RESEARCH ARTICLE

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Acyclic Diene Metathesis (ADMET) Polymerization of 2,2,6,6-Tetramethylpiperidine-1-sulfanyl (TEMPS) Dimers

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The preparation of polymers containing sulfur–nitrogen bond derivatives, particularly 2,2,6,6-tetramethylpiperidine-1-sulfanyl (TEMPS) dimers (i.e., BiTEMPS), has been limited to free-radical or conventional step-growth polymerization as result of the inherent thermal lability of the BiTEMPS unit. Accordingly, a novel poly(diaminodisulfide) possessing the BiTEMPS functional group is synthesized via acyclic diene metathesis (ADMET) polymerization at 65–75 °C within 3 h with precise control over the primary polymer structure. Polymer is isolated with an M_n of 20 400 g mol^{-1} and $Đ$ of 1.9. Importantly, detailed nuclear magnetic resonance (NMR), size exclusion chromatography, attenuated total reflectance Fourier transform infrared (ATR-IR) in addition to elemental analysis studies of the BiTEMPS polymer confirm the successful polymerization, and show that the BiTEMPS unit remains intact during the polymerization process. Furthermore, the previously unexplored UV-responsiveness of the BiTEMPS decorated polymer backbone is investigated for the very first time.

1. Introduction

An important milestone for polymer science was celebrated in the year of 2020: the 100th anniversary of the seminal paper published in 1920 by Hermann Staudinger.[1] Since then, with the aid of a series of synthetic breakthroughs, a plethora of chemistries suitable for the synthesis of various polymers have been developed.[2] Indeed, among this broad synthetic plethora, numerous advances have been made concerning the synthesis of polymers with functional groups containing heteroatoms within the main chain. This reaches from carbon–oxygen bonds (e.g., ethers, esters, and carbonates) to carbon–nitrogen (e.g., imines,[3] hydrazones,[4] and oximes[5]). Interestingly, their sulfur-containing analogues,[6] have been underestimated for long time, although the intrinsic characteristics of these polymers are offering a myriad of superior properties (e.g., degradation, flame retardancy, film-forming ability, good solubility in polar solvents, and high refractivity with small chromatic dispersions amongst other) compared to the carbon-derivatives. This is particularly the case for sulfur–nitrogen based polymers. The distinctive characteristics of the sulfur–nitrogen based polymers result from the unique chemical properties of the sulfur–nitrogen bond (e.g., its polar character and the multiple valence states of sulfur). As one of the most intriguing dynamic covalent bonds featuring a simple redox chemistry, the disulfide bond has a crucial importance in organic and polymer chemistry.[7] On the contrary, the amino- and diaminodisulfide functional groups (*–S–S–N–* and *–N–S–S–N–*, respectively) are rarely studied in organic chemistry, and the respective polymers are very much in their infancy. At the same time, diaminodisulfide and its derivatives represented with the formula *–N–S–S–N–*, are known for their low S–S bond dissociation energies (e.g., BDE of 180 kJ mol^{-1} for the simplest diaminodisulfide $H_2N–S–S–NH_2$) in reference to diaryl and dialkyl disulfide bonds (190–230 and 250–290 kJ mol^{-1}, respectively). In spite of this, diaminodisulfides are stable and readily handled at ambient temperature as a result of the high stability of the respective thiyl radicals that are formed via catalyst free-thermally induced reversible dissociation. Literature survey also clearly depicts that polymers with sulfur–nitrogen bond (particularly, poly(sulfenamide)s, poly(diaminosulfide)s, and poly(diaminodisulfide)s[8,9]) could be considered as sleeping beauties and (re)appear to be promising for new materials that combine the advantages of sulfur and nitrogen solely. While, the first synthesis of organic molecules decorated with disulfidediamine dates back to 1895,[10] it took almost a century until a pioneering study on polymeric diaminodisulfide derivatives was reported in 1991.[11] Whilst the study failed to provide any complementary characterization of the reported poly(diaminodisulfide) derivatives, the first report dealing with the in-depth characterization of this polymer class dates back to 2012.[12] In a recent study, Otsuka and co-workers,[13]

