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Rapid Bonding/Debonding on Demand: Reversibly Cross-Linked Functional Polymers via Diels-Alder Chemistry

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Introduction. The design of reversibly linked and crosslinked polymeric materials that are able to change their physical characteristics rapidly, within a well-defined temperature interval and in a cyclic fashion, continues to be a highly investigated area in materials research.^{1,2} Lying at the core of such research is the exploitation of reversible covalent bonds within a polymer network. To date, there has been a wealth of chemistries that have been investigated within this context, such as thiol-driven sulfide coupling,³ photoreversible olefin cycloadditions,⁴ carbene dimerization,⁵ nucleophilic addition of isocyanates with imidazoles,⁶ and thermally cleavable alkoxyamines.⁷ However, the most widely investigated technique by far has been Diels-Alder (DA) chemistry.⁸⁻¹⁴ The use of DA cycloadditions (most specifically those between various maleimide and furan derivatives) in such technology has greatly been facilitated by both the commercial availability and chemical accessibility of such functional groups. To illustrate two very recent examples, low molecular weight star-shaped molecules were prepared by Aumsuwan and Urban¹⁵ in which a maleimide-furan cycloadduct formed the linkage between the arms of the star and its core. From a variable-temperature ¹H NMR and ATR-IR spectroscopic analysis, the forward star-forming DA reaction was determined to proceed at 40 °C. The stars could subsequently be unmade through a 90 °C retro-DA reaction. In the other example, Syrett et al. synthesized maleimide- and furancapped polymers via atom transfer radical polymerization (ATRP) which could be linked (60 °C, 24 h) and unlinked (110 °C, 24 h).¹⁶

We have recently reported a particularly rapid version of hetero-DA chemistry where a highly electron-deficient dithioester undergoes a [4 + 2] cycloaddition with cyclopentadiene (Cp) derivatives quantitatively within a few minutes under ambient conditions.¹⁷ The rapidity of the reaction has since been employed in the facile modular construction of block copolymers^{17,18} and in surface modifications.^{19,20} Although we have already explored the quantitative reversion of such chemistry by thermal treatment,^{21,22} it is with a recent report that we truly investigated its reversibility within the context of color switching in polymeric materials.²³ While the forward reaction is swift, the resulting cycloadducts are temperature stable up to a relatively moderate temperature range (60–90 °C), depending on the dithioester-Cp combination utilized. Beyond this temperature, an effective retro-DA reaction sets in, leading to a quantitative reformation of the starting materials.

A characteristic of DA chemistry that renders it highly attractive in such technologies is the wide variety of diene dienophile pairs that can potentially be utilized, which allows one to fine-tune the temperature profile in which bonding and debonding take place. To date, particularly ultrarapid hetero-DA chemistry has not been reported in the preparation of reversible cross-linked polymeric structures. Thus, we herein report the synthesis of a novel poly(methyl methacrylate) (PMMA) chain bearing Cp functionality at both chain ends and a trifunctional pyridinyldithioformate linker molecule (see Scheme 1), which are able to rapidly and reversibly cross-link on demand within a highly accessible temperature range.

Experimental Part. Materials. The ATRP initiator 1,2bis(bromoisobutyryloxy)ethane was synthesized according to the literature.²⁵ Methyl methacrylate (MMA, Acros) was passed through a short column of basic alumina and stored at -19 °C prior to use. Copper(I) bromide (Fluka) was purified by sequential washing with sulfurous acid, acetic acid, and ethanol, followed by drying under reduced pressure. Copper(II) bromide (Fluka), 2,2'-bipyridyl (bpy, Sigma-Aldrich), 4-bromomethylbenzoic acid (Acros), 2-(chloromethyl)pyridine hydrochloride (Aldrich), 1,8-diazabicycloundec-7ene (DBU, Fluka), N,N'-dicyclohexylcarbodiimide (DCC, Aldrich), 4-(dimethylamino)pyridine (DMAP, Aldrich), nickelocene (Strem), potassium tert-butoxide (Merck), tributylphosphine (Alridch), sodium iodide (Fluka), sodium phenylsulfinate (Aldrich), elemental sulfur, p-toluenesulfonic acid (Aldrich), trifluoroacetic acid (TFA, Sigma-Aldrich), and 1,1,1-tris(hydroxymethyl)propane were all purchased at the highest available purity and used as received.

