PS _{50wt%} , 9.3k-co-PnBA _{20k}) _z	50	9.3	20	69	1.7
(PS _{70wt%} , 9.3k-co-PnBA _{20k}) _z	70	9.3	20	69	1.6
(PS _{70wt%} , 14k-co-PnBA _{24k}) _z	70	13	24	90	1.7
(PS _{80wt%} , 14k-co-PnBA _{24k}) _z	80	13	24	86	1.7
(PS _{90wt%} , 14k-co-PnBA _{24k}) _z	90	13	24	84	1.7
(PS _{60wt%} , 14k-co-PnBA _{24k}) _z	60	13	24	87	1.7
(PS _{70wt%} , 32k-co-PnBA _{24k}) _z	70	32	24	95	1.8

Table C7. T_g data of PS dithiol calculated using Flory–Fox equation (1) compared to observed.

Sample	PS w_1	EtLp w_2	T_g observed (°C)	T_g calculated (°C)
PS _{32k}	0.91	0.09	76	79
PS _{14k}	0.76	0.24	48	52
PS _{9.3k}	0.73	0.27	28	43

°C

(1)

observed.

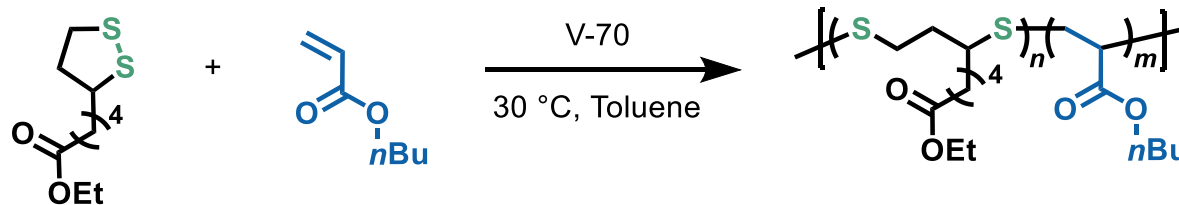
Sample	PS w ₁	PnBA w ₂	EtLp w ₃	T _g observed (°C)	T _g calculated (°C)
(PS _{60wt%} , 14k-co-PnBA _{24k}) _z	0.55	0.26	0.19	24	14
(PS _{70wt%} , 14k-co-PnBA _{24k}) _z	0.60	0.21	0.19	43	22
(PS _{80wt%} , 14k-co-PnBA _{24k}) _z	0.68	0.13	0.19	53	35

$$T_{g,PS} = 100\text{ }^{\circ}\text{C}$$

(2)

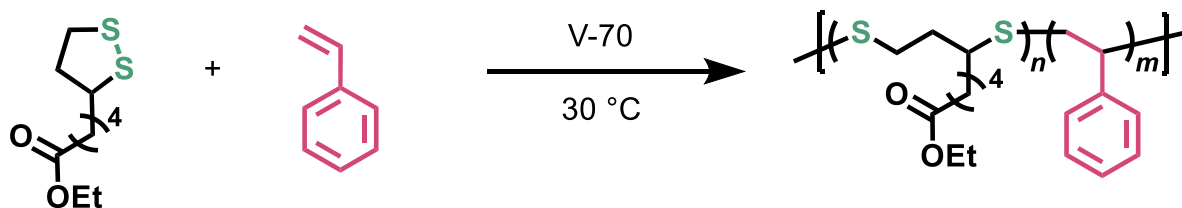
Procedures

Example procedure for ethyl lipoate copolymerization with butyl acrylate. 80:20 mol%

nBA:LpOEt

nBA (17.5 g, 136.5 mmol, 320 equiv.), ethyl lipoate (8.0 g, 34.1 mmol, 80 equiv.), V-70 (0.132 g, 0.427 mmol, 1 equiv.), and dry toluene (60 mL, 2 M) were added to a 100 mL round bottom flask equipped with stir bar and capped with rubber septa. Reaction mixture immediately cooled to 0 °C using an ice bath and degassed with argon for 60 minutes. An aliquot was taken for a time = 0 h point to monitor conversion. Reaction mixture heated to 30 °C until nBA conversion reached 50 mol% (approx. 3 – 4 h). Reaction mixture was precipitated into 1 L of 0 °C MeOH then the MeOH was decanted. Precipitation was repeated twice more by redissolving precipitate into DCM (about 50 mL) and precipitated into 1 L of 0 °C MeOH. Sample dried under high vacuum. Product obtained was a clear, colorless, viscous oil. SEC THF M_n = 110 kDa, M_w = 190 kDa, D = 1.7.

Example procedure for ethyl lipoate copolymerization with styrene. 90:10 mol% St:LpOEt

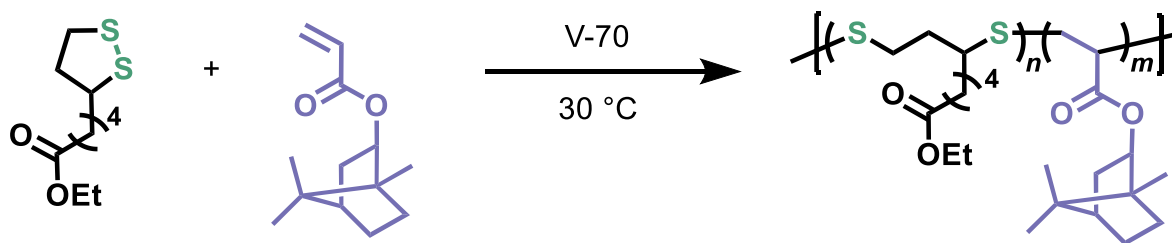


Styrene (30 g, 288 mmol, 360 equiv.), ethyl lipoate (7.5 g, 32 mmol, 40 equiv.), and V-70 (0.247 g, 0.8 mmol, 1 equiv.) were added to a 100 mL round bottom flask equipped with stir bar and capped with rubber septa. Reaction mixture immediately cooled to 0 °C using an ice bath and degassed with argon for 60 minutes. An aliquot was taken for a time = 0 h point to monitor conversion. Reaction mixture heated to 30 °C until St conversion reached 70 mol% (approx. = 24 h). Reaction mixture was dissolved into 50 mL DCM and precipitated into 1 L of 0 °C MeOH then the MeOH was decanted. Precipitation was repeated twice more by redissolving precipitate into DCM (about 50 mL) and precipitated into 1 L of 0 °C MeOH.

Sample dried under high vacuum. Product obtained was a white solid. SEC THF $M_n = 86$ kDa, $M_w = 200$ kDa, $\bar{D} = 2.3$.

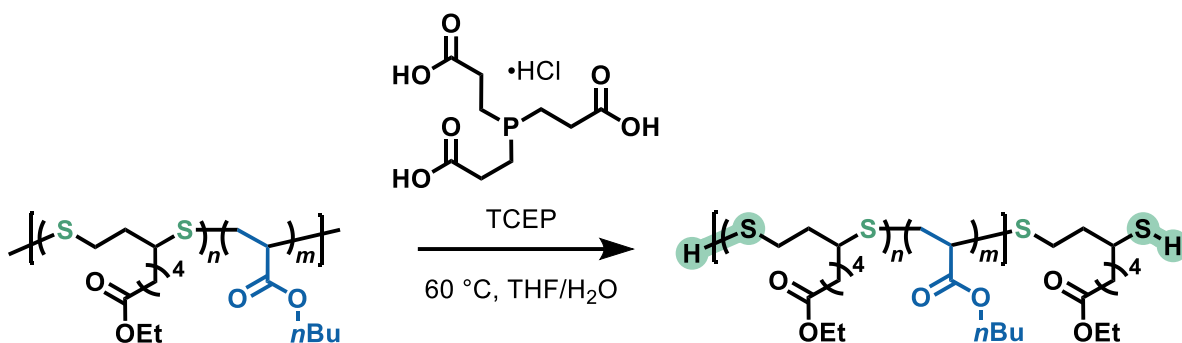
Example procedure for ethyl lipoate copolymerization with isobornyl acrylate. 70:30 mol%