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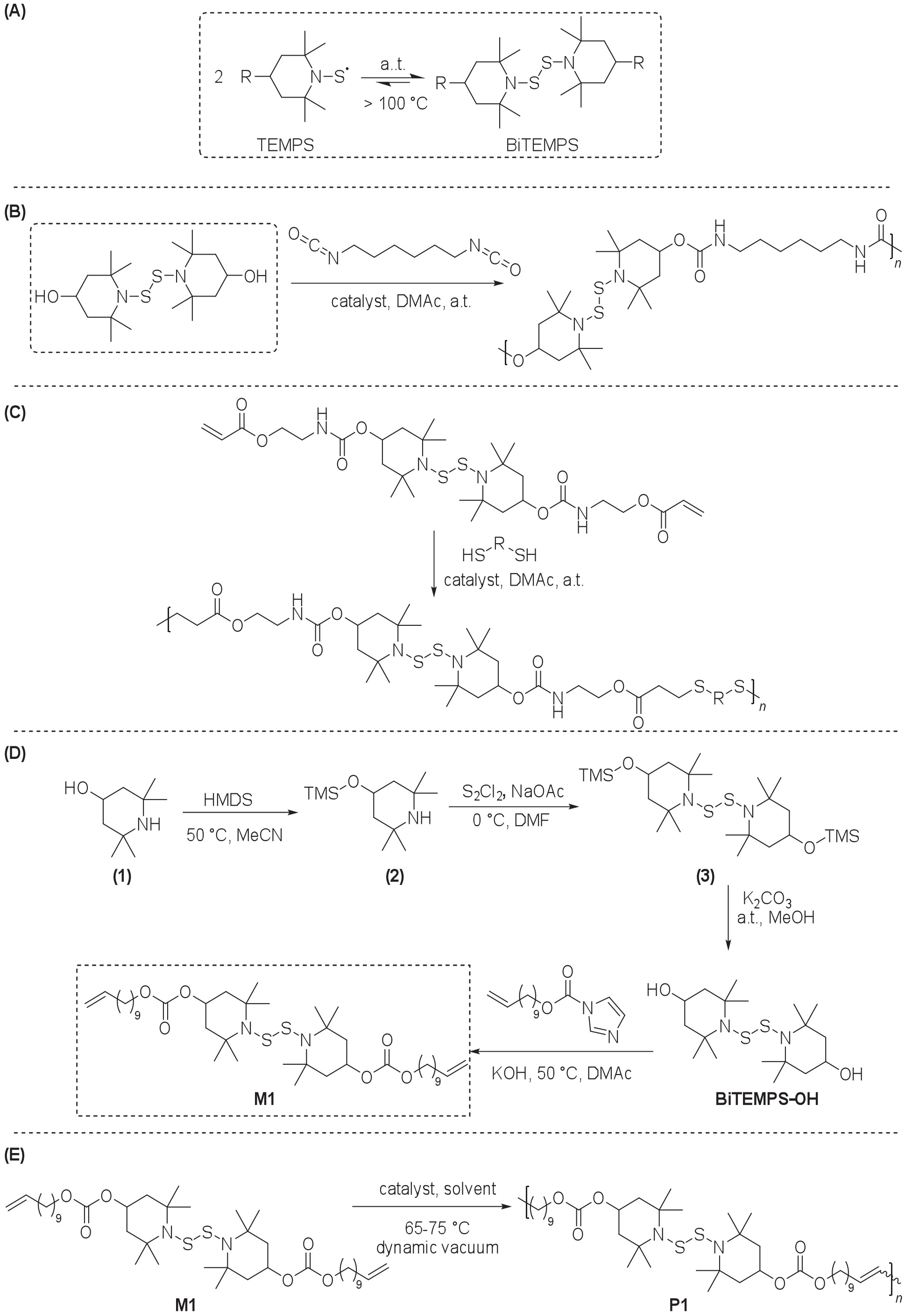

Scheme 1. Schematic representation of: A) characteristic dissociation of **BiTEMPS**; B,C) Previously reported synthesis approaches for the preparation of **BiTEMPS** containing polymers; D) The synthesis of a new tailor-made α,ω-diene functionalized **BiTEMPS** monomer **M1** and E) its subsequent polymerization via ADMET chemistry to afford polymer **P1**.