Characterization. ¹*H NMR spectroscopy* was performed using a Bruker AM 250 spectrometer at 250 MHz for hydrogen nuclei and 100 MHz for carbon nuclei. All samples were dissolved in either CDCl₃ or DMSO d_6 . The δ -scale is referenced to the internal standard trimethylsilane (TMS, δ = 0.00 ppm).

Size exclusion chromatography (SEC) measurements were performed on a Polymer Laboratories (Varian) PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel $5\,\mu$ m bead-size guard column (50 × 7.5 mm), one PLgel 5 μ m Mixed E column (300 × 7.5 mm), three PLgel 5 μ m Mixed C columns (300 × 7.5 mm), and a differential refractive index detector using THF as the eluent at 35 °C with a flow rate of 1 mL min⁻¹. The SEC system was calibrated using linear poly(styrene) standards ranging from 160 to 6 × 10⁶ g mol⁻¹ and linear poly(methyl methacrylate) standards ranging from 700 to 2 × 10⁶ g mol⁻¹. Molecular weights relative to PMMA are reported in the current contribution.

Mass spectra were recorded on a LXQ mass spectrometer (ThermoFisher Scientific) equipped with an atmospheric pressure ionization source operating in the nebulizer-assisted electrospray mode. The instrument was calibrated in the m/z range 195–1822 using a standard comprising caffeine, Met-Arg-Phe-Ala acetate (MRFA), and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 4.5 kV and a dimensionless sweep gas flow rate of 2 and a dimensionless sheath gas flow rate of

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^{*a*} The α, ω -functionalization of the PMMA proceeds via our recently reported nickelocene procedure.²⁴

12 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature were set to 60 V, 110 V, and 275 °C, respectively. The LXQ was coupled to a Series 1200 HPLC system (Agilent) that consisted of a solvent degasser (G1322A), a binary pump (G1312A), and a highperformance autosampler (G1367B), followed by a thermostated column compartment (G1316A). Separation was performed on two mixed bed GPC columns (Polymer Laboratories, Mesopore 250×4.6 mm, particle diameter 3μ m) with precolumn (Mesopore 50×4.6 mm) operating at 30 °C. THF at a flow rate of 0.3 mL min^{-1} was used as the eluent. The mass spectrometer was coupled to the column in parallel to an RI detector (G1362A with SS420x A/D) in a setup described previously.²⁶ A 0.27 mL min⁻¹ aliquot of the eluent was directed through the RI detector and 30 μ L min⁻ infused into the electrospray source after postcolumn addition of a 0.1 mM solution of sodium iodide in methanol at $20 \,\mu L \,min^{-1}$ by a microflow HPLC syringe pump (Teledyne ISCO, Model 100DM). The polymer solutions $(20 \,\mu L)$ with a concentration of close to 3 mg mL⁻¹ were injected into the HPLC system.

UV-vis spectroscopy was performed using a Cary 300 Bio UV/vis photospectrometer (Varian) equipped with a temperature-controlled sample cell. Absorption was measured in toluene solution (3 mg mL⁻¹) at a wavelength of 522 nm at temperatures ranging from 30 to 100 °C (using a 0.5 °C min⁻¹ heating rate).