IBA:LpOEt



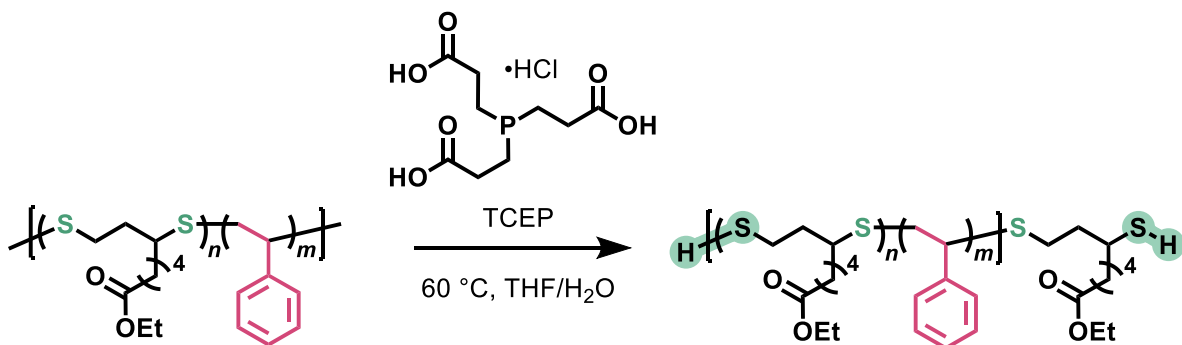
IBA (1.0 g, 4.8 mmol, 280 equiv.), ethyl lipoate (0.48 g, 2.1 mmol, 120 equiv.), V-70 (5.3 mg, 0.017 mmol, 1 equiv.), and dry toluene (3.5 mL, 2 M) were added to a 20 mL vial equipped with stir bar and capped with septa. Reaction mixture immediately cooled to 0 °C using an ice bath and degassed with argon for 60 minutes. An aliquot was taken for a time = 0 h point to monitor conversion. Reaction mixture heated to 30 °C until IBA conversion reached 50 mol% (approx. 3 – 4 h). Reaction mixture was precipitated into 1 L of 0 °C MeOH then the MeOH was decanted. Precipitation was repeated twice more by redissolving precipitate into DCM (about 50 mL) and precipitated into 1 L of 0 °C MeOH. Sample dried under high vacuum. Product obtained was a clear, colorless, viscous oil. SEC THF $M_n = 50$ kDa, $M_w = 85$ kDa, $\bar{D} = 1.7$.

Example procedure for disulfide bond reduction with TCEP•HCl. PnBA dithiol



18 g PnBA parent copolymer was added to a 500 mL round bottom flask equipped with magnetic stir bar and dissolved in 200 mL THF. In a separate 20 mL vial, 2.6 g of TCEP (5 eq. if expecting 10 kDa dithiol polymer) was dissolved in 20 mL DI water. The TCEP solution was added to the PnBA parent copolymer flask. Reaction mixture was capped, stirred, and heated at 60 °C. Reaction was monitored by SEC until the molecular weight no longer decreased (typically 24 h). Solution was cooled to room temperature and THF removed under vacuum. Reaction mixture was diluted with 250 mL DCM and washed with 200 mL of saturated NaHCO₃ aq., 200 mL DI water, and 200 mL brine. The organic layer was dried with anhydrous MgSO₄ and concentrated under vacuum to obtain the dithiol polymer.

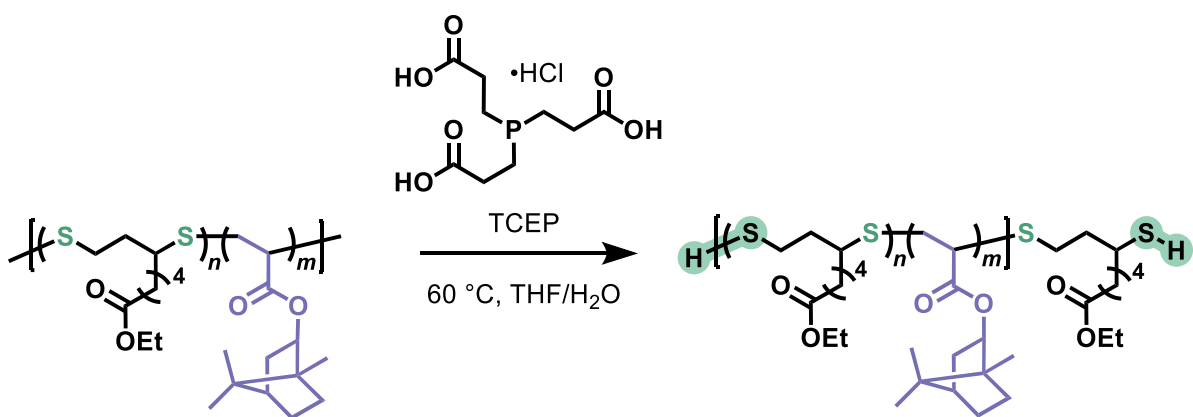
Example procedure for disulfide bond reduction with TCEP•HCl. PS dithiol



20 g PS parent copolymer was added to a 500 mL round bottom flask equipped with magnetic stir bar and dissolved in 200 mL THF. In a separate 20 mL vial, 3 g of TCEP (5 eq. if expecting

10 kDa dithiol polymer) was dissolved in 20 mL DI water. The TCEP solution was added to the PS parent copolymer flask. Reaction mixture was capped, stirred, and heated at 60 °C. Reaction was monitored by SEC until the molecular weight no longer decreased (typically 24 h). Solution was cooled to room temperature and THF removed under vacuum. Reaction mixture was diluted with 250 mL DCM and washed with 200 mL of saturated NaHCO₃ aq., 200 mL DI water, and 200 mL brine. The organic layer was dried with anhydrous MgSO₄ and concentrated under vacuum to obtain the dithiol polymer.

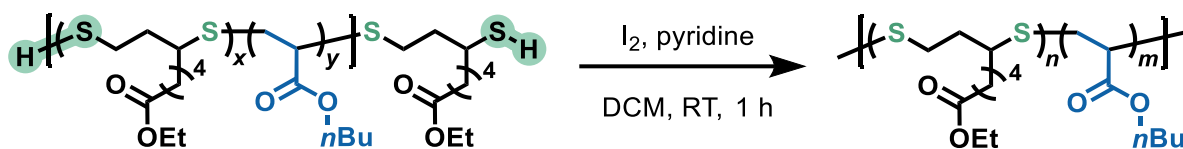
Example procedure for disulfide bond reduction with TCEP•HCl. PIBA dithiol



1.0 g PIBA parent copolymer was added to a 20 mL vial equipped with magnetic stir bar and dissolved in 10 mL THF. In a separate 4 mL vial, 0.18 g of TCEP (5 eq. if expecting 8 kDa dithiol polymer) was dissolved in 1 mL DI water. The TCEP solution was added to the PIBA parent copolymer vial. Reaction mixture was capped, stirred, and heated at 60 °C. Reaction was monitored by SEC until the molecular weight no longer decreased (typically 24 h). Solution was cooled to room temperature and THF removed under vacuum. Reaction mixture was diluted with 20 mL DCM and washed with 20 mL of saturated NaHCO₃ aq., 20 mL DI

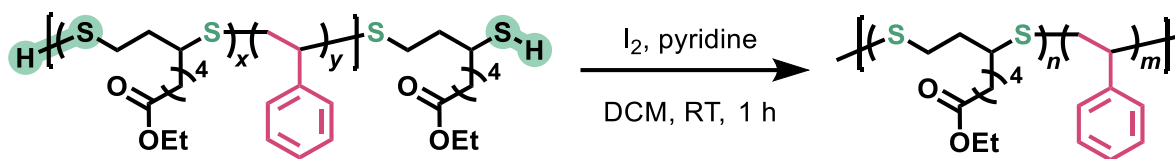
water, and 20 mL brine. The organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the dithiol polymer.

Example procedure repolymerization of dithiol polymer using iodine/pyridine PnBA



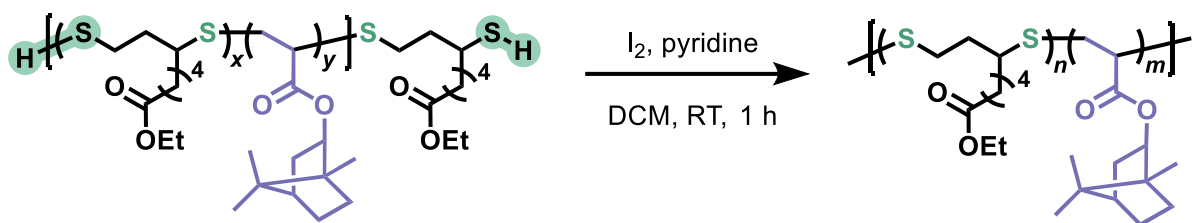
0.10 g of the PnBA dithiol (24 kDa, 0.0042 mmol) was added to a 4 mL vial equipped with magnetic stir bar and dissolved in 0.5 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.064 g iodine, 0.040 g pyridine, and 10 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 0.18 mL (1.0 equivalents, 0.0042 mmol iodine, and 2.0 equivalents, 0.0083 mmol pyridine relative to polymer chain) of the iodine/pyridine stock solution was added to the PnBA dithiol solution dropwise. The vial was capped and stirred for 1 h. Reaction mixture was transferred to a 45 mL centrifuge tube and diluted with DCM until there was 20 mL DCM total. The organic layer was washed with 20 mL of 1 M $\text{Na}_2\text{S}_2\text{O}_3$, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the repolymerized polymer.

