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Mechanically Facilitated Retro [4 + 2] Cycloadditions

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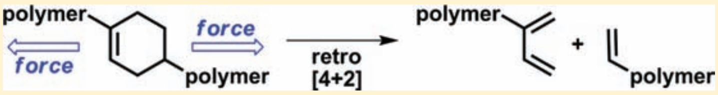
S *Supporting Information*



ABSTRACT: Poly(methyl acrylate)s (PMAs) of varying molecular weights were grown from a [4 + 2] cycloaddition adduct of maleimide with furan containing two polymerization initiators. Subjecting the corresponding PMA (>30 kDa) chains to ultrasound at 0 °C resulted in a retro [4 + 2] cycloaddition reaction, as observed by gel permeation chromatography (GPC) and UV−vis spectroscopy, as well as labeling of the liberated maleimide and furan moieties with appropriate chromophores featuring complementary functional groups. Similar results were obtained by sonicating analogous polymers that were grown from a thermally robust [4 + 2] cycloaddition adduct of maleimide with anthracene. The generation of anthracenyl species from these latter adducts allowed for the rate of the corresponding mechanically activated retro [4 + 2] cycloaddition reaction to be measured. No reduction in the number average molecular weight (M_n) or liberation of the maleimide, furan, or anthracene moieties was observed (i) for polymers containing the cycloaddition adducts with M_n < 20 kDa, (ii) for high molecular weight PMAs (M_n > 60 kDa) featuring terminal cycloaddition adducts, or (iii) when the cycloaddition adducts were not covalently linked to a high molecular weight PMA. Collectively, these results support the notion that the aforementioned retro [4 + 2] cycloaddition processes were derived from a vectorially opposed mechanical force applied to adducts embedded within the polymer chains.

INTRODUCTION

Ultrasound has recently been demonstrated as a powerful technique for directing bond dissociation[1] and isomerization[2] reactions through high energy pathways. For example, Moore has shown that sonicating solutions of benzocyclobutenes appropriately outfitted with polymer chains facilitates thermally and photochemically disallowed electrocyclic ring-opening reactions.[2a] In these enabling processes, the ultrasound induces the formation and growth of microbubbles, which later collapse. The dissolved polymer segments closest to these collapsing bubbles move at higher velocities than those that are more distal, causing the polymer chain to elongate.[3] For polymers of sufficiently high molecular weight, the tension formed can selectively activate certain chemical processes, often at centrally located sites where the force is maximized. Ultimately, this process translates mechanical force into unique chemical reactivity.[1,2,4] Despite the extreme temperatures and pressures that may form in solutions under sonication, extensive control experiments have supported the notion that the aforementioned activation processes are derived from mechanical force.[5]

Although ultrasound has been used to facilitate other pericyclic rearrangements, including spiropyran-to-merocyanine isomerizations[2b] and dihalocyclopropane ring-openings,[2c,e] we report herein the first use of mechanical force to facilitate retro [4 + 2] reactions.[6] Beyond establishing new tools for controlling molecular processes with high activation barriers and fundamentally new reactivities, mechanical methods for forming reactive cycloaddition partners are expected to find applications in self-healing materials that use the physical processes associated with the formation of damage to initiate essential repair processes.[7]

Diels and Alder disclosed the first cycloaddition reaction in 1928,[8] modifications of which have subsequently found extraordinary utility in synthetic organic chemistry for the formation of carbo- and heterocycles.[9] Many cycloaddition reactions are reversible when heated, a feature that has been used to generate reactive species in situ.[10] However, such retro cycloadditions, especially those which involve carbocycles, typically require elevated temperatures. While the applied heat often results in undesired side reactions, frequently to the detriment of the desired reactivity,[11] Barner-Kowollik has elegantly demonstrated[12] that the activation temperature may be finely tuned through structural modifications. We envisioned overcoming prohibitively high thermal barriers associated with retro cycloadditions using mechanical force. Our hypothesis was that the application of ultrasound-induced tensile stress to polymer chains properly attached to a cycloaddition adduct should destabilize the ground state of the system or lower the activation barrier, facilitating the entropy-driven cycloreversion process at relatively low temperatures. To test our hypothesis, a variety of retro [4 + 2] cycloaddition reactions involving derivatives of two dienes (furan and anthracene) and a common dienophile (maleimide) were investigated.

RESULTS AND DISCUSSION

Initial efforts were directed toward polymerizing methyl acrylate (MA) from the known[13] oxanorbornene-based, difunctional initiator **DA1**[14] using Cu-mediated single-electron-transfer living

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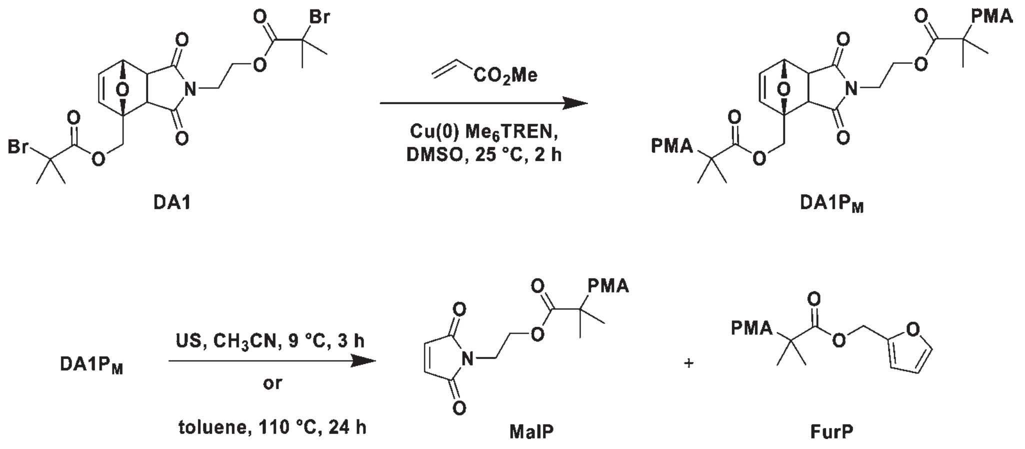
Scheme 1. Synthesis and Selective Dissociation of $DA1P_M$[a]



[a] PMA = poly(methyl acrylate). US = ultrasound.

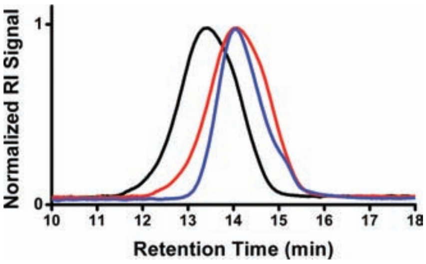


Figure 1. GPC traces of $\mathbf{DA1P_{70}}$ before (black) and after sonication (blue) or reflux (red).