Synthesis of Bis(cyclopentadienyl) Poly(methyl methacrylate) (PMMA-Cp₂). Methyl methacrylate (MMA), 1,2-bis(bromoisobutyryloxy)ethane (initiator), copper(I) bromide (Cu^IBr), copper(II) bromide (Cu^{II}Br), and 2,2'-bipyridine (bpy) were added to a round-bottom flask in the ratio 50/1/0.105/0.01250/0.25. Acetone was subsequently added such that the resulting mixture was 50 vol % acetone. Nitrogen was then bubbled through the mixture for 40 min to remove residual oxygen. The mixture was subsequently sealed under nitrogen and placed in a thermostated oil bath set to 50 °C. After 2 h, the polymerization was stopped by cooling the mixture in an ice bath and exposure to oxygen. The mixture was then passed through a short column of neutral alumina to remove the copper catalyst. α, ω -functional poly(methyl methacrylate) (PMMA-Br₂) was isolated by 2-fold precipitation in cold *n*-hexane. GPC (THF): $M_n = 3500 \text{ g mol}^{-1}$, PDI = 1.2.

According to our previously reported nickelocene Cpfunctionalization procedure,²⁴ α, ω -functional PMMA-Br₂, sodium iodide, tributylphosphine, and nickelocene in the ratio 1/12/4/8 were dissolved, under nitrogen, in anhydrous THF such that the solution was 0.1 M with respect to the polymer. The ambient temperature reaction was allowed to proceed for at least 12 h before the reaction mixture was passed through a short column of basic alumina. PMMA-Cp₂ was the isolated by a 2-fold precipitation in cold *n*-hexane.

Synthesis of 4-((Pyridine-2-carbonothioylthio)methyl)benzoic Acid. Step I: A mixture of 2-(chloromethyl)pyridine hydrochloride (10 mmol, 1.64 g), sodium phenylsulfinate (15 mmol, 2.46 g), and a catalytic amount of tetrapropylammonium bromide (2 mmol, 0.53 g), DBU (10 mmol, 1.52 g) in CH₃CN (10 mL), was refluxed for 12 h. The solvent was subsequently removed under vacuum, and the residue was dissolved in CH₂-Cl₂, washed with brine, and dried over MgSO₄ and the solvent removed. The crude product was obtained in quantitative yield, as a white solid and was used without purification in the next step.

Step II: A mixture of sulfone (8.51 mmol, 1.9 g) (from step I) and elemental sulfur (24.3 mmol, 0.78 g) was placed into THF (10 mL) under magnetic stirring. After addition of *t*-BuOK (24.3 mmol, 2.72 g), the color of the solution changed to dark brown. The reaction was stirred at ambient temperature for 12 h. Subsequently, 4-methylbenzoic acid (12.15 mmol, 2.6 g) in THF (10 mL) was added dropwise to the solution, and stirring was continued for 5 h. The color changed to reddishpink. The product was washed with aqueous HCl (2 N) and extracted in CH₂Cl₂. The crude product was finally purified by extraction with acetone (45% yield).

¹H NMR (DMSO-*d*₆, 250 MHz): δ /ppm = 4.63 (s, 2H, S-C*H*₂), 7.51–7.54 (m, 2H, Ar*H*), 7.67–7.71 (m, 1H, pyr*H*), 7.87–7.91 (m, 2H, pyr*H*), 7.95–8.26 (m, 2H, Ar*H*), 8.62–8.64 (m, 1H, pyr*H*), 13.0 (s, 1H, –COO*H*). ¹³C NMR (DMSO-*d*₆, 100 MHz): δ /ppm = 40.1, 121.89, 127.87, 129.42, 129.5, 137.78, 140.67, 148.34, 155.37, 166.94, 226.09. The ¹H and ¹³C NMR spectra can be found in the Supporting Information (Figures S1 and S2).