Example procedure repolymerization of dithiol polymer using iodine/pyridine PS



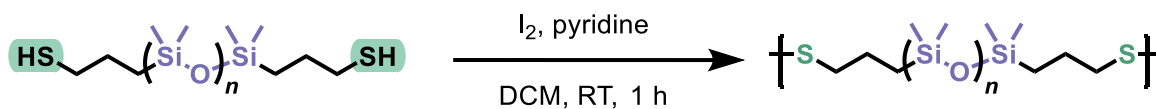
0.10 g of the PS dithiol (13 kDa, 0.0077 mmol) was added to a 4 mL vial equipped with magnetic stir bar and dissolved in 0.5 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.064 g iodine, 0.040 g pyridine, and 10 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 0.40 mL (1.3 equivalents, 0.010 mmol iodine, and 2.6 equivalents, 0.026 mmol pyridine relative to polymer chain) of the iodine/pyridine stock solution was added to the PS dithiol solution dropwise. The vial was capped and stirred for 1 h. Reaction mixture was transferred to a 45 mL centrifuge tube and diluted with DCM until there was 20 mL DCM total. The organic layer was washed with 20 mL of 1 M $Na_2S_2O_3$, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous $MgSO_4$ and concentrated under vacuum to obtain the repolymerized polymer.

Example procedure repolymerization of dithiol polymer using iodine/pyridine PIBA



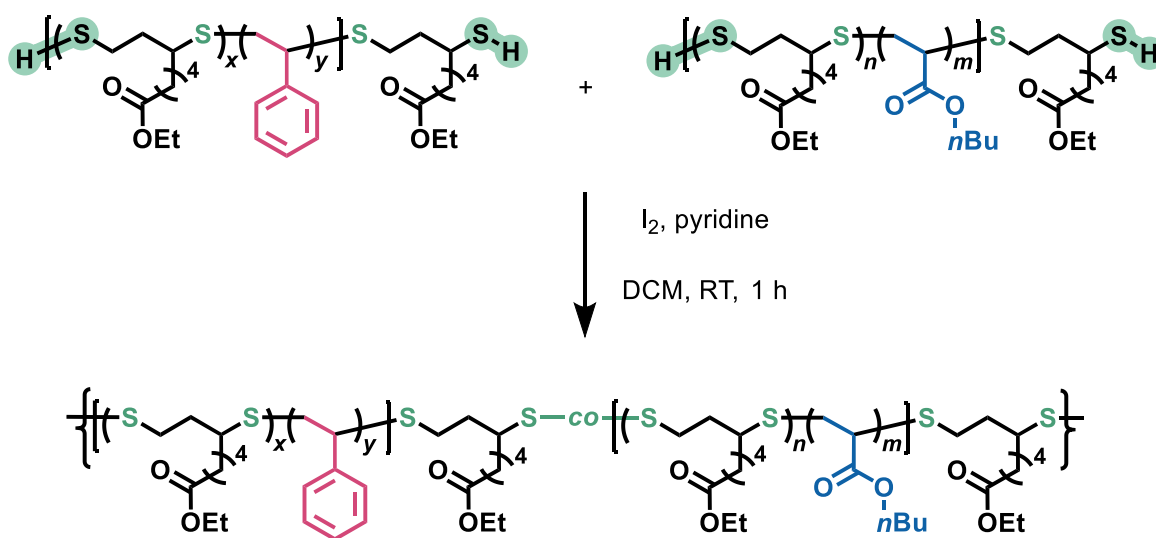
0.10 g of the PIBA dithiol (8 kDa, 0.013 mmol) was added to a 4 mL vial equipped with magnetic stir bar and dissolved in 0.5 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.064 g iodine, 0.040 g pyridine, and 10 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 0.60 mL (1.2 equivalents, 0.015 mmol iodine, and 2.4 equivalents, 0.030 mmol pyridine relative to polymer chain) of the iodine/pyridine stock solution was added to the PIBA dithiol solution dropwise. The vial was capped and stirred for 1 h. Reaction mixture was transferred to a 45 mL centrifuge tube and diluted with DCM until there was 20 mL DCM total. The organic layer was washed with 20 mL of 1 M $\text{Na}_2\text{S}_2\text{O}_3$, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the repolymerized polymer.

Example procedure repolymerization of dithiol polymer using iodine/pyridine PDMS



0.10 g of the PDMS dithiol (5.5 kDa, 0.018 mmol) was added to a 4 mL vial equipped with magnetic stir bar and dissolved in 0.5 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.064 g iodine, 0.040 g pyridine, and 10 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 1.45 mL (2.0 equivalents, 0.036 mmol iodine, and 4.0 equivalents, 0.072 mmol pyridine relative to polymer chain) of the iodine/pyridine stock solution was added to the PDMS dithiol solution dropwise. The vial was capped and stirred for 1 h. Reaction mixture was transferred to a 45 mL centrifuge tube and diluted with DCM until there was 20 mL DCM total. The organic layer was washed with 20 mL of 1 M Na₂S₂O₃, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous MgSO₄ and concentrated under vacuum to obtain the repolymerized polymer.

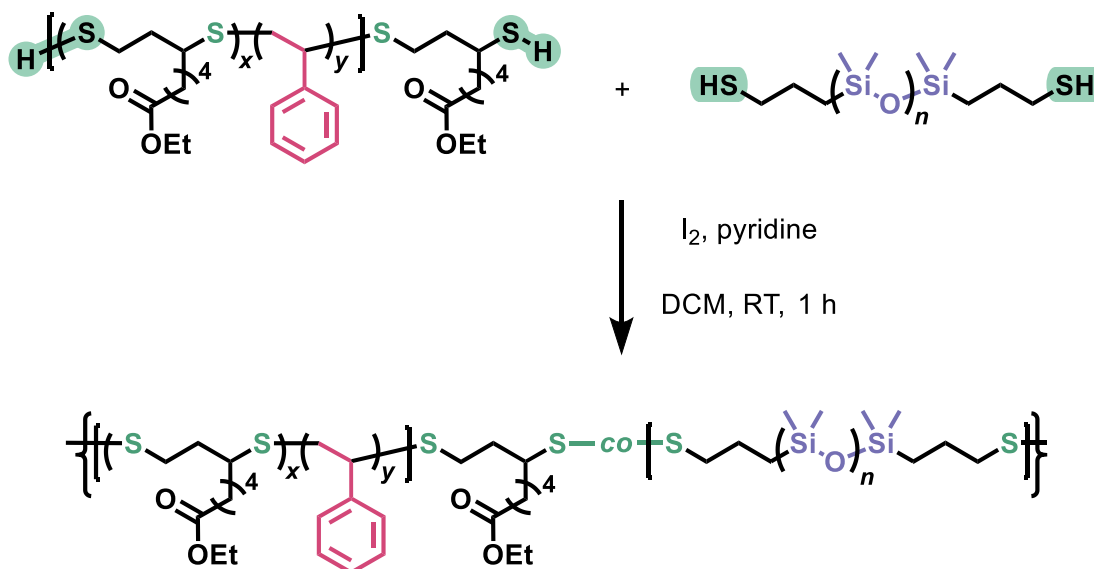
Example procedure repolymerization of dithiol polymer for (PS_{70wt%, 13k}-co-PnBA_{24k})_z



1.4 g of the PnBA dithiol (24 kDa, 0.058 mmol) and 0.60 g PS dithiol (13 kDa, 0.046 mmol) was added to a 20 mL vial equipped with magnetic stir bar and dissolved in 4 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.064 g iodine, 0.040 g pyridine, and 10 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 5.2 mL of the iodine/pyridine stock solution was added to the dithiol solution dropwise (calculated from needing 2.8 mL for the PnBA and 2.4 mL for the PS). The vial was capped and stirred for 1 h. Reaction mixture was split and transferred to two 45 mL centrifuge tubes and each diluted with DCM until there was 20 mL DCM total per centrifuge tube. For each centrifuge tube, organic layer was washed with 20 mL of 1 M $\text{Na}_2\text{S}_2\text{O}_3$, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the repolymerized polymer. The multiblock copolymer

was further purified by dissolving in DCM and precipitating into 0°C MeOH. MeOH was decanted and product was dried under vacuum.

Example procedure repolymerization of dithiol polymer for (PS_{50wt%, 18k}-co-PDMS_{5.5k})_z



1.0 g of the PDMS dithiol (5.5 kDa, 0.18 mmol) and 1.0 g PS dithiol (18 kDa, 0.056 mmol) was added to a 40 mL vial equipped with magnetic stir bar and dissolved in 7 mL DCM. In a separate 20 mL vial, a 0.025 M iodine and 0.05 M pyridine stock solution mixture was prepared by adding 0.128 g iodine, 0.080 g pyridine, and 20 mL DCM into the 20 mL vial and shaken until iodine was fully dissolved. 17.4 mL of the iodine/pyridine stock solution was added to the dithiol solution dropwise (calculated from needing 14.5 mL for the PDMS and 2.9 mL for the PS). The vial was capped and stirred for 1 h. Reaction mixture was split and transferred to two 45 mL centrifuge tubes and each diluted with DCM until there was 20 mL DCM total per centrifuge tube. For each centrifuge tube, organic layer was washed with 20 mL of 1 M Na₂S₂O₃, mixture shaken, then centrifuged for 10 min at 3500 rpm to help separate the layers. The aqueous layer was removed, and 20 mL of 1 M HCl was added, mixture shaken, then

centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of DI water was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, and 20 mL of brine was added, mixture shaken, then centrifuged for 10 min at 3500 rpm. The aqueous layer was removed, organic layer was dried with anhydrous MgSO_4 and concentrated under vacuum to obtain the repolymerized polymer. The multiblock copolymer was further purified by dissolving in DCM and precipitating into 0°C MeOH. MeOH was decanted and product was dried under vacuum.