enriched the toolbox of the monomers applicable for the synthesis of poly(diaminodisulfide)s by developing 2,2,6,6-tetramethylpiperidine-1-sulfanyl (TEMPS) dimers (e.g., **BiTEMPS**) as a new class of dynamic covalent chemistry (**Scheme 1**A). The **BiTEMPS** unit, first reported by Bennett et al. in 1967,[14] is recognized as a stable covalent bond at ambient temperature, which allows the exchange of the disulfide bonds above 80 °C. By virtue of their unique dissociation features, **BiTEMPS** were initially utilized as cross-linking point within polymer networks to impart a thermally induced healing property.[15] Despite the elegant achievements based on the dynamic behavior of **BiTEMPS** derivatives,[16] such as the fusion of different cross-linked polymers,[17] the topological rearrangement from linear to cyclic polymers,[18,19] and synthesis of end-functionalized polymers,[20] to the best of our knowledge, the protocols utilized for the preparation of **BiTEMPS** containing polymers has been limited to conventional free-radical or step-growth polymerization approaches. Critically, due to the thermal lability of the **BiTEMPS** unit at temperatures above 80 °C,[14] previously reported polymerizations were essentially performed at ambient temperatures (Scheme 1B,C).

Thus, within this study, in order to broaden the toolbox of **BiTEMPS** polymer synthesis facilitated by modern polymer syntheses, acyclic diene metathesis (ADMET) polymerization[21] was adopted. ADMET is appreciated for its mild and highly functional group tolerant character, thus it appeared as a suitable approach to polymerize a new tailor-made α,ω-diene functionalized **BiTEMPS** monomer (**M1** in Scheme 1D). Without doubt, ADMET polymerization has received attention as an efficient polycondensation strategy for the construction of polymers with precise control over the primary polymer structure. Indeed, a key to afford a polymer with well-defined chain structure requires a careful design and synthesis of the ADMET monomer, i.e., **BiTEMPS** derived monomer (**M1** in Scheme 1D). Accordingly, the general strategy for the preparation of the essential monomer **M1** started from commercially available 4-hydroxy-2,2,6,6-tetramethylpiperidine (**1**), which was first protected to yield 2,2,6,6-tetramethyl-4-((trimethylsilyl)oxy) piperidine (**2**) in the presence of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (refer to Section SA.2.1–S2.5 in the Supporting Information). The sodium acetate catalyzed reaction of (**2**) with S_2Cl_2 delivered compound (**3**), which in turn was deprotected by base mediated removal of the TMS protecting group to afford bis(4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)disulfide (**BiTEMPS-OH**). For the ADMET polymerization (Scheme 1E), it is prerequisite that the monomer possesses two terminal alkene functionalities as polymerization process is based on the metathesis reaction of the two terminal olefins in order to form an internal C=C double bond. Accordingly, a suitable monomer for ADMET polymerization was synthesized by placing a carbonate moiety in between the terminal alkene derivative and **BiTEMPS** functionality by reaction of **BiTEMPS-OH** with 1,1′-carbonyldiimidazole (i.e., CDI) activated 10-undecen-1-ol (**4**). Crucially, it is important to mention that the latter is a subsidiary product of castor oil.[22] The resulting monomer **M1** was obtained with a reasonable overall yield of 55%. Nuclear magnetic resonance (NMR) spectroscopy was used in order to confirm the chemical structures of the monomer precursors (i.e., (2), (3), and **BITEMPS-OH**) along monomer **M1** (refer to **Figure 1**A and Figures S1–S12 in the Supporting Information section, and red line in Figure 1A). Ultraviolet–visible (UV–vis, red line in Figure 1B) and attenuated total reflectance Fourier transform infrared (ATR-IR, Figure 1C; Figures S17 and S18, Supporting Information) spectroscopy were additionally utilized to asset the structure and optical properties of **M1**. For instance, the main band at 244 nm and an additional small band at approximately 287 nm was observed for **M1** (red line in Figure 1B).