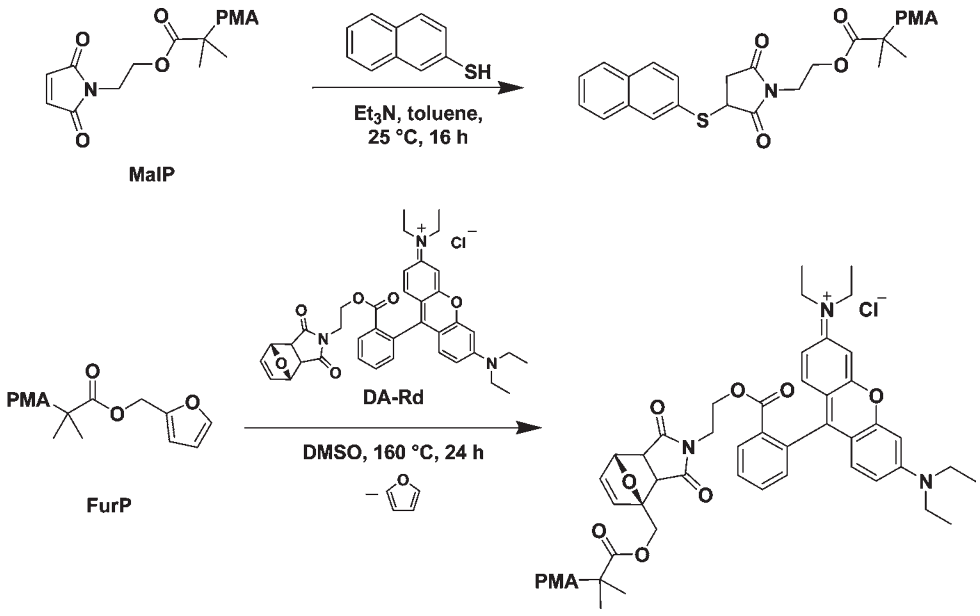
radical polymerization (SET LRP),[15] as shown in Scheme 1. Using an initial monomer to initiator ratio of ca. 800:1, a polymer ($\mathbf{DA1P_{70}}$) with a number average molecular weight (M_n) of 69 kDa and a polydispersity index (PDI) of 1.3, as determined by gel permeation chromatography (GPC), was obtained in 99% yield after 2 h at 25 °C. After further characterization by UV–vis spectroscopy (see below), $\mathbf{DA1P_{70}}$ was dissolved in CH_3CN ($[\mathbf{DA1P_{70}}]_0$ = 10 mg mL^{-1}), transferred to a Suslick cell, and subjected to sonication for 3 h in an ice bath.[16] The volatiles were then removed under reduced pressure, and the residual polymeric material was washed with methanol and characterized by GPC. The M_n of the polymer obtained after sonication decreased to 37 kDa with only a slight increase in polydispersity (PDI = 1.4), a result consistent with cleavage of the polymer near its midpoint (Figure 1).

It has recently been demonstrated that poly(methyl methacrylate) (PMMA) analogues of $\mathbf{DA1P_{70}}$ undergo dissociation via retro [4 + 2] cycloaddition at elevated temperatures.[13] Hence, a preliminary experiment was designed to gauge whether the reduction in molecular weight observed in the ultrasound experiment described above was consistent with a thermally activated retro [4 + 2] cycloaddition process. To test, a toluene solution of $\mathbf{DA1P_{70}}$ ($[\mathbf{DA1P_{70}}]_0$ = 10 mg mL^{-1}) was heated to 110 °C for 24 h. The solvent was then removed under reduced pressure, and the resulting material was determined by GPC to exhibit an M_n = 35 kDa and a PDI = 1.5, similar to the postsonicated polymer described above (Figure 1, red line).

To gain further insight into whether the products of the observed ultrasound-induced chain scission process were due to a mechanically facilitated retro [4 + 2] cycloaddition reaction, we reasoned that the expected furan and maleimide moieties presumably liberated upon sonication of $\mathbf{DA1P_{70}}$ could be selectively labeled with diagnostic chromophores possessing complementary functionality. Considering that thiols have been successfully coupled to maleimides via Michael addition[17] and that naphthalene has a unique UV–vis signature,[18] 2-naphthalenethiol was chosen as an appropriate coupling partner for any maleimides generated upon the cleavage of $\mathbf{DA1P_{70}}$.[19] To test our supposition, the polymer isolated after the sonication of $\mathbf{DA1P_{70}}$ was divided into two fractions.[16] The first fraction was analyzed by GPC equipped with a UV detector set to measure the amount of light absorbed at 285 nm (a λ_{abs} of naphthalene), and the second fraction was treated with excess 2-naphthalenethiol (21 equiv relative to oxanorbornene moiety in $\mathbf{DA1P_{70}}$) as well as triethylamine (5 equiv relative to oxanorbornene moiety) in toluene at 25 °C for 16 h (Scheme 2). The treated polymer (Figure 2 left, blue line), which was isolated by precipitation from methanol, exhibited a significantly increased absorbance at 285 nm, as compared to the untreated polymer (black line). Similar increases in absorbance were observed when the UV–vis spectra of the aforementioned polymers were recorded over a broad range of wavelengths. Likewise, the full absorption spectrum of the polymer treated with 2-napthalenethiol (Figure 2 right, blue line) exhibited new signals at λ_{abs} = 285 and 250 nm, consistent with the attachment of a naphthalene moiety; these signals were not observed in the spectrum of the untreated polymer (black).

A series of control experiments was performed to gain additional support for the notion that 2-napthalenethiol selectively reacted with a maleimide moiety generated under ultrasound in the aforementioned reaction. First, a mixture of $\mathbf{DA1P_{70}}$, 2-naphthalenethiol, and triethylamine (in identical ratios as described above) was stirred in toluene for 16 h at 25 °C to rule out nonspecific physisorption. The material isolated at the conclusion of this experiment exhibited a UV–vis spectrum that was identical to that of pretreated $\mathbf{DA1P_{70}}$ (Figure S15). Second, to determine if the thermally facilitated dissociation of $\mathbf{DA1P_{70}}$ would afford products that exhibited reactivity similar to those obtained from the analogous sonication experiment, $\mathbf{DA1P_{70}}$ was refluxed in toluene at 110 °C for 24 h, and the resulting reaction mixture was divided into two fractions. The first fraction was characterized directly by GPC, whereas the second fraction was reacted with 2-naphthalenethiol and

Scheme 2. Selective Labeling of Maleimide and Furan Moieties Generated upon the Dissociation of $\mathbf{DA1P_M}$[a]



[a] **MalP** and **FurP** were generated from $\mathbf{DA1P_M}$; see text. PMA = poly(methyl acrylate).