Characterization data

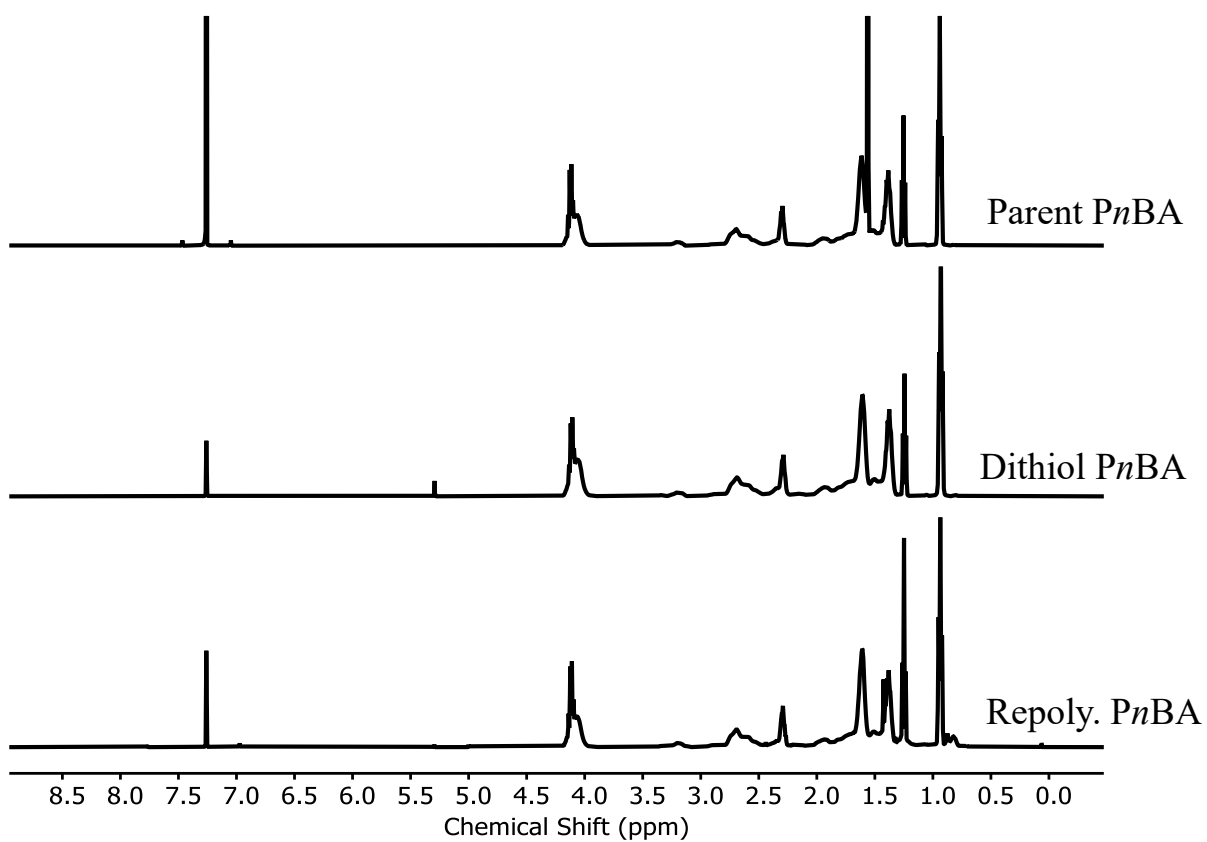


Figure C1. Example of PnBA parent (top), dithiol (middle), and repolymerized (bottom) ^1H -NMR having similar spectra.

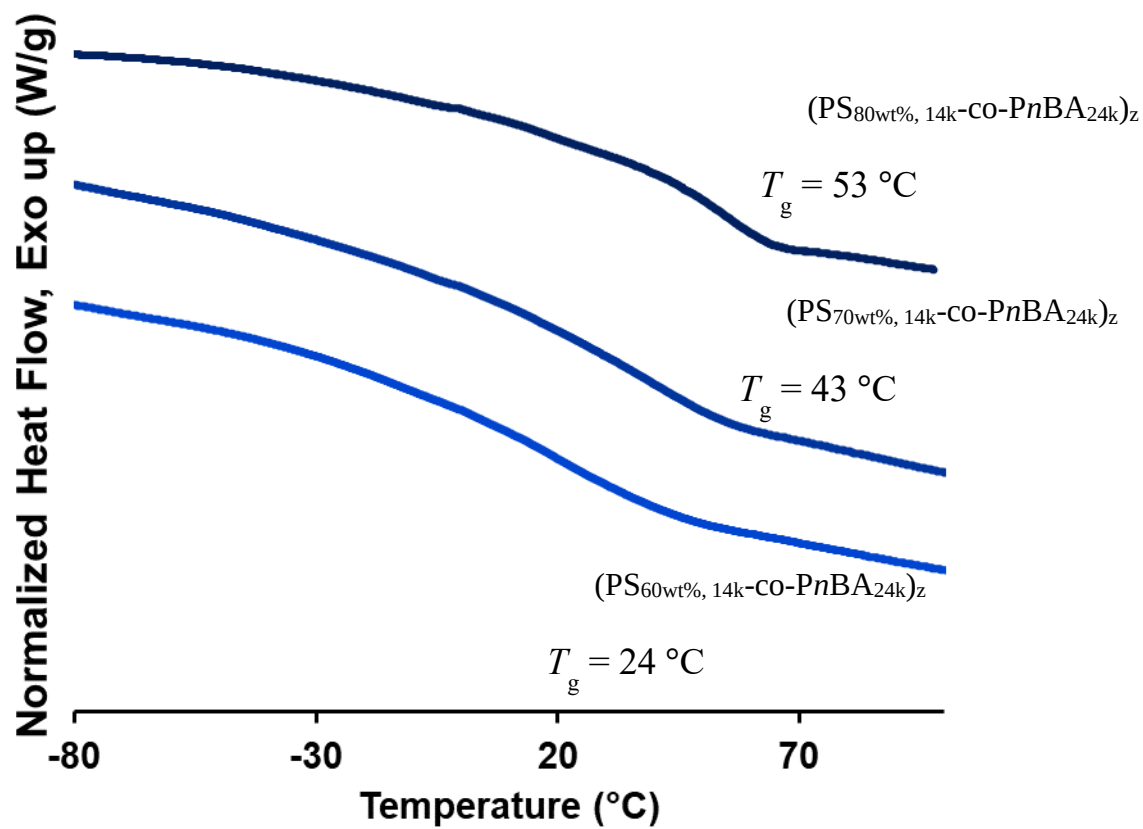


Figure C2. DSC traces of (PS_{14k}-co-PnBA_{24k})_z multiblock copolymers at different PS wt% incorporations.

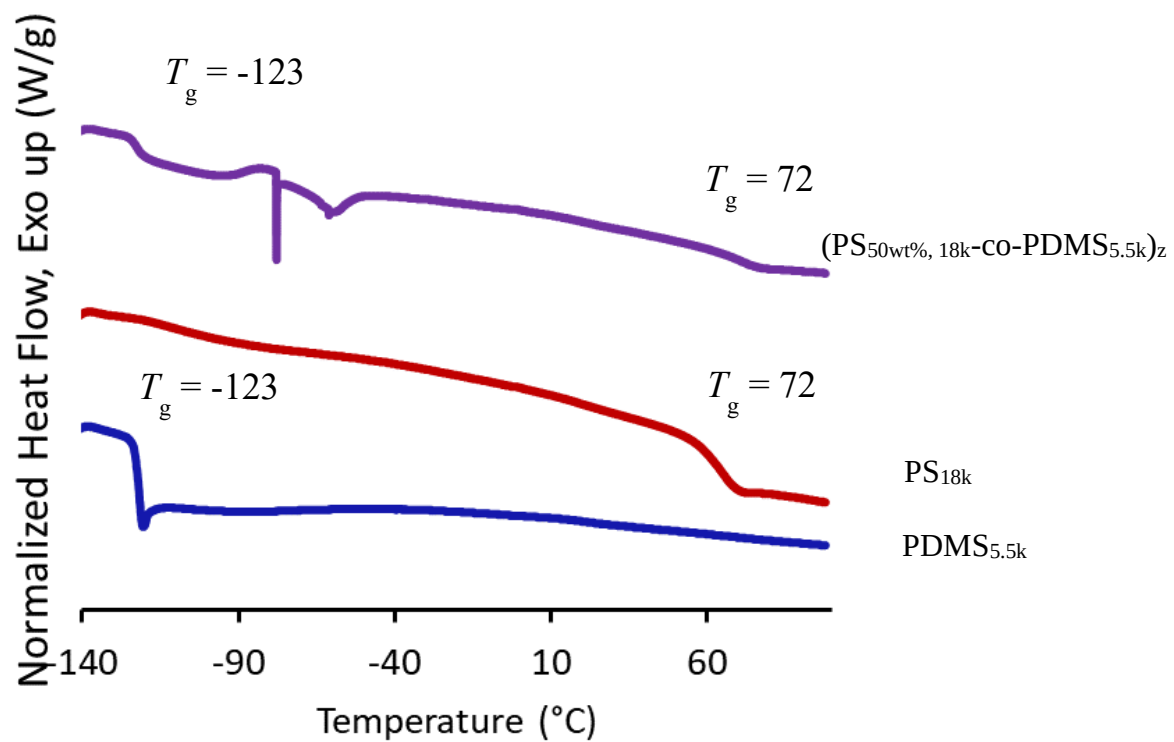


Figure C3. DSC traces for $(PS_{50wt\%}, 18k\text{-co-PDMS}_{5.5k})_z$ multiblock copolymer compared to dithiols