Synthesis of the Trifunctional Linker. 1,1,1-Tris(hydroxymethyl)propane (TMP) (0.072 g, 0.536 mmol), 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS) (0.118 g, 0.402 mmol), and (dimethylamino)pyridine (DMAP) (0.025 g, 0.201 mmol) were dissolved in 10 mL of CH₂Cl₂. 4-((Pyridine-2-carbonothioylthio)methyl)benzoic acid (0.581 g, 2.01 mmol) was dissolved in 3 mL of DMF and then added to the solution. After 10 min, dicyclohexylcarbodiimide (DCC) (0.622 g, 3.01 mmol) in 2 mL of dichloromethane was added to this solution. The reaction mixture was stirred overnight at ambient temperature. It was subsequently filtered and evaporated, and the remaining product was purified by column chromatography over silica gel eluting with hexane/ethyl acetate (6:4) to obtain pure red solid trilinker, yielding 0.301 g (59%). ¹H NMR (250, CDCl₃): δ (ppm) 8.61–8.59 (d, 3H, pyr*H*), 8.32-8.29 (d, 3H, pyrH), 7.94-7.91 (d, 6H, ArH), 7.83-7.76 (m, 3H, pyr*H*), 7.50–7.47 (m, 3H, pyr*H*), 7.44–7.41 (d, 6H, ArH), 4.57 (s, 6H, S-CH₂), 4.47 (s, 6H, O-CH₂), 1.79-1.70 (q, 2H, CH_2CH_3), 1.07–1.00 (t, 3H, CH_2CH_3). ¹³C NMR $(CDCl_3, 100 \text{ MHz}): \delta/\text{ppm} = 6.6 (CH_2CH_3), 22.76 (CH_2CH_3),$ 24.59 (C_q), 39.71 (CH₂O), 64.06 (CH₂S), 121.30 (C_{ar}), 125.89 $(C_{ar,py})$, 128.47 (C_{ar}) , 128.86 (C_{ar}) , 135.99 $(C_{ar,py})$, 140.02 (C_{ar}) , 146.39 $(C_{ar,py})$, 155.14 $(C_{ar,py})$, 164.44 (C=O), 226.09 (C=S). ESI-MS+Na (m/z) calcd 970.12; found 970.08. The ¹H NMR and MS spectra of the trilinker are depicted in Figure 2. The ¹³C NMR spectrum can be found in the Supporting Information (please refer to Figure S3, which also contains the peak assignments).

Cross-Linking (Bonding) between $PMMA-Cp_2$ and Trifunctional Linker. PMMA-Cp₂ and trifunctional linker were mixed in 1:1 ratio with respect to functional groups in chloroform such that the concentration of polymer was 0.05 M. 1.5 equiv of trifluoroacetic acid (TFA) was added, and the resulting mixture shaken at ambient temperature for 10 min. The solvent was removed and the residue directly analyzed by SEC prior to gelation.

De-Cross-Linking (Debonding) between $PMMA-Cp_2$ *and Trifunctional Linker*. The resulting cross-linked polymer was placed in toluene and heated to above 80 °C for 5 min. During this time, the colorless toluene turned pink in color, indicative of the release of the trifunctional linker via a retro-Diels–Alder cycloaddition and the polymer dissolved.

Re-Cross-Linking (Rebonding) between PMMA-Cp₂ and Trifunctional Linker. The non-cross-linked polymer was dissolved in chloroform as described above and additional TFA added (1.5 equiv). The solvent was removed within the



Figure 1. ESI-MS spectra of the starting α, ω -functional PMMA-Br₂ (a) and the corresponding α, ω -functional PMMA-Cp₂ (b). Note that both a single and double charged distribution of the polymeric materials are visible. Minor impurities due to side products formed in the ATRP process (bimolecular termination and elimination) are also visible.

space of 1 min, and the residue was directly analyzed by SEC prior to gelation.

Solid-State Cross-Linking. PMMA-Cp₂ and trifunctional linker were mixed in 1:1 ratio with respect to functional groups. Upon the addition of 1.5 equiv of TFA, the mixture was thoroughly mixed with a mortar and pestle. Fully cross-linked (i.e., completely insoluble) material resulted within the space of seconds.