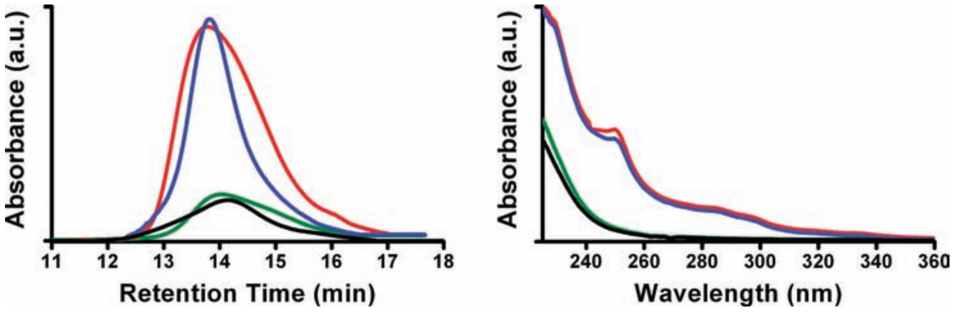


Figure 2. GPC traces as visualized using UV detection at 285 nm (left) and the full UV−vis spectra (right) of $\mathbf{DA1P_{70}}$ after sonochemical (blue) or thermal (red) activation followed by treatment with 2-naphthalenethiol (see text for details). For comparison, the GPC traces and absorption spectra of the polymers obtained after sonochemical (black) or thermal (green) activation of $\mathbf{DA1P_{70}}$ (but not treated with 2-napthalenethiol) are also shown. All spectra were acquired at an initial polymer concentration of 11 mg mL^{-1} in THF.

triethylamine as described above. The treated fraction exhibited an increased absorbance at 285 nm when analyzed by GPC equipped with a UV detector (red line, Figure 2, left). This spectroscopic result was similar to that observed for the material obtained from the sonication of $\mathbf{DA1P_{70}}$ and subsequently treated with 2-naphthalenethiol (blue line). In contrast, the fraction that was only refluxed in toluene (i.e., not treated with 2-naphthalenethiol) exhibited an absorption profile similar to that of pretreated $\mathbf{DA1P_{70}}$ (green line). Further analysis by UV−vis spectroscopy (Figure 2, right) revealed the formation of new signals at λ = 285 and 250 nm for the treated polymer (red line), as compared to its starting material (green line). Collectively, these results were consistent with the selective reaction between 2-naphthalenethiol and a maleimide moiety generated from $\mathbf{DA1P_{70}}$ during the aforementioned sonication experiment.

As a complement to the maleimide labeling experiments described above, efforts were also directed toward labeling the liberated furans with a chromophore possessing a complementary functionality. A broad range of dienes, including those appended to polymer chains,[13] have been shown to react with rhodamine-B-functionalized maleimides to afford products that strongly absorb at 550 nm (a $\lambda_{\max}$ of rhodamine-B).[20] We hypothesized that if the sonication of a solution of $\mathbf{DA1P_{70}}$ resulted in the liberation of a furan moiety, subsequent reaction of the reactive species with **DA-Rd**, an oxanorbornene compound known to liberate a maleimide-functionalized rhodamine-B at elevated temperatures,[13] would result in an identifiable product (Scheme 2).[21] To test our supposition, $\mathbf{DA1P_{70}}$ was subjected to sonication as previously described and then poured into excess methanol to facilitate the precipitation and isolation of the product.[16] To confirm that dissociation had occurred, the postsonicated material was analyzed by GPC and found to exhibit a reduced molecular weight (36 kDa, PDI = 1.4) as compared to its starting material. The residual material was then divided into two fractions. The first fraction was analyzed using a gel permeation chromatograph equipped with a UV−vis detector, whereas the second fraction was dissolved in DMSO ($[\text{polymer}]_0$ = 25 mg mL^{-1}), heated at 160 °C in the presence of **DA-Rd** (10 equiv relative to oxanorbornene moiety in **DA1P$_{70}$**) for 24 h, and then isolated by precipitation into methanol to remove any unbound rhodamine-B species.[22] Subsequent GPC analysis using UV detection at 550 nm revealed a significant increase in the absorbance exhibited by the fraction treated with **DA-Rd** (Figure 3, blue line), consistent with the cycloaddition of a rhodamine-B-functionalized maleimide to the polymer bound furan. In contrast, no change in absorbance was observed for the untreated fraction of **DA1P$_{70}$** obtained after sonication (black line), as compared to its starting material.

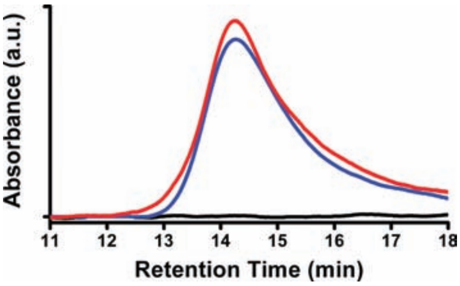


Figure 3. GPC traces visualized by UV detection at 550 nm of **DA1P$_{70}$** after sonication (black). Upon treatment of the sonicated polymer with **DA-Rd**, the absorbance measured at 550 nm increased (blue), consistent with the reaction of a polymer bound furan with the rhodamine-B tagged maleimide.[21] Refluxing **DA1P$_{70}$** with **DA-Rd** resulted in a comparable absorbance increase at 550 nm (red). All spectra were acquired at an initial polymer concentration of 11 mg mL^{-1} in THF.