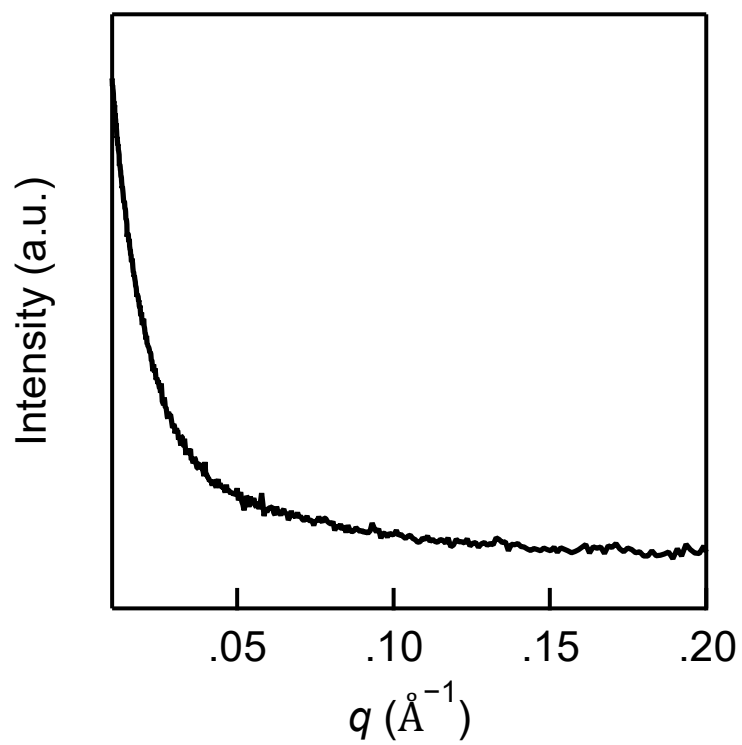


Figure C4. SAXS data of multiblock: $(\text{PS}_{70\text{wt}\%}, 14\text{k-CO-PnBA}_{24\text{k}})_z$

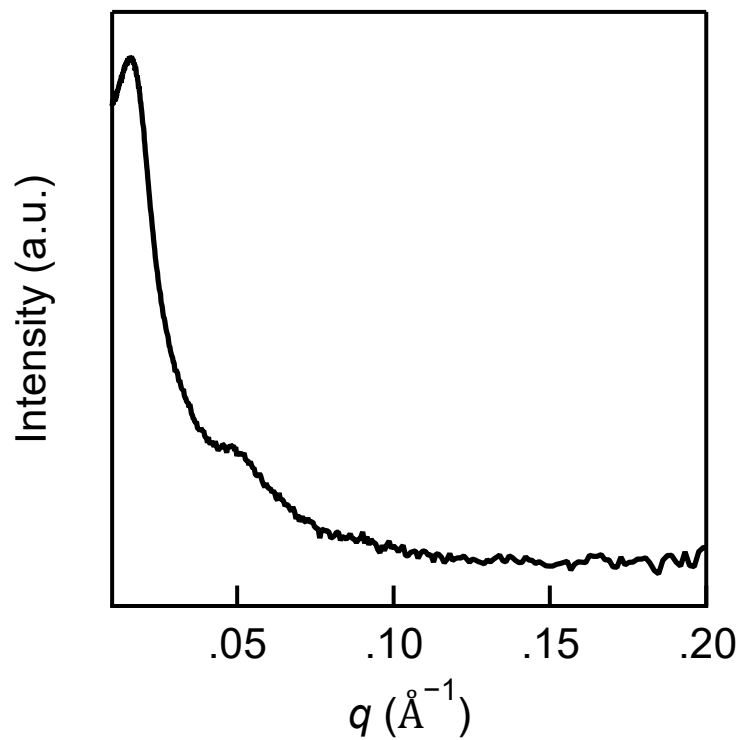


Figure C5. SAXS data of multiblock: $(\text{PS}_{25\text{wt}\%, 18\text{k}}\text{-co-PDMS}_{5.5\text{k}})_z$

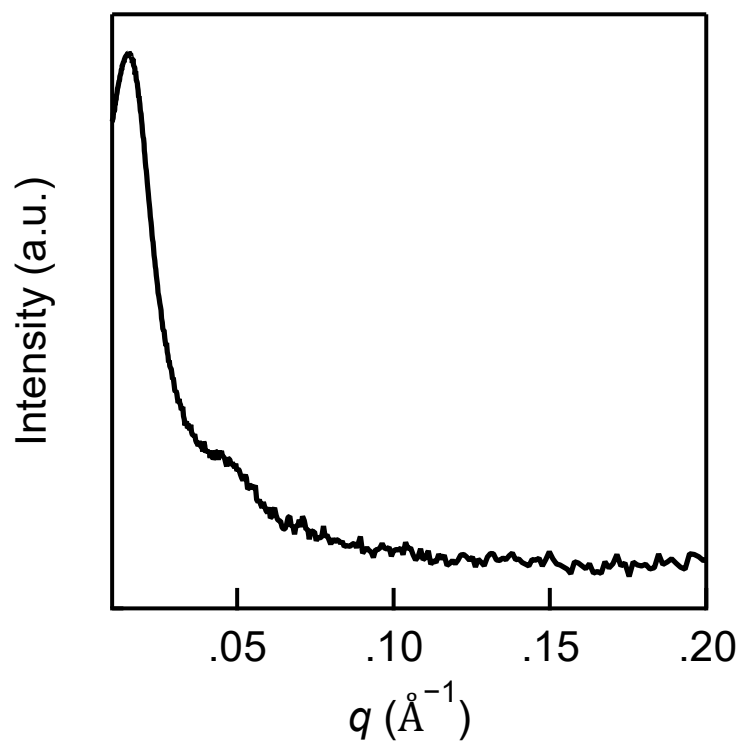


Figure C6. SAXS data of multiblock: $(\text{PS}_{50\text{wt}\%}, 18\text{k-CO-PDMS}_{5.5\text{k}})_z$