[23] Along this, the band at 1236 cm^{-1} in the ATR-IR spectrum could be assigned to the antisymmetric stretching mode of N–S. The latter particularly confirms the presence of **BiTEMPS** unit in compounds **BiTEMPS-OH** and **M1** (compare Figure S18 in the Supporting Information).[24] For the ADMET polymerization of **M1**, Hoveyda–Grubbs second generation catalyst (HG-II; a ruthenium alkylidene complex, depicted in Scheme S1 in the Supporting Information), was selected as the polymerization catalyst. Indeed, HG-II is known for its high stability to air and moisture, in addition to its tolerance to diverse functional groups along high activity.[25] In order to drive the equilibrium toward the formation of polymer, the polymerization reaction was carried out under dynamic vacuum (1.0–0.1 mbar). It is important to mention that polymerizations were performed in solution instead of bulk in order to overcome limitations due to high viscosity in reaching high molar mass.[26] Polarclean (ethyl-5-(dimethylamido) -2-methyl-5-oxopentanoate) was the choice of solvent as it is recognized as an eco-friendly solvent, featuring a high boiling point and a lower toxicity than toluene, *o*-chlorobenzene or *N, N*-dimethylformamide. After reacting monomer **M1** with HG-II catalyst (2.0 mol%/molecule), under dynamic vacuum (1.0–0.1 mbar) at a temperature range from 65 to 75 °C in Polarclean (0.6 м) for 3 h, the targeted polymer **P1** was isolated with an M_n of 20 400 g mol^{-1} ($Đ$ of 1.9, as determined by size exclusion chromatography (SEC) relative to polystyrene standards in tetrahydrofuran (THF) as eluent, black line in Figure 1D). Note that, the polymerization of **M1** was also conducted in *o*-chlorobenzene under the same experimental conditions as for **P1**, nevertheless the SEC analysis revealed the formation of polymer **P2** with considerable low molar mass, i.e., M_n of 5300 g mol^{-1} and $Đ$ of 1.5 (grey line in Figure 1D). While, polymer **P1** was soluble in dichloromethane (DCM), chloroform, THF and 1,4-dioxane, and completely insoluble in acetonitrile, diethyl ether, dimethyl sulfoxide (DMSO), methanol, and water, the polymerization solvent, i.e., Polarclean could be easily removed from the reaction mixture by washing the precipitated polymer with ice-cold methanol. On the one hand, ^1H NMR (black line in Figure 1A) and ATR-IR (black line in Figure 1C) analysis confirmed the chemical structure of the polymer, whereas UV–vis measurements displayed the optical properties of the polymer. In other words, two main bands at 229 and 276 nm appeared in the spectrum of **P1** (black line in Figure 1B). On the other hand, the formation of a polymer was indicated as the magnetic resonances of the terminal olefins of **M1** (red line Figure 1A) at 5.86–5.74 and 5.03–4.89 ppm almost vanished. Besides, the magnetic resonances of the internal −HC=CH− double bond formed after the polymerization appeared at 5.42–5.32 ppm (black line in Figure 1A). Moreover, the characteristic magnetic resonances arising from the **BiTEMPS** units (signals f, g, and h at 2.09–1.99, 1.65, and 1.57 ppm, respectively) were also detected. In similar manner, the characteristic vibration of **M1** (red line in Figure 1C) attributed to the terminal olefin bond, which reveals bands in the 3078 and 1642 cm^{-1} wavenumber regions (corresponding to carbon–hydrogen stretching and bending vibrations of the =C−H group, respectively), were not present in the polymer **P1** (black line). On the contrary, the dihedral bend arising from the vibrations of the –S–S– stretch remained substantially in the same region, i.e., 528 and 533 cm^{-1}, respectively for **M1** and **P1**. Furthermore, it is of crucial importance to mention that complementary to ^1H NMR and ^{13}C NMR spectroscopic analysis (Figure S13, Supporting Information), 2D NMR (Figures S14–S16, Supporting Information) and elemental analysis also manifested that the **BiTEMPS** functionality persisted intact. The experimentally obtained elemental