Table 1. Selected Molecular Weight Data[a]

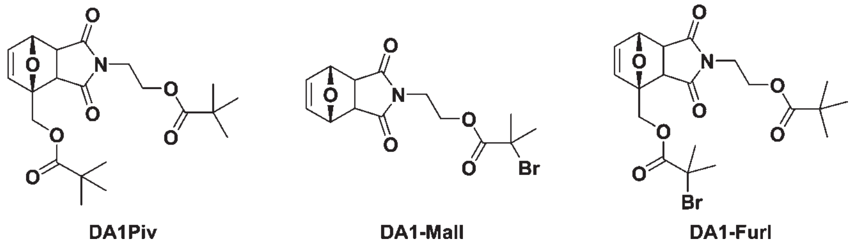
	presonication		postsonication[b]		postreflux[c]	
polymer	M_n [kDa][d]	PDI[e]	M_n [kDa][d]	PDI[e]	M_n [kDa][d]	PDI[e]
DA1P$_{70}$	69	1.3	37	1.4	35	1.5
DA1P$_{60}$	60	1.3	33	1.4	34	1.5
DA1P$_{50}$	50	1.3	30	1.5	29	1.6
DA1P$_{40}$	41	1.2	40	1.2	22	1.4
DA1P$_{30}$	30	1.2	31	1.3	17	1.4
DA1P$_{20}$	19	1.3	19	1.3	8.9	1.4

[a] Nomenclature: **DA1** refers to the [4 + 2] cycloaddition adduct between furan and maleimide, and the M in **P$_M$** corresponds to the polymer's approximate number average molecular weight (M_n) in kDa. [b] The polymer was dissolved in CH_3CN (10 mg mL^{-1}) and subjected to sonication for 3 h (see ref 16). [c] The polymer was dissolved in toluene (10 mg mL^{-1}) and refluxed for 24 h (110 °C). [d] M_n refers to the number average molecular weight of the polymer analyzed. [e] The polydispersity index (PDI) was calculated using the equation PDI = M_w/M_n, where M_w is the weight average molecular weight. M_n and M_w were determined as their polystyrene equivalents by GPC (eluent = THF).

To confirm that the labeling process was due to the reaction of **DA-Rd** with a liberated furan moiety, **DA1P$_{70}$** was refluxed in the presence of **DA-Rd** (in ratios identical to those described above) in DMSO for 24 h (160 °C) and then isolated by collecting the solids that precipitated upon pouring the reaction mixture into excess methanol. Analysis of the thermally activated polymer by GPC using UV detection at 550 nm (Figure 3, red line) revealed an increased absorbance that was comparable to the signal observed for the polymer obtained after sonicating **DA1P$_{70}$** and treatment with **DA-Rd**. Collectively, these results suggested to us that the aforementioned sonication experiment successfully facilitated the dissociation of **DA1P$_{70}$** via a retro [4 + 2] cycloaddition process which liberated a reactive furan moiety.

It has been previously demonstrated that sonochemically induced transformations are dependent on the length of the polymer chains used to facilitate the respective mechanochemical processes.[1,2] Thus, to gain additional support for the notion that the aforementioned retro [4 + 2] cycloaddition reactions were facilitated by mechanical force, a series of PMA chains of various molecular weights (**DA1P$_M$**) were synthesized by SET LRP from **DA1** by varying the monomer to initiator ratios. After these materials were characterized by GPC, they were individually subjected to sonication in CH_3CN,[16] as described above, and then reanalyzed by GPC; the results are summarized in Table 1. While polymers with M_n > 40 kDa resulted in reductions in molecular weight similar to that observed for **DA1P$_{70}$**, the sonication of the polymers with M_n < 40 kDa resulted in no significant change in the M_n (Figure S3). Similarly, the **DA1P$_M$** polymers were also individually refluxed for 24 h in toluene and then analyzed by GPC. A reduction in the M_n was observed for each of the thermally activated polymers, although the measured PDIs were consistently higher than the polymers obtained postsonication (see Table 1 and Scheme 1).[23]

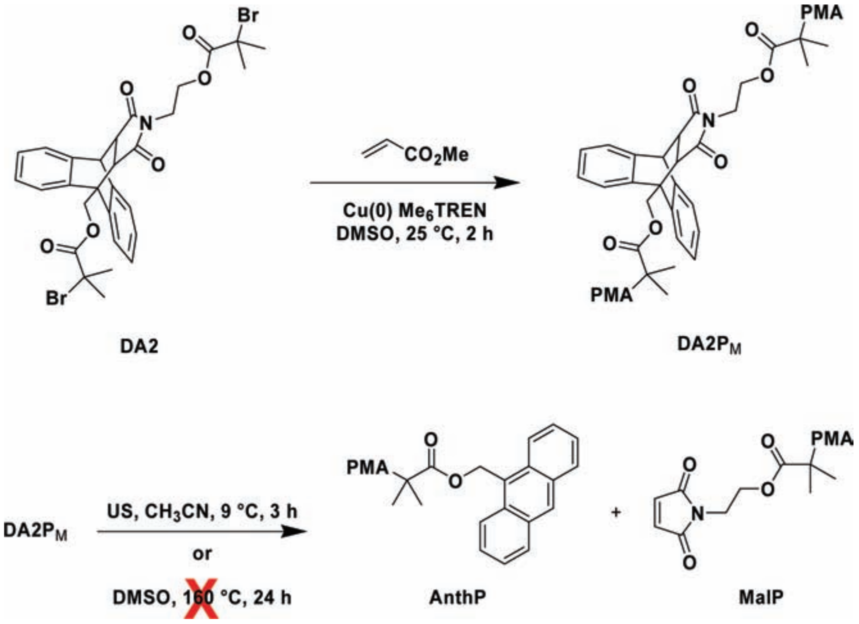
As an additional control, a small molecule analogue of **DA1P$_M$**, which featured pivalate end groups in lieu of polymer chains, **DA1Piv**, was synthesized and studied (Figure 4).[14] Refluxing **DA1Piv** in toluene at 110 °C for 24 h resulted in a product that exhibited ^{1}H NMR signals at δ = 6.70 ppm as well as at 6.29 and 6.27 ppm ($CDCl_3$), which were assigned to the maleimide and furan components expected for the retro cycloaddition of this adduct, respectively (Figure S9, top).[13] In contrast, ^{1}H NMR spectroscopic analysis of the crude product mixture obtained after subjecting **DA1Piv** to the aforementioned sonication conditions[16] revealed no decomposition products (Figure S9, bottom). As no activation was observed for the small molecule **DA1Piv** and the relatively short polymer chains (M_n < 40 kDa) under sonication, we concluded that the attachment of high molecular weight polymers to the [4 + 2] cycloaddition adduct of maleimide with furan was necessary to mechanically facilitate its dissociation.



DA1Piv **DA1-MalI** **DA1-FurI**

Figure 4. Structures of the small molecule control **DA1Piv** and the initiators **DA1-MalI** and **DA1-FurI**.[14]

Scheme 3. Synthesis and Selective Dissociation of $DA2P_M$[a]



[a] PMA = poly(methyl acrylate). US = ultrasound.