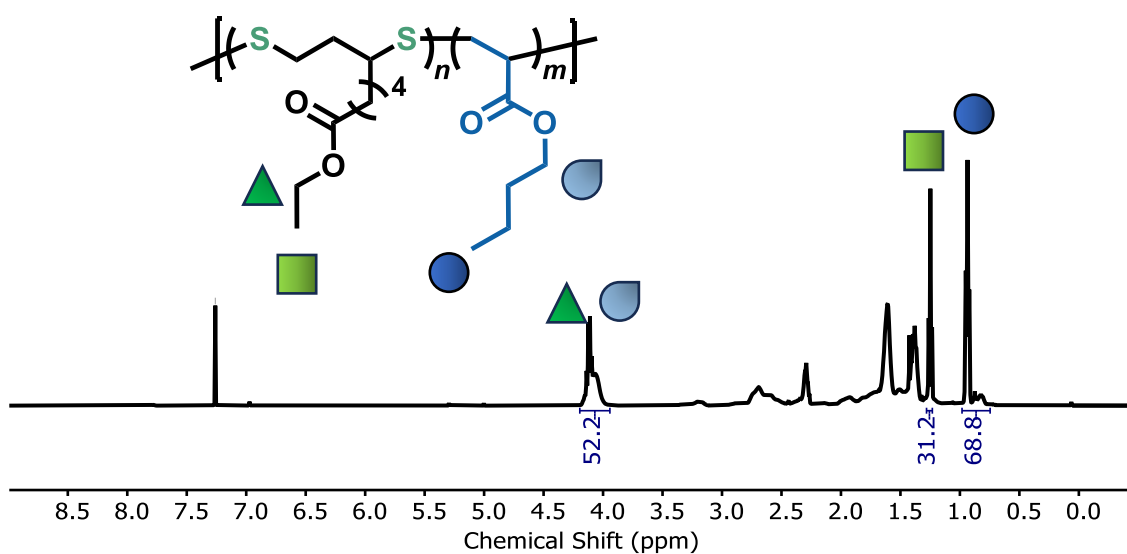


Figure C9. ^1H -NMR of PnBA repolymerized polymer in deuterated chloroform

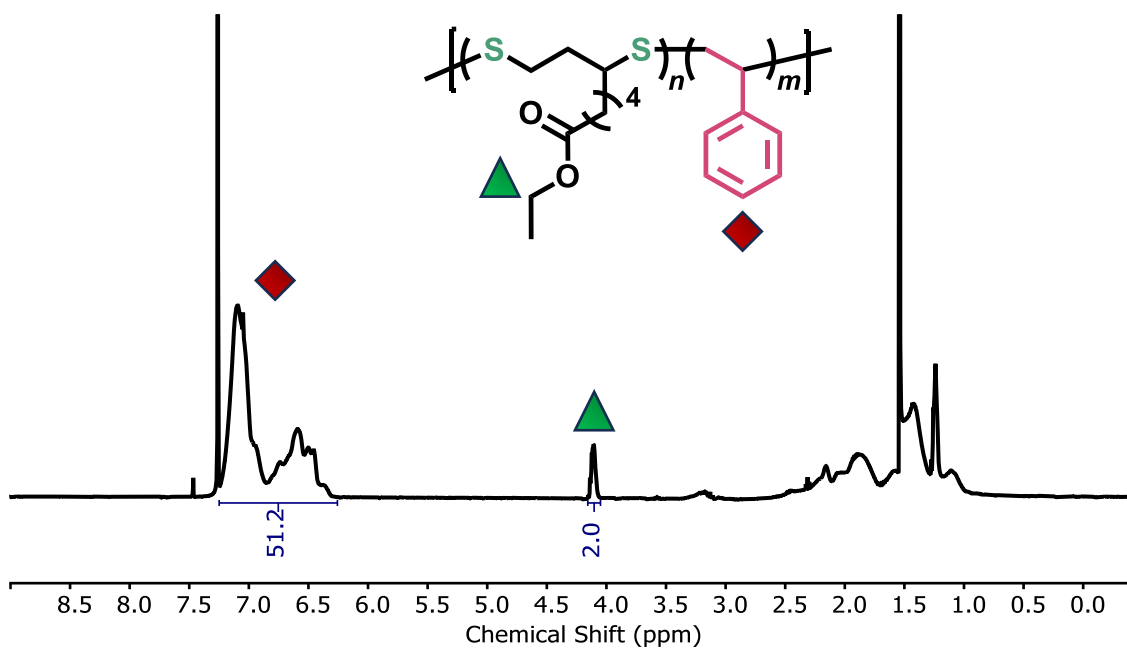


Figure C10. ^1H -NMR of PS parent polymer in deuterated chloroform

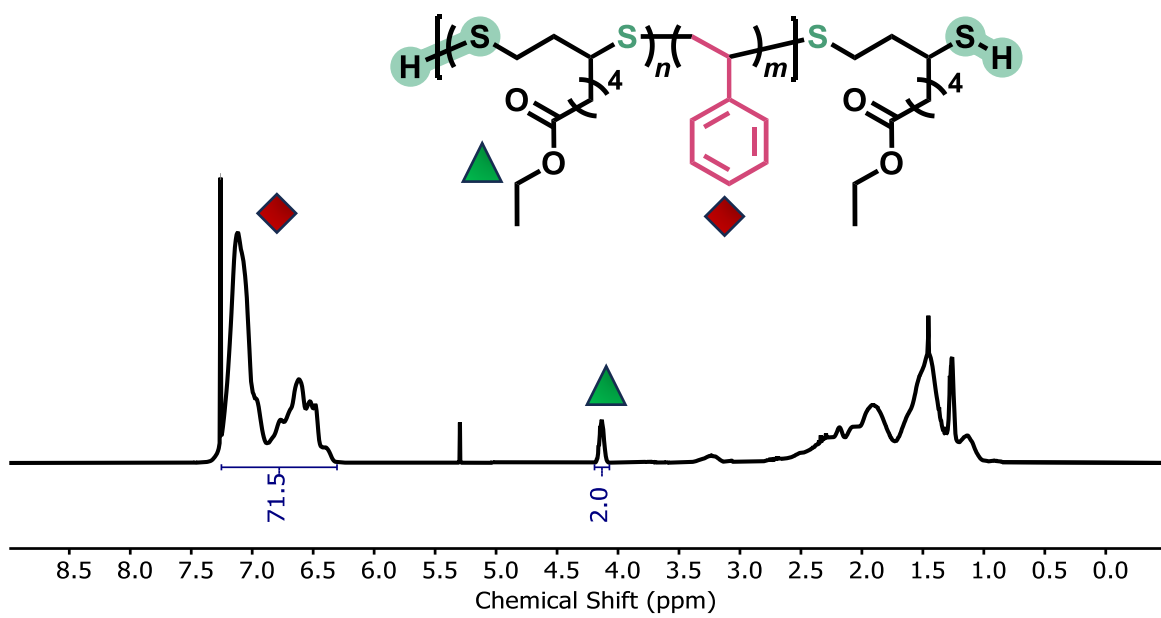


Figure C11. ¹H-NMR of PS dithiol polymer in deuterated chloroform

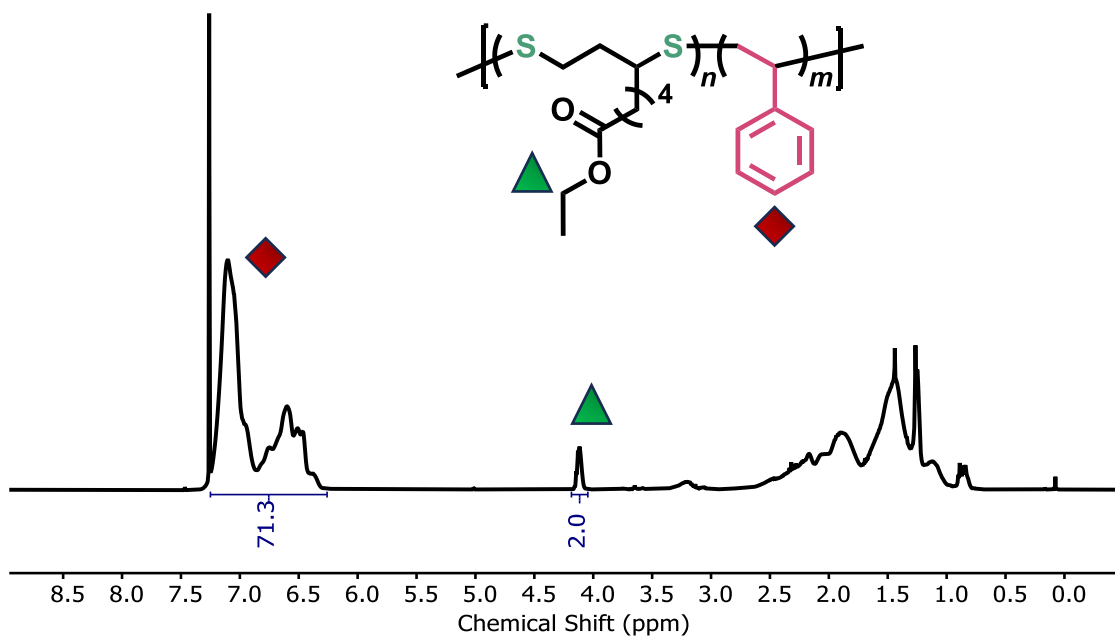


Figure C12. ¹H-NMR of PS repolymerized polymer in deuterated chloroform

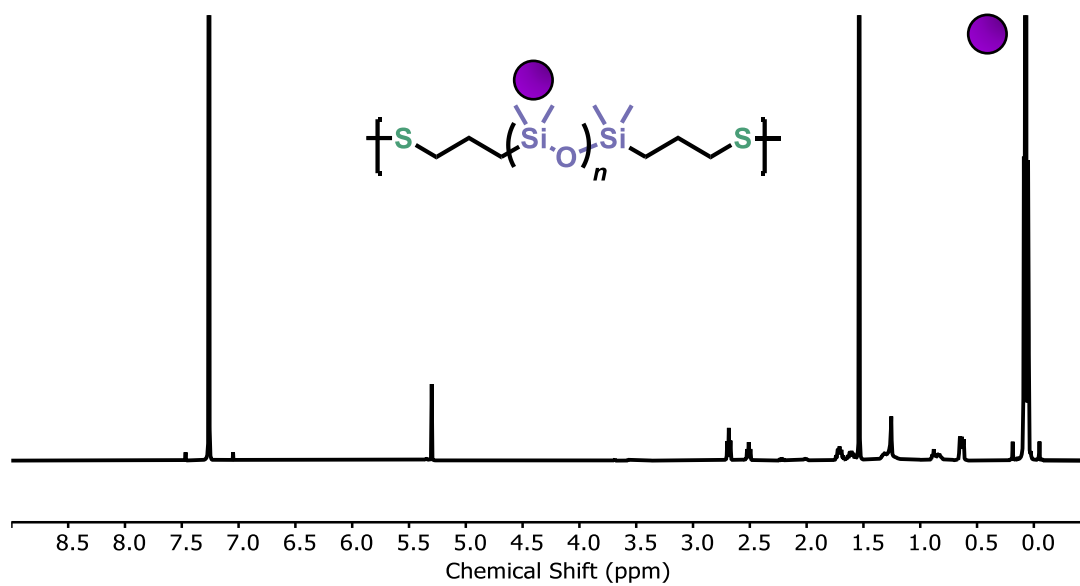