Results and Discussion. In the current study, reversibly crosslinked polymeric structures were generated utilizing rapid hetero-Diels–Alder (HDA) chemistry. Unlike the majority of reports, in which maleimide and furan DA chemistry is used as the reversible linking mechanism, the present use of the highly reactive Cp moiety and pyridinyldithioformate allows for facile ambient temperature conjugations to be performed within the space of several minutes at ambient temperatures rather than several hours at elevated temperatures. Herein, α, ω -Cp-functional PMMA is reversibly and rapidly cross-linked by reaction with a tripyridinyldithioformate functional linker molecule.

Bis(cyclopentadienyl) poly(methyl methacrylate) (PMMA-Cp₂) was synthesized from the corresponding dibromo precursor. Dibromo poly(methyl methacrylate) (PMMA-Br₂) was obtained via ATRP of methyl methacrylate using the difunctional initiator 1,2-bis(bromoisobutryloxy)ethane. Subsequently, the PMMA-Br₂ was transformed into the targeted



Figure 2. ¹H NMR spectrum (a) and ESI-MS spectrum (b) of the trilinker. The ¹³C NMR spectrum of the trilinker can be found in the Supporting Information (see Figure S3).

PMMA-Cp₂ via nucleophilic substitution of the bromide moieties with cyclopentadienyl moieties via our facile and recently reported nickelocene pathway.²⁴ The quantitative conversion of PMMA-Br2 into PMMA-Cp2 was monitored via ESI-MS, which is a very convenient technique in determining low molecular weight polymer end-group functionalization. Figure 1 depicts the comparison of the ESI-MS spectra of the starting PMMA-Br₂ and PMMA-Cp₂. As can be observed, a shift of the dominant series of signals to lower m/z values is complete and consistent with the targeted transformation. All minor species, which are associated with various minor byproduct of the ATRP process such as bimolecular coupling and elimination species,²⁴ are carried through the substitution process. A comparison of the experimentally observed and the theoretically calculated m/z values for the dominant series is presented in Table S1 in the Supporting Information.

The dienophilic trifunctional linker is based upon the dithioester molecule 4-((pyridine-2-carbonothioylthio)methyl)benzoic acid, the synthesis of which has been appropriated from a two-step procedure reported in the literature.²⁷ In the first step, commercially available 2-(chloromethyl)pyridine hydrochloride is transformed into the corresponding sulfone by reaction with sodium phenylsulfinate in the presence of DBU and tetrapropylammonium bromide. The targeted sulfone was isolated in quantitative yields and used without further purification for the next step. The second step was carried out by reacting the above sulfone with sulfur (S_8) in the presence of potassium tert-butoxide, and subsequent alkylation with 4-methylbenzoic acid yielded the desired 4-((pyridine-2-carbonothioylthio)methyl) benzoic acid. The ¹H and ¹³C NMR of 4-((pyridine-2-carbonothioylthio)methyl)benzoic acid are shown in Figures S1 and S2 in the Supporting Information. The trifunctional linker was obtained via esterification of 1,1,1-tris(hydroxymethyl)propane with 4-((pyridine-2-carbonothioylthio)methyl))benzoic acid in the presence of DCC, 4-(dimethylamino)pyridinium-4-toluenesulfonate (DPTS), and DMAP. The trifunctional linker was purified via column chromatography, and the purity was determined by ¹H NMR spectroscopy and ESI-MS (Figure 2).

In order to generate cross-linked structures under ambient conditions, the trilinker core was reacted with PMMA- Cp_2 in a 1:1 ratio with respect to functional groups using chloroform as the solvent and TFA as a catalyst. The linkages that



Figure 3. Structure of the linkages formed during the HDA reaction. For simplification, not all regio-/stereoisomers are depicted.

are formed via the HDA reaction are depicted in Figure 3. Within a maximum time frame of 30 min at ambient temperatures completely cross-linked structures were synthesized, as indicated by their lack of solubility. When the cross-linking reaction was performed in the solid state, fully cross-linked material was formed within the space of seconds. Therefore, in order to perform a SEC analysis to visualize the changes in molecular weight that occur, the crude reaction mixtures were quickly diluted with THF prior to the gel point (< 10 min) and directly analyzed. Figure 4a depicts the SEC distribution of the starting trifunctional linker and PMMA-Cp₂ having a molecular weight of 990 and 3500 g mol⁻¹, respectively. After a reaction time of 10 min, the molecular weight of the system markedly increases to $12\,700$ g mol⁻¹. It is also noted that the polydispersity of the system increases from 1.21 to 2.57. Both of these observations are indicative of the progression of rapid cross-linking reactions.