Considering that the mechanical force applied to a polymer chain under sonication is believed to be maximized near its midpoint,[1,2] further evidence for a mechanically facilitated process was obtained by studying two relevant, semitelechelic polymers: one where the terminus of the polymer chain was attached to the maleimide and another where the terminus was attached to the furan component of the respective cycloaddition adduct. The first end-functionalized polymer **DA1-MalP$_{78}$** (M_n = 78 kDa; PDI = 1.2) was prepared by polymerizing MA using SET LRP from the cycloaddition adduct of an initiator-functionalized maleimide with furan (**DA1-MalI**)[14] (Figure 4). After **DA1-MalP$_{78}$** was sonicated in CH_3CN (10 mg mL^{-1}) as described above,[16] the resulting product showed minimal change in molecular weight (M_n = 75 kDa) and no change in PDI as compared to its starting material (Figure S6, left). The sonicated polymer was also subjected to the 2-napthalenethiol labeling experiment previously described for **DA1P$_{70}$**, and GPC as well as UV−vis spectroscopy of the isolated products did not show the presence of a naphthalene moiety coupled to the polymer (Figure S16). In contrast, when **DA1-MalP$_{78}$** was refluxed in toluene and then treated with 2-napthalenethiol, a naphthalene moiety was observed by UV−vis spectroscopy (Figure S16). A second oxanorbornene end-functionalized polymer **DA1-FurP$_{60}$** (M_n = 60 kDa; PDI = 1.2) was prepared by polymerizing MA using SET LRP from the cycloaddition product of maleimide and an initiator-functionalized furan (**DA1-FurI**).[14] Sonication of **DA1-FurP$_{60}$** resulted in a polymer that exhibited a M_n = 59 kDa and a slightly increased polydispersity (PDI = 1.3) as compared to its starting material (Figure S6, right).[16] Collectively, these results suggested to us that the cycloaddition adduct must be embedded within the polymer chain to experience the force necessary for ultrasound-induced mechanical activation.

While the results described above supported our hypothesis that mechanical activation facilitated a retro [4 + 2] cycloaddition process in the **DA1P$_M$** polymers, we desired a system that would produce an observable signal upon cycloreversion to further confirm the observed reactivity. Our emphasis focused on systems based on anthracene, which absorbs light at three wavelengths between 340 and 400 nm, a unique spectroscopic signature that facilitates its identification.[24] Moreover, the cycloaddition adducts of maleimide with anthracene are known and readily accessible.[25] Hence, we selected a polymer-functionalized adduct between these two species that was expected to generate a distinct, quantifiable signal upon cycloreversion.

SET LRP was used to grow PMA chains from the known[13] difunctional initiator **DA2** (see Scheme 3). By varying the initial monomer to initiator ratio, polymers with a range of different molecular weights, M_n = 13−71 kDa, and narrow PDIs (1.2 − 1.3) were prepared and characterized by GPC (see Scheme 2 and Table 2). Sonication of **DA2P$_{70}$**,[16] the highest molecular weight polymer synthesized, resulted in a material with a reduced molecular weight as compared to its starting material (from M_n = 71 to 34 kDa), as determined by GPC. Analysis of the postsonicated material by UV−vis spectroscopy revealed absorbances characteristic of anthracene at λ = 387, 366, and 348 nm (Figure 5, right).[21] The concomitant reduction in molecular weight and appearance of new UV absorbances suggested to us that the dissociation of the anthracene/maleimide adduct proceeded through a process that was consistent with a retro [4 + 2] cycloaddition process.

It was recently discovered that polymers obtained by growing poly(methyl methacrylate) from **DA2** were thermally robust: refluxing these materials in DMSO for 24 h resulted in <20% dissociation.[13] Similarly, our attempt to facilitate the retro [4 + 2] cycloaddition of **DA2P$_{70}$** by refluxing in DMSO for 24 h (160 °C) was unsuccessful as the product isolated from this experiment was unchanged as compared to the starting material, as determined by GPC (M_n = 71 kDa). In addition, the UV−vis spectra of the isolated polymers did not exhibit any signals that could be assigned to an anthracenyl moiety (Scheme 3 and Figure 5). In light of the results obtained from the sonication experiments described above, where **DA2P$_{70}$**

underwent dissociation under ultrasound, we concluded that mechanical stress may be used to overcome the prohibitively high thermal barriers associated with certain retro [4 + 2] cycloaddition reactions.[26]

To determine if a maleimide moiety was also generated during the mechanically facilitated retro [4 + 2] cycloaddition process, postsonicated **DA2P$_{70}$** was treated with 2-naphthalenethiol, as described above for **DA2P$_{M}$**. Analysis of the treated polymers using a gel permeation chromatograph equipped with a UV detector showed an increase in the absorbance at 285 nm (Figure S14C), similar to that observed for the **DA1P$_{70}$** polymer that was sonicated and subsequently treated with 2-naphthalenethiol.[27] Nonspecific physisorption and other side reactions were ruled out by treating and then analyzing (presonicated) **DA2P$_{70}$** with 2-naphthalenethiol and triethylamine in toluene at 25 °C for 24 h (Figure S15). The successful labeling of the mechanically dissociated polymer with a naphthalene moiety was consistent with the generation of a maleimide bound polymer upon exposure of **DA2P$_{M}$** to ultrasound.

To further support that an ultrasound-induced mechanically facilitated retro [4 + 2] cycloaddition process was occurring in the aforementioned sonication experiments, three additional **DA2P$_{M}$** polymers of varying molecular weights (Table 2) were individually sonicated,[16] and the products of these experiments were analyzed by GPC as well as UV−vis spectroscopy.[1,2,4] Analysis of the postsonicated **DA2P$_{45}$** and **DA2P$_{30}$** revealed that the starting materials underwent a reduction in molecular weight by GPC and afforded products that exhibited signals attributable to the presence of an anthracenyl moiety by UV−vis spectroscopy (Figure S21). In contrast, the shorter **DA2P$_{13}$** did not exhibit a change in molecular weight upon being subjected to sonication, and these polymers exhibited UV absorption profiles that were similar to their starting material. Moreover, the product obtained after sonicating a small molecule analogue featuring pivalate groups in lieu of polymer chains, **DA2Piv** (Figure 6), exhibited a UV absorbance spectrum and ^{1}H NMR signals similar to those of its starting material (Figure S11).[16] Collectively, these results suggested to us that polymer chains of sufficient molecular weight are necessary for the polymer prepared from **DA2** to experience sufficient force to undergo activation under ultrasound (Table 2).

Table 2. Selected Molecular Weight Data[a]

	presonication		postsonication[b]		
polymer	M_n [kDa][c]	polymer	M_n [kDa][c]	PDI[d]	
DA2P$_{70}$	71	1.3	34	1.4	
DA2P$_{45}$	44	1.2	18	1.3	
DA2P$_{30}$	31	1.2	14	1.3	
DA2P$_{13}$	13	1.2	13	1.4	

[a] Nomenclature: **DA2** refers to the [4 + 2] cycloaddition adduct between anthracene and maleimide, and the M in **P$_{M}$** corresponds to the approximate number average molecular weight (M_n) in kDa. [b] The polymer was dissolved in CH_3CN (10 mg mL^{-1}) and subjected to sonication for 3 h (see ref 16). [c] M_n refers to the number average molecular weight of the polymer analyzed. [d] The polydispersity index (PDI) was calculated using the equation PDI = M_w/M_n, where M_w is the weight average molecular weight. M_n and M_w were determined as their polystyrene equivalents by GPC (eluent = THF).