Figure C13. ^1H -NMR of PDMS repolymerized polymer in deuterated chloroform

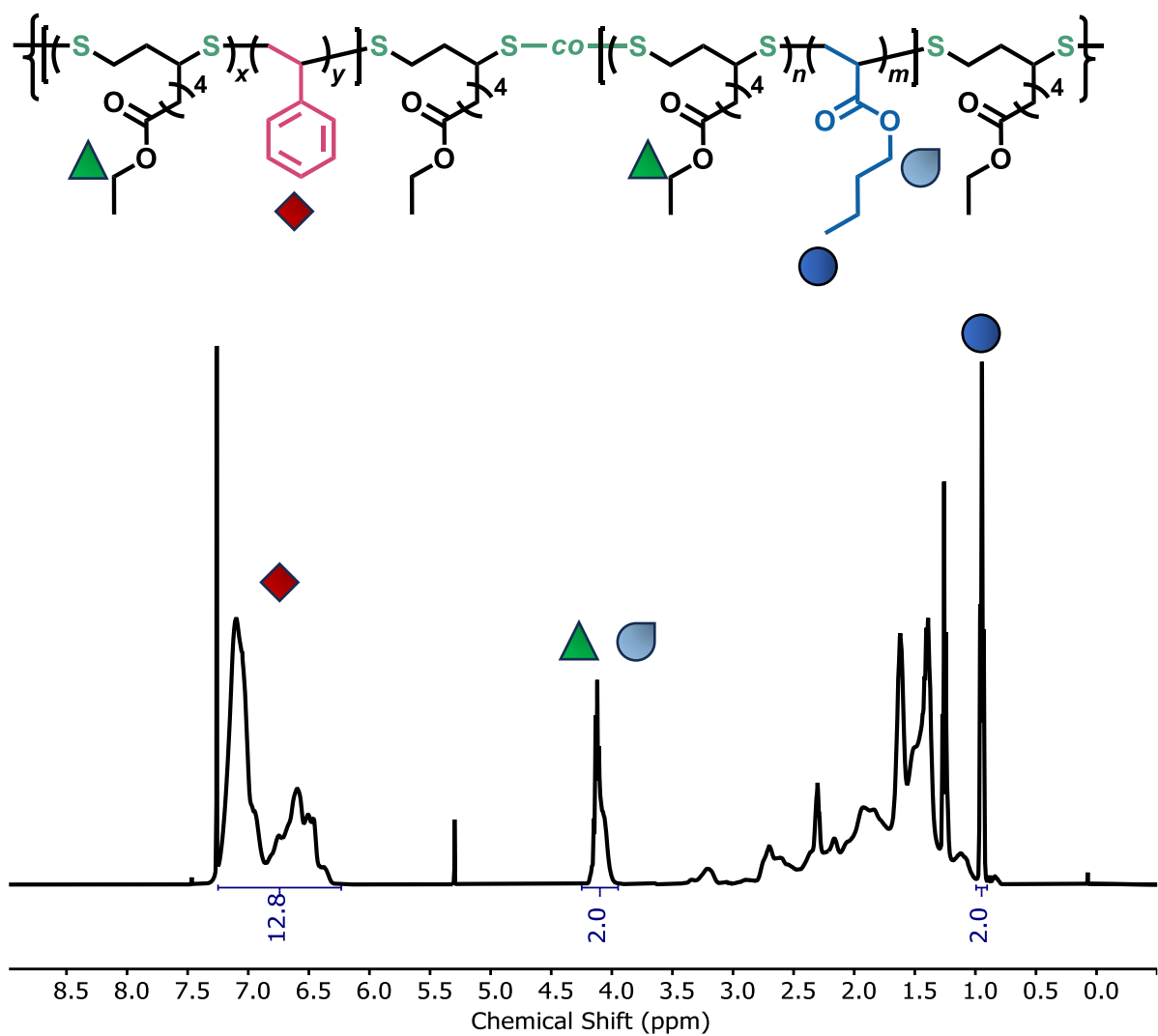


Figure C14. $^1\text{H-NMR}$ of $(\text{PS}_{70\text{wt}\%,9.3\text{k}}\text{-co-PnBA}_{20\text{k}})_z$ multiblock copolymer in deuterated chloroform

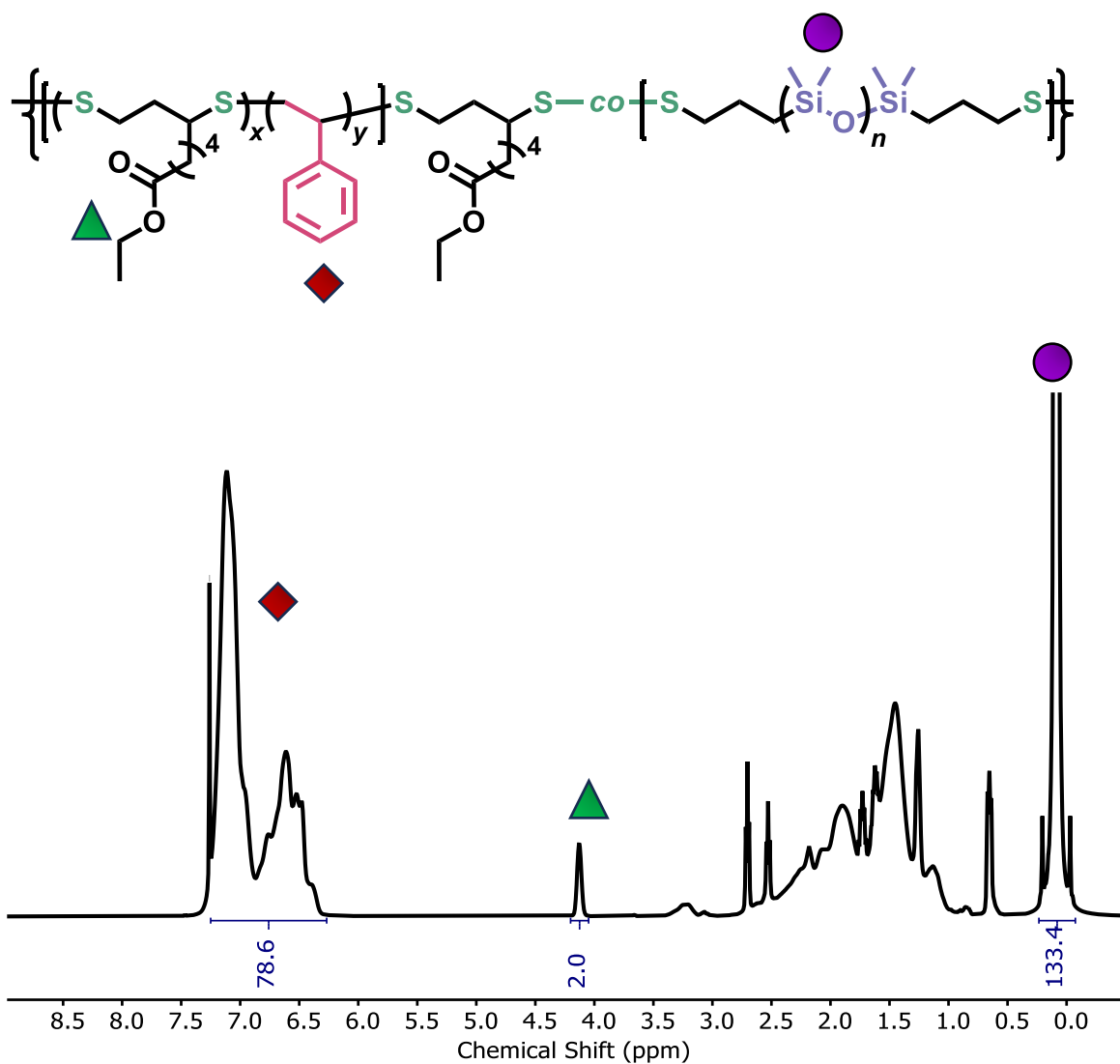


Figure C15. ^1H -NMR of $(\text{PS}_{50\text{wt}\%,18\text{k}}\text{-co-PDMS}_{5.5\text{k}})_z$ multiblock copolymer in deuterated chloroform