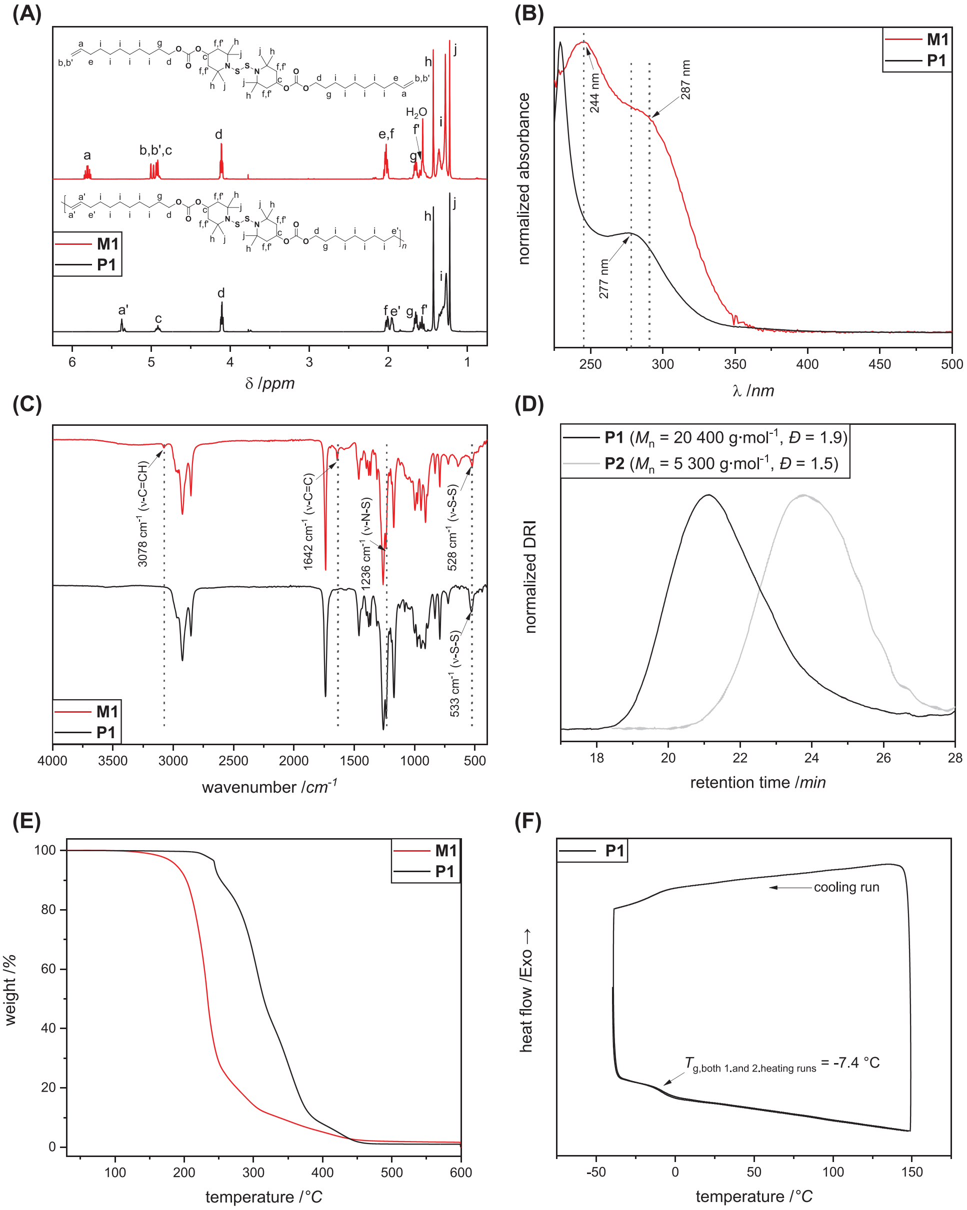

Figure 1. A) ^{1}H NMR spectra (up, 500 MHz, $CDCl_3$, 298 K) of **M1** (red line) and **P1** (bottom, black line). B) Absorption traces of **M1** (red line), **P1** (black line) DCM (c = 0.2 mg mL^{-1}). C) ATR-IR traces of **M1** (red line) and **P1** (black line). D) SEC traces of metathesis polymers **P1** ($M_{n,SEC}$ = 20 400 g mol^{-1}, $Đ_{SEC}$ = 1.9, black line) and **P2** ($M_{n,SEC}$ = 5300 g mol^{-1}, $Đ_{SEC}$ = 1.5, grey line), synthesized in Polarclean and *o*-chlorobenzene, respectively. E) Thermogravimetric analysis (TGA) of **M1** (red line) and **P1** (black line) from 25 to 600 °C with a heating rate of 5 K min^{-1} under nitrogen flow. F) The heating–cooling–heating thermal profiles via DSC of polymer **P1**.

composition of **P1** (C: 68.1%, H: 9.6%, S: 8.0%, N: 3.3%) was in accordance with the theoretically calculated values (C: 64.8%, H: 9.8%, S: 8.7%, N: 3.8%), thus once more indicating the compatibility of ADMET chemistry with the **BiTEMPS** unit.