Further evidence of mechanical activation was obtained from the synthesis and study of two semitelechelic polymers: in one example, one end-group of a PMA was attached to an anthracenyl moiety; in the second example, one end-group of the PMA was attached to a maleimide moiety (Figure 6). **DA2-AnthP$_{65}$** (M_n = 65 kDa, PDI = 1.2) was prepared by growing PMA from the [4 + 2] cycloaddition product of 9-anthrylmethyl-2-bromo-2-methyl propionate and *N*-propyl maleimide (**DA2-AnthI**). Sonication[16] of **DA2-AnthP$_{65}$** resulted in minimal change in molecular weight and polydispersity (M_n = 64 kDa; PDI = 1.3) as compared to the starting material (Figure S7, right). Furthermore, the UV−vis absorption profile of the material obtained postsonication was similar to that exhibited by the presonicated **DA2-AnthP$_{65}$** (Figure S8).[28] A second, end-functionalized polymer **DA2-MalP$_{70}$** (M_n = 69 kDa, PDI = 1.3) was prepared by growing chains of PMA from the respective cycloaddition adduct of a maleimide functionalized with a polymerization initiator and anthracene (**DA2-MalI**). Sonication[16] of **DA2-MalP$_{70}$** resulted in a material that exhibited a minimal change in molecular weight and polydispersity (M_n = 67 kDa; PDI = 1.3) when compared to its starting material, as determined by GPC (Figure S7, left). To determine if the sonication of **DA2-MalP$_{70}$** generated a

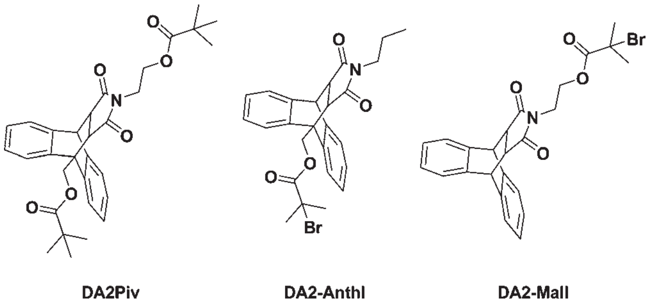


Figure 6. Structures of the small molecule control **DA2Piv** and the initiators **DA2-AnthI** and **DA2-MalI**.

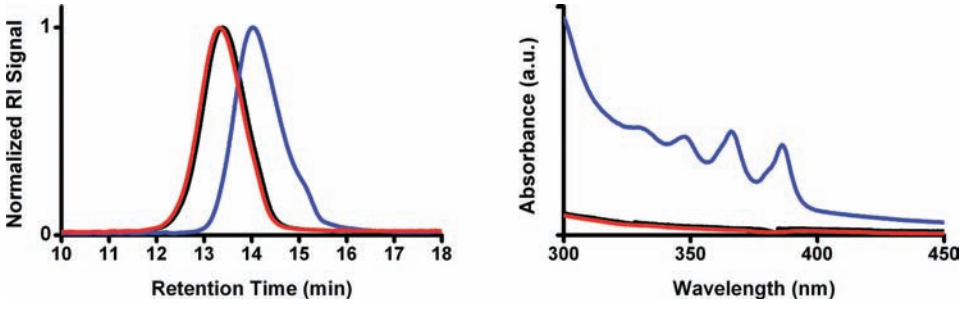


Figure 5. GPC traces (left) and the UV−vis spectra (right) of **DA2P$_{70}$** before (black) and after sonication (blue) and refluxing in DMSO (red). The UV−vis spectra were acquired at a polymer concentration of 11 mg mL^{-1} in THF.

maleimide moiety, the postsonicated material was treated with 2-napthalenethiol using the conditions described above. Analysis of the treated polymer by UV−vis spectroscopy revealed an absorbance profile similar to that of the starting material (Figure S17). Collectively, these results suggested to us that the cycloaddition adduct of anthracene with maleimide must be embedded near the midpoint of a high molecular weight polymer chain to experience the force necessary for activation.

Because the retro [4 + 2] cycloaddition of the $\mathbf{DA2P_M}$ polymers resulted in a quantifiable UV−vis signal, the rates of the aforementioned mechanically facilitated retro [4 + 2] cycloaddition reactions were measured. Assuming that the $\mathbf{DA2P_M}$ polymers undergo irreversible cleavage under the sonochemical conditions employed, the corresponding dissociation process may be described using eq 1:

$$\mathbf{DA2P} \rightarrow \mathbf{AnthP} + \mathbf{MalP} \tag{1}$$

where **DA2P** is the starting material and **AnthP** is the observable product obtained upon mechanically induced cleavage. Thus, the dissociation reaction should follow first-order kinetics with the rate given by eq 2:

$$\ln([\mathbf{DA2P}]_o) = kt - \ln([\mathbf{DA2P}]_o - [\mathbf{AnthP}]) \tag{2}$$

where $[\mathbf{DA2P}]_o$ is the initial concentration of the anthracene maleimide adduct.[29] To measure the rate of the dissociation reaction, the increase in the concentration of **AnthP** was monitored over time.[30] Aliquots were removed periodically during individual sonication experiments involving $\mathbf{DA2P_M}$ and analyzed at 366 nm (a λ_{abs} of anthracene) using a gel permeation chromatograph equipped with a UV detector. A smooth increase in the intensity of the absorbance of the polymers was observed throughout the sonication experiment for $\mathbf{DA2P_M}$, where $M_n > 30$ kDa (see Figure 7 for $M = 70$). Plotting the natural log of $[\mathbf{DA2P}]_o/([\mathbf{DA2P}]_o - [\mathbf{AnthP}])$ for each aliquot collected over time enabled the determination of the dissociation rates for various $\mathbf{DA2P_M}$ studied (Figure 8, left; see Figure S4 for GPC traces of the other $\mathbf{DA2P_M}$ polymers studied).