Aside from the rapid nature of the above cycloadditions, another advantage of the use of the reactive Cp moiety is the reduction in temperature at which the retro-HDA reaction occurs. In previous investigations, open-chain dienes were utilized, the HDA adducts of which underwent reversion at temperatures exceeding 120 °C.^{21,22} At such temperatures, the liberated dithioesters readily decompose which precludes such systems to be used in a continually reversible fashion.



Figure 4. (a) Visualizing the changes in molecular weight in the cross-linking system by SEC. (b) Graphical representation of the bonding/debonding on demand, which occurs within minutes in either direction. (c) UV/vis monitoring of the onset of debonding (i.e., the reaction solution becomes colored again) at close to 80 °C ($\lambda = 522$ nm).

 Table 1. Characterization of the Bonded and Debonded Polymer

 Systems, Demonstrating the Switching Behavior in Both the

 Observed Molecular Weight and the Polydispersity Index

polymer	$M_{ m n,SEC}/ m g\ mol^{-1}$	PDI
PMMA-Cp ₂	3500	1.20
bond	12700	2.57
debond	3800	1.26
bond	10200	2.14

In the present study, the retro- or debonding reactions were performed at temperatures between 80 and 100 °C. Referring back to Figure 4a, it is noted that heating the highly linked structure for no more than 5 min at > 80 °C results in debonding taking place. One can clearly observe not only the reduction in molecular weight of the system ($M_{\rm n} = 3800 \text{ g mol}^{-1}$) but also an increase in the signal representing the trilinker molecule, indicating its release into solution. The final part of Figure 4a depicts an attempt at rebonding the above debonded sample. The debonded polymer/trilinker mixture was dissolved in fresh chloroform, and a catalytic amount of TFA was added. Analysis of the reaction mixture via SEC reveals that an increase in molecular weight $(10\,200\,\mathrm{g\,mol}^{-1})$ and polydispersity (2.14) occurred, thus confirming the ability of the system to bond, debond, and rebond on demand. The system is graphically depicted in Figure 4b. Furthermore, the molecular weight data for the above study are included in Table 1.

The onset of debonding was also monitored via UV/vis spectroscopy. In an initial qualitative trial, fully cross-linked material was suspended in toluene. Upon heating with a hand-held heat gun, the material gradually dissolved and the toluene solution turned pink, indicating the release of the starting trilinker molecule. Performing the same reaction quantitatively inside a UV/vis spectrophotometer allowed for the absorbance of the solution to be monitored as a function of temperature. Figure 4c depicts the results of such an analysis, and it is observed that a sharp increase in the absorbance of the system occurs at around 80 °C (the solution returns the color of the dithioester), corresponding to the rapid onset of debonding.

Conclusions. The reversibility of rapid HDA reactions has been exploited for the generation of a highly reversibly stimuli-responsive cross-linked polymeric network. The ambient temperature cross-linking of PMMA (bonding) could be reversed upon thermal treatment (debonding) and subsequently re-formed (rebonding) again at ambient temperature. Although accessibility to the HDA functionalities is not the same as the widely used maleimide/furan derivatives, the provision and continued development of such systems will ultimately lead to significant advances in such fields as coatings, adhesives, and self-healing polymeric materials.

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Supporting Information Available: ¹H and ¹³C NMR spectra of 4-((pyridine-2-carbonothioylthio)methyl)benzoic acid, the ¹³C NMR spectrum of the trilinker, and individual peak assignments for the mass spectra depicted in Figure 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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