Accurate thermal characterization is essential for appropriate application-oriented explorations of this novel polymer. The decomposition temperature (T_d), defined as the temperature at 5% weight loss, was determined by thermogravimetric analysis (TGA). As shown in Figure 1E, an one-step degradation pattern, was observed with a T_d of ≈244 °C under inert conditions (i.e., nitrogen), with no char residue. The thermal transitions of **P1** were also investigated by differential scanning calorimetry (DSC, Figure 1F). It was detected that the glass transition temperature T_g, observed during the second heating measurement via DSC analysis, was reflecting amorphous behaviour with a T_g of close to −7.4 °C.

The disulfide exchange reactions have been recognized as a crucial development within the field of dynamic covalent chemistry.[27] Those reactions can be initiated in a number of ways; for instance, thermally,[13] chemically,[28] in the presence of metal[29] or phosphine catalysts,[30] as well as sonication.[31] In similar manner, upon irradiation with UV light, disulfide bonds are homolytically cleaved to give two thiyl radicals which could recombine through the manipulation of reaction conditions.[32]

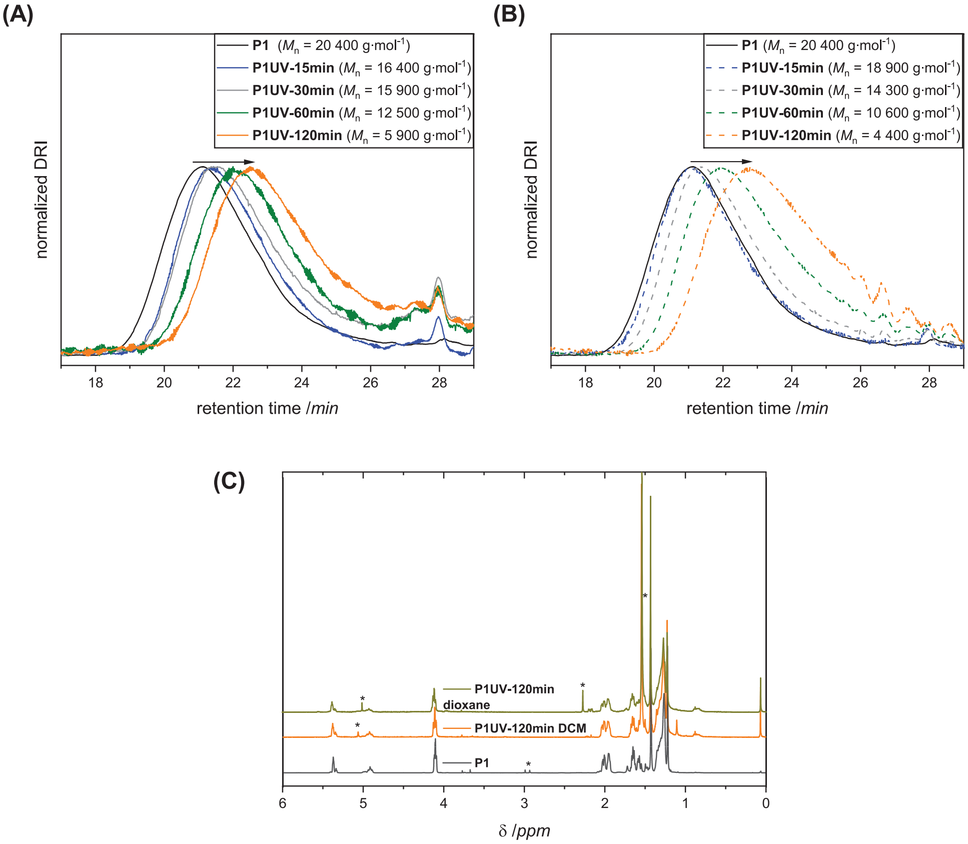

Figure 2. UV-induced stimuli-responsiveness of polymer **P1**: A) The change of the SEC chromatogram of **P1** (black line) before and after treatment with UV irradiation in DCM (**P1UV-x min**, where *x* indicates the time interval when a sample was withdrawn from the reaction mixture; **P1UV-15 min** (blue line), **P1UV-30 min** (grey line), **P1UV-60 min** (green line), and **P1UV-120 min** (orange line)); B) The change of the SEC chromatogram of **P1** (black line) before and after treatment with UV irradiation in 1,4-dioxane (**P1UV-15 min** (blue dashed line), **P1UV-30 min** (grey dashed line), **P1UV-60 min** (green dashed line), and **P1UV-120 min** (orange dashed line)); C) ^{1}H NMR spectra (bottom, 500 MHz, $CDCl_3$, 298 K) of **P1UV-120 min** in DCM (orange line) and 1,4 dioxane (olive green line), respectively, compared to **P1** (black line).

Nevertheless, the light induced exchange reaction of conventional aliphatic and aryl disulfide bonds typically requires UV light at wavelengths below 300 nm (e.g., λ_{max} = 254 nm).[32a] on the contrary, the formation of thiyl radicals strongly depends on the BDE of the S–S bond, which can be modulated chemically by the use of proper derivatives. Due to the low BDE of the S–S bond in **BiTEMPS** (109–130 kJ mol^{-1}),[33] it would be expected that the formation of the TEMPS thiyl radicals and their respective exchange reaction could take place at UV light wavelength above 300 nm; most importantly at ambient temperature and without external stimuli. In fact, after irradiation