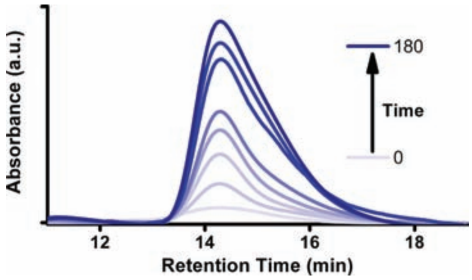


Figure 7. GPC traces visualized with UV detection at 366 nm of $\mathbf{DA2P_{70}}$ (20 mg mL^{-1}) during sonication, where $t = 0$ (light blue) to 180 min (dark blue) exhibited an increase in the absorbance of the polymer at 366 nm, consistent with the generation of an anthracenyl end group.

For the highest molecular weight analyzed, $\mathbf{DA2P_{70}}$, the rate constant of adduct dissociation was determined to be $5.2 \pm 0.1 \times 10^{-3}$ min^{-1}; lower rate constants were measured for $\mathbf{DA2P_{45}}$ ($3.8 \pm 0.1 \times 10^{-3}$ min^{-1}) and $\mathbf{DA2P_{30}}$ ($2.2 \pm 0.1 \times 10^{-3}$ min^{-1}), as expected.[1,2,4,31] The lowest molecular weight material analyzed, $\mathbf{DA2P_{13}}$, did not exhibit a significant increase in absorbance, a result that was consistent with the aforementioned GPC analyses, indicating that $\mathbf{DA2P_{13}}$ did not undergo chain dissociation under ultrasound. Overall, the rate constants measured inversely correlated with the polymers' molecular weight, and polymers below 30 kDa did not undergo activation (Figure 8, right). Collectively, these kinetic data further confirmed that the observed retro [4 + 2] cycloaddition was facilitated by mechanical force.[1,2]

Finally, to explore the potential of the aforementioned polymers in self-healing applications, the postsonicated $\mathbf{DA1P_M}$ and $\mathbf{DA2P_M}$ materials were heated under concentrated conditions to ascertain the abilities of the dissociated products to recouple with each other. Previous studies have shown that heating poly(methyl methacrylate)s containing furyl or anthracenyl end groups with polymeric analogues containing complementary maleimide end groups at 60 °C in the bulk resulted in materials that exhibited relatively high molecular weights. The corresponding processes were attributed to a forward cycloaddition reaction involving the end groups of the aforementioned polymers.[13]

To determine if the postsonicated materials described above exhibited similar behavior, the $\mathbf{DA1P_M}$ polymers, where $M_n >$ 40 kDa, and the $\mathbf{DA2P_M}$ polymers, where $M_n > 30$ kDa, were individually subjected to the aforementioned sonication conditions to effect chain scission.[16] The resulting products were characterized by GPC to confirm that the products of these reactions displayed a reduced molecular weight as compared to their starting materials. Following concentration, the products were heated in the bulk at 60 °C for 48 h and then analyzed by GPC (as well as UV−vis spectroscopy for $\mathbf{DA2P_M}$). As shown in Figure 9 and enumerated in Table 3, the postsonicated $\mathbf{DA1P_{70}}$ and $\mathbf{DA2P_{70}}$ products showed an increase in molecular weight

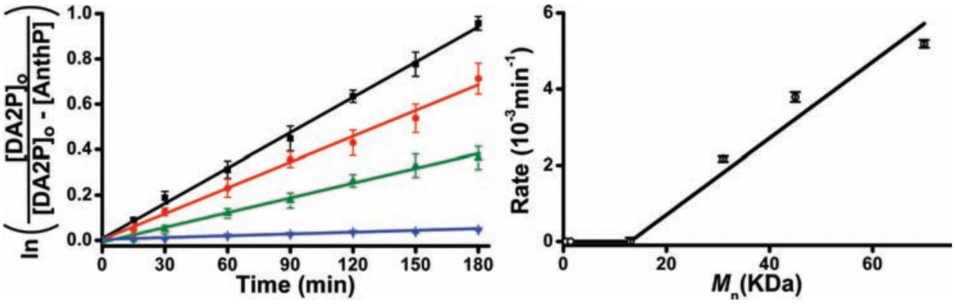


Figure 8. (left) First-order rate plots for $\mathbf{DA2P_{70}}$ (black), $\mathbf{DA2P_{45}}$ (red), $\mathbf{DA2P_{30}}$ (green), and $\mathbf{DA2P_{13}}$ (blue). (The corresponding GPC traces may be found in Figure S4.) $[\mathbf{DA2P}]_0$ refers to the initial concentration of the cycloaddition adduct in the $\mathbf{DA2P_M}$ polymer; $[\mathbf{AnthP}]$ refers to the concentration of an anthracenyl species that was liberated after sonication at the time indicated on the x axis. (right) Plot of the rate coefficients of various mechanically facilitated retro [4 + 2] cycloaddition reactions as a function of M_n. All data points and error bars were calculated from the average and standard deviation of three separate experiments.

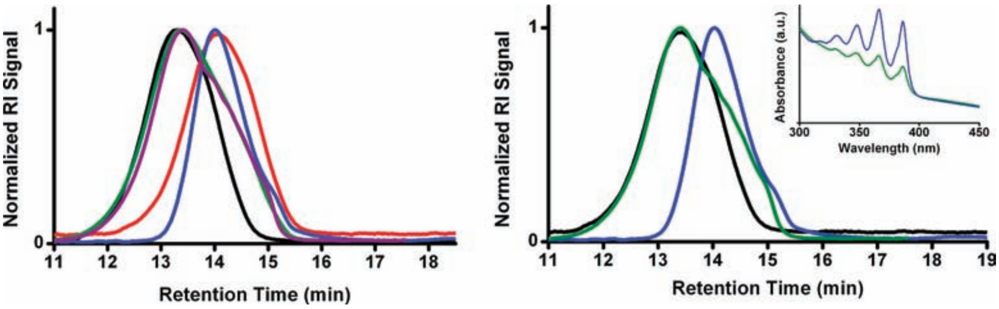


Figure 9. Overlaid GPC traces of (black) **DA1P$_{70}$** (left) and **DA2P$_{70}$** (right) polymers and traces of the same materials after sonochemical (blue) and thermal (red) activation (see text). Chain coupling was observed after heating the sonochemically (green) and thermally activated (purple) polymers in the bulk. The inset (right) shows the disappearing UV−vis absorbances of the anthracenyl species after the sonochemically activated polymer (blue) was heated in the bulk to effect chain coupling (green). The UV−vis spectra were acquired in THF at a polymer concentration of 11 mg mL^{-1} in THF.