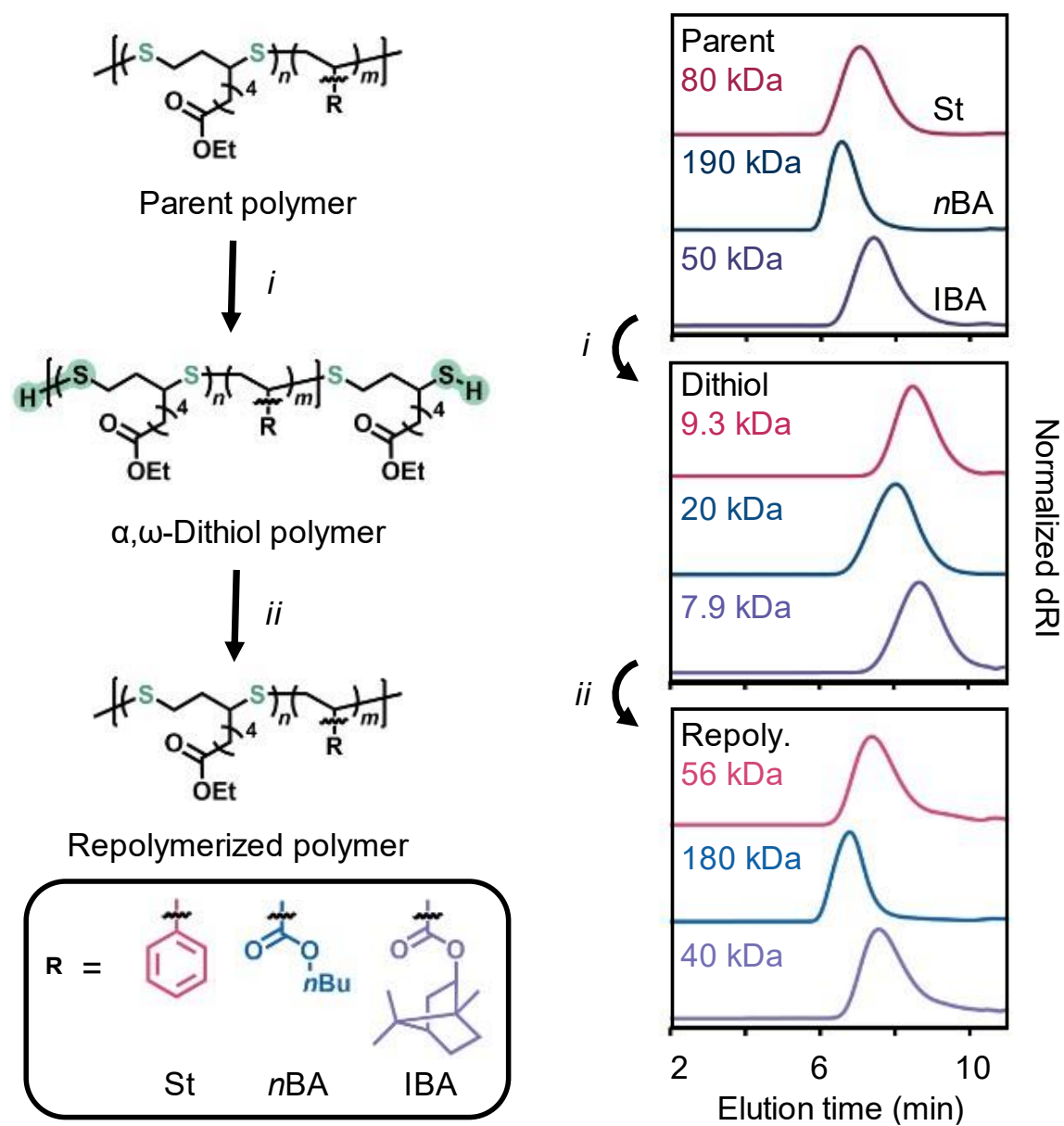


Figure C16. SEC THF of *Pn*BA, PS, and PIBA parent, dithiol, and repolymerized

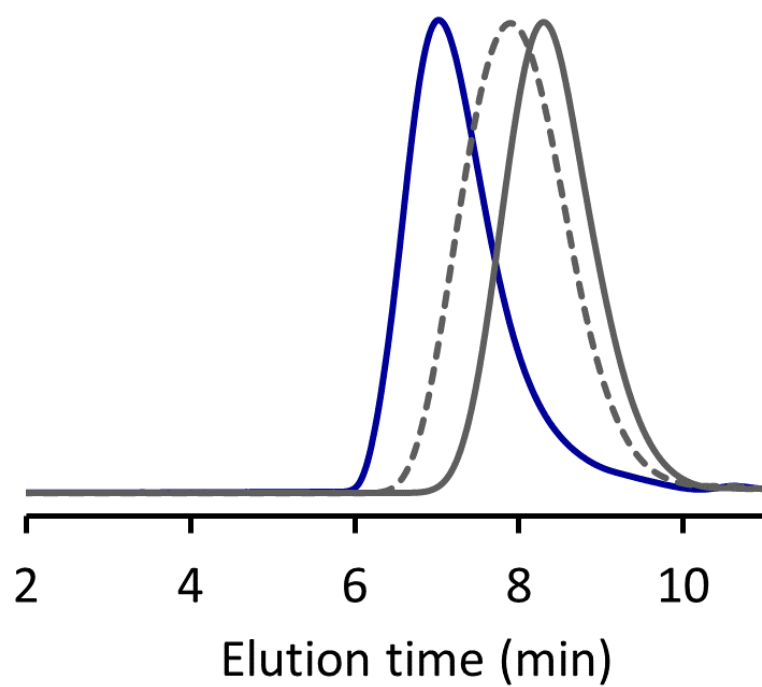


Figure C17. Example SEC THF of dithiol traces $\text{PS}_{13\text{k}}$ (solid grey) and $\text{PnBA}_{24\text{k}}$ (dotted grey) to blue multiblock copolymer $(\text{PS}_{70\text{wt\%, } 13\text{k}}\text{-co-PnBA}_{24\text{k}})_z$

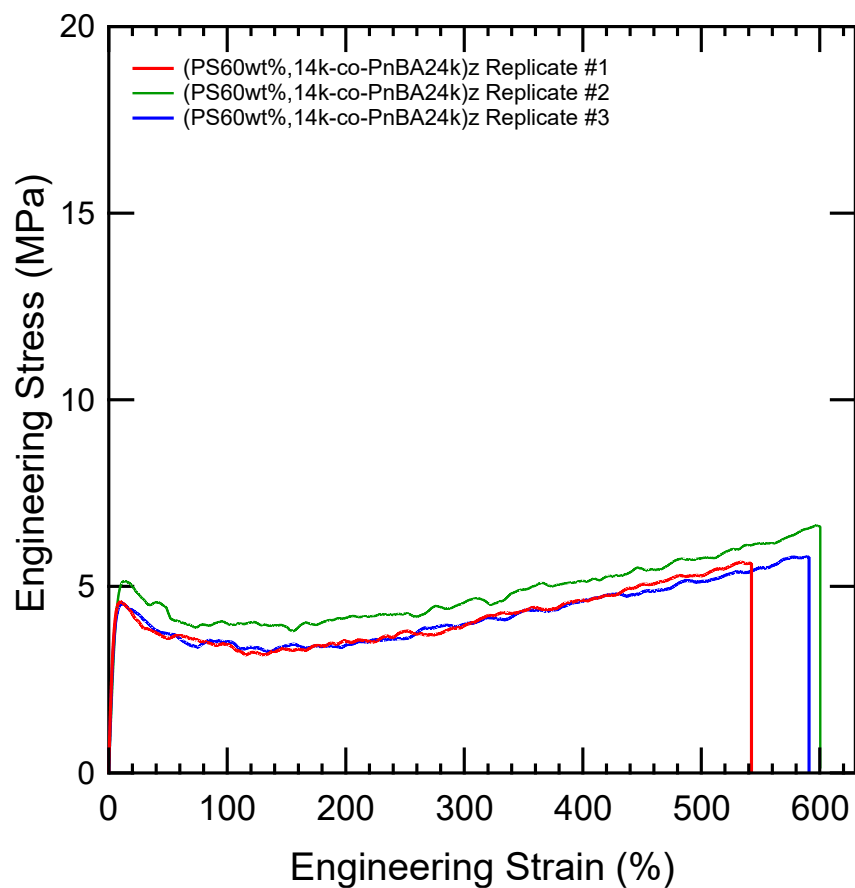


Figure C18: Triplicate data for mechanical testing of (PS_{60wt%}, 14k-co-PnBA_{24k})_z

References

- (1) Raeisi, M.; Tsarevsky, N. V. Radical Ring-opening Polymerization of Lipoates: Kinetic and Thermodynamic Aspects. *J. Polym. Sci.* **2021**, 59 (8), 675–684.