with UV light (λ_{max} = 320 nm) for 2 h in DCM (1.0 g L^{-1}), the initial peak of **P1** (M_n = 20 400 g mol^{-1}) in the SEC chromatogram gradually shifted with decrease in the apparent number average molar mass to a higher retention time, (**P1UV-15 min** (M_n = 16 400 g mol^{-1}) – **P1UV-120 min** (M_n = 5900 g mol^{-1}) in **Figure 2**A). The reaction was also monitored with ^{1}H NMR. Figure 2C displays the comparative ^{1}H NMR spectra of **P1** (black line) and **P1UV-120 min** (orange line) and is clearly showing that no significant change was observed in the position and the respective intensities of the relevant magnetic resonances arising from the **BiTEMPS** unit, thus implying that the chemical composition of the polymer remained unchanged. Importantly, we repeated the UV-experiments in UV-unreactive solvents such as acetonitrile and 1,4-dioxane after eliminating their stabilizers. While, the reaction failed to take place in acetonitrile due to the limited solubility of **P1** in the respective solvent (Figure S19, Supporting Information), switching the solvent to the slightly less polar 1,4-dioxane facilitated the respective exchange reaction to occur to similar extent in the same manner to the reaction performed in DCM (compare Figure 2B,C). Accordingly, the results clearly revealed the previously unexplored UV-responsiveness of the **BiTEMPS** decorated polymer backbone.

To conclude, we have demonstrated the first attempt for the polymerization of the temperature-sensitive **BiTEMPS** decorated monomers above ambient temperatures. An α,ω-diene functional **BiTEMPS** was synthesized, fully characterized and polymerized by ADMET chemistry at temperature range from 65 to 75 °C under dynamic vacuum. The ADMET polymerization allowed the construction of polymers with precise control over the primary polymer structure, and thus endeavour macromolecules with sulfur–nitrogen bonds that show prominent light-induced responsiveness. The latter being yet not explored for polymers bearing **BiTEMPS** units. Importantly, detailed NMR, SEC, ATR-IR in addition to elemental analysis studies confirmed the successful polymerization, and showed that the thermally labile **BiTEMPS** moiety remained intact during the polymerization process. Further studies (e.g., electron paramagnetic resonance (EPR) measurements) focusing on the thermal and UV dissociation properties of the synthesized **BiTEMPS** polymers are currently underway. Last but not at least, potential applications in the field of biomedicine and energy are foreseen for those polymers.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2,2,6,6-tetramethylpiperidine-1-sulfanyl (TEMPS) dimers, ADMET, BiTEMPS, poly(diaminodisulfide)s, sulfur–nitrogen polymers

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