Table 3. Selected Molecular Weight Data for Various Coupling Experiments[a]

	postsonication[a]		postcoupling[b]	
polymer	M_n [kDa][c]	PDI[d]	M_n [kDa][c]	PDI[d]
DA1P$_{70}$	37	1.4	55	1.7
DA1P$_{60}$	33	1.4	40	2.0
DA1P$_{50}$	30	1.5	38	1.6
DA2P$_{70}$	34	1.4	57	1.5
DA2P$_{45}$	18	1.3	34	1.8
DA2P$_{30}$	14	1.3	25	1.9

[a] The corresponding starting materials were dissolved in CH_3CN (10 mg mL^{-1}) and subjected to sonication for 3 h (see ref 16). [b] The corresponding postsonicated materials were heated in the bulk at 60 °C for 48 h. [c] M_n refers to the number average molecular weight of the polymer. [d] The polydispersity index (PDI) was calculated using the equation PDI = M_w/M_n, where M_w is the weight average molecular weight. The M_n and M_w were determined as their polystyrene equivalents by GPC (eluent = THF).

after being heated in the bulk (see Figures S19−S21 for the GPC traces of the other **DA1P$_M$** and **DA2P$_M$** polymers studied). Additional support for chain coupling was obtained from the UV−vis analysis of the **DA2P$_M$** originated polymers, which revealed a decrease in the intensity of the absorbances assigned to an anthracenyl species after coupling (Figure 9, inset). The ability of these materials to recombine after mechanical activation underscores the potential for their use in the aforementioned applications.[7,32]

CONCLUSION

We have shown that mechanical force may be used to facilitate retro [4 + 2] cycloaddition reactions. The formation of the expected dienes (furan or anthracene) and dienophile (maleimide) coupling partners was confirmed chemically as well as spectroscopically. For both types of adducts, the maleimide species liberated upon cycloreversion were selectively labeled with a functionalized naphthalene moiety. The corresponding furans liberated upon sonication of the **DA1P$_M$** polymers were identified through labeling experiments involving a rhodamine-B functionalized with a complementary maleimide, and the appearance of an anthracenyl species upon the sonication of the **DA2P$_M$** was confirmed by UV−vis spectroscopy. Comprehensive control experiments performed on a series of small molecule analogues, derivatives below the molecular weight threshold required for mechanical activation, as well as appropriately end-functionalized derivatives enabled us to preclude a thermal process. In addition, thermally facilitated chain coupling was observed for the polymers that were successfully cleaved under ultrasound, underscoring the potential for using these materials in self-healing and other stimulus-responsive applications. Collectively, these results establish ultrasound as a powerful method for enabling retro [4 + 2] cycloaddition reactions and that adducts with prohibitive thermal activation barriers may be readily dissociated using mechanical force. In a broader perspective, the results presented herein provide new avenues for engaging complex pericyclic rearrangement reactions and generating reactive species from thermally robust cycloaddition adducts.

ASSOCIATED CONTENT

Supporting Information. Synthetic details and characterization of compounds, tables and figures summarizing control experiments, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) A maleimide-functionalized PMA (**MalP$_{90}$**) was grown via SET LRP from 2-bromo-2-methyl-propionic acid 2-(2,5-dihydro-2,5-dioxo-1*H*-pyrrol-1-yl)ethyl ester (**MalI**), which afforded a 90 kDa polymer (PDI = 1.2). This maleimide end-functionalized polymer was treated with 2-naphthalenethiol (21 equiv relative to maleimide moiety) and triethylamine (5 equiv relative to maleimide moiety) in toluene at 25 °C for 24 h. The resulting product was isolated by precipitation from methanol to remove any unbound naphthalene and analyzed by GPC as well as UV−vis spectroscopy (Figure S13). An increase in absorbance at 285 nm was observed, which was consistent with the attachment of naphthalene to the maleimide end group.

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(21) In addition, a furyl end-functionalized PMA (**FurP$_{70}$**) was grown via SET LRP from 2-furanylmethyl-(2-bromo-isobutyrate) (**FurI**), which resulted in a polymer that exhibited a M_n = 70 kDa (PDI = 1.3). The furyl end-functionalized polymer was refluxed in DMSO (20 mg mL^{-1}) in the presence of **DA-Rd** (10 equiv relative to the furyl species) for 24 h (160 °C). The product of this reaction was isolated by precipitation from methanol to remove any unbound rhodamine-B species and analyzed by GPC with UV−vis detection (Figure S18). The increase in absorbance observed at λ = 550 nm was consistent with the attachment of the rhodamine-B-functionalized maleimide to the furyl end group.

(22) The high temperature was necessary to liberate the furan-functionalized product from the retro [4 + 2] cycloaddition of the rhodamine-B-functionalized oxanorbornene and to promote the forward [4 + 2] cycloaddition with the polymer bound furan.

(23) As further confirmation of these results, the maleimide labeling experiments were performed using the **DA1P$_M$** polymers of varying molecular weights. For the **DA1P$_M$** above the molecular weight threshold necessary for sonochemical activation (M_n > 40 kDa), the resulting polymers exhibited increased absorbances at λ = 285 nm, as determined by GPC with UV−vis detection, and exhibited a UV−vis profile that was consistent with the labeling of an exposed maleimide with 2-napthalenethiol. Polymers below the molecular weight threshold (M_n < 40 kDa) displayed UV−vis spectra similar to those of their respective starting materials (Figure S14). After being refluxed in toluene for 24 h (110 °C), all of the **DA1P$_M$** polymers were successfully labeled with 2-napthalenethiol.

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[4 + 2] cycloadditions may be due to ground-state destabilization of the adduct or lowering of the activation barrier for the cycloreversion process.

(27) As an additional control experiment, **DA2P$_{70}$** was refluxed in DMSO for 24 h (160 °C), and the resulting product was isolated by precipitation from methanol followed by collection via filtration. Subsequent treatment of the isolated material with 2-napthalenethiol showed no increase in the absorbance of the polymer at 285 nm by GPC with UV detection and no change in UV−vis spectra as compared to the starting material, indicating that a maleimide species was not generated (Figure S14C).

(28) Refluxing **DA2-AnthP$_{65}$** in DMSO for 24 h (160 °C) resulted in minimal retro [4 + 2] cycloaddition, as evidenced by the observation of a slight increase in the absorbance of the polymer at 550 nm and the weak absorbances characteristic of anthracene (Figure S8).

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(30) See the Supporting Information for additional details.

(31) All data points and error bars were calculated from the average and standard deviation, respectively, of three separate experiments.

(32) To compare the effects of mechanically induced chain scission versus those that were thermally induced, the **DA1P$_M$** polymers were refluxed in toluene at 110 °C to facilitate the retro [4 + 2] cycloaddition reaction. After it was confirmed that these materials underwent chain cleavage by GPC, the resulting polymers products were heated in the bulk at 60 °C for 48 h. Subsequent characterization by GPC revealed an overall increase in molecular weight that was consistent with chain coupling.