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Controlled Synthesis of a Homopolymer Network Using a Well-Defined Single-Component Diels–Alder Cyclopentadiene Monomer

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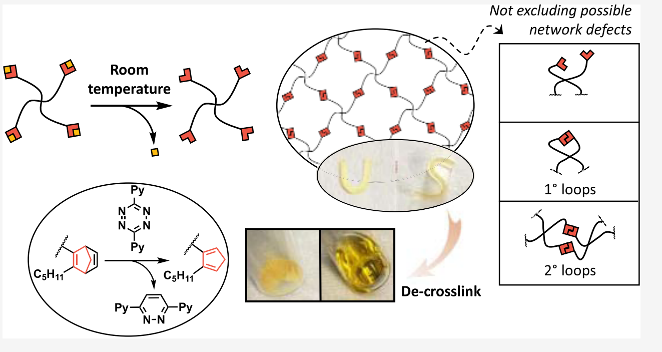
ABSTRACT: Cyclopentadiene is known for its high reactivity and propensity to dimerize, making monomer synthesis and polymerization notoriously challenging. In fact, despite its long history and compelling chemistry, only two reports have appeared in the literature since the first attempt to homopolymerize cyclopentadiene by Staudinger in 1926. Herein, we present a strategy not only to synthesize, isolate, and homopolymerize a well-defined tetracyclopentadiene monomer but also to de-cross-link the network homopolymer. Mechanical properties are also investigated, including creep–recovery, shape memory, and tensile behaviors. Interestingly, the tensile test reflects a tough and elastic material, in contrast to prior Cp-based homopolymer networks. This work provides a versatile platform to access and study new cyclopentadiene-based and better-defined homopolymer networks with potential applications ranging from shape memory polymers to degradable thermosets.



■ INTRODUCTION

There is a long history in the synthesis of polymer networks dating back to vulcanization of natural rubber in the 19th century.[1] Today, polymer networks are among the most widely studied and broadly used synthetic materials with a range of exceptional properties. While most cross-linked polymer networks are heterogenous and lack controlled structures, recent advances in controlling polymer network topology and studying defective topological structures have enabled access to polymer networks with optimized elasticity, fracture toughness, stimuli responsiveness, and minimization of defects.[2,3] Furthermore, these materials facilitate structure–property relationship studies,[2−6] which are essential for tailored designs and optimized functions of advanced materials. One of the most widely adopted strategies to construct well-defined polymer networks (e.g., model or near-ideal networks) is "end-linking," where two different multifunctional monomers are linked through a step-growth reaction.[7] The efficient methods include a mixture of precursor telechelic linear polymers (A_2) and multifunctional cross-linkers (B_f with $f > 2$) or multifunctional precursor polymers with a controlled chain length (A_f and B_f). A pioneering example is Matsunaga and Sakai's tetrafunctional PEG model network formation using A_4 + B_4 that cannot form primary loops, leading to a material with remarkably high mechanical strength.[8] Johnson and co-workers also reported an elegant strategy through the slow addition of B_f to A_2 during network formation, which allows for the capping of each B functionality with excess A groups.[9] This approach results in a significant reduction in primary loop defects and improved shear storage moduli compared to networks synthesized by conventional batch mixing.

From a design perspective, there are generally three critical requirements to achieve near-ideal or model networks: controlled molecular weights between the two junctions, perfect stoichiometry, and quantitative curing behaviors.[7,10] Among these factors, reaching a stoichiometric balance between A and B functions has remained a challenging task.[7,11−15] In this work, we explore an alternative approach to better-defined polymer networks based on a single-component dual-role monomer, cyclopentadiene (Cp). Cp has a unique property in that it can serve both as a diene and dienophile in quantitative Diels–Alder (DA) cycloadditions,[16,17] thereby eliminating the internal imbalance/stoichiometry from the two-component multifunctional monomers. While the formation of loop defects and structural diversity of DA adducts will prevent ideal network formation, the dynamic retro-DA/DA reaction provides a potential pathway to remove defects. The fast, self-reactivity of Cp led to the first single-component network formation in 1926 by Hermann Staudinger,[18] the "father of macromolecular chemistry" (Figure 1a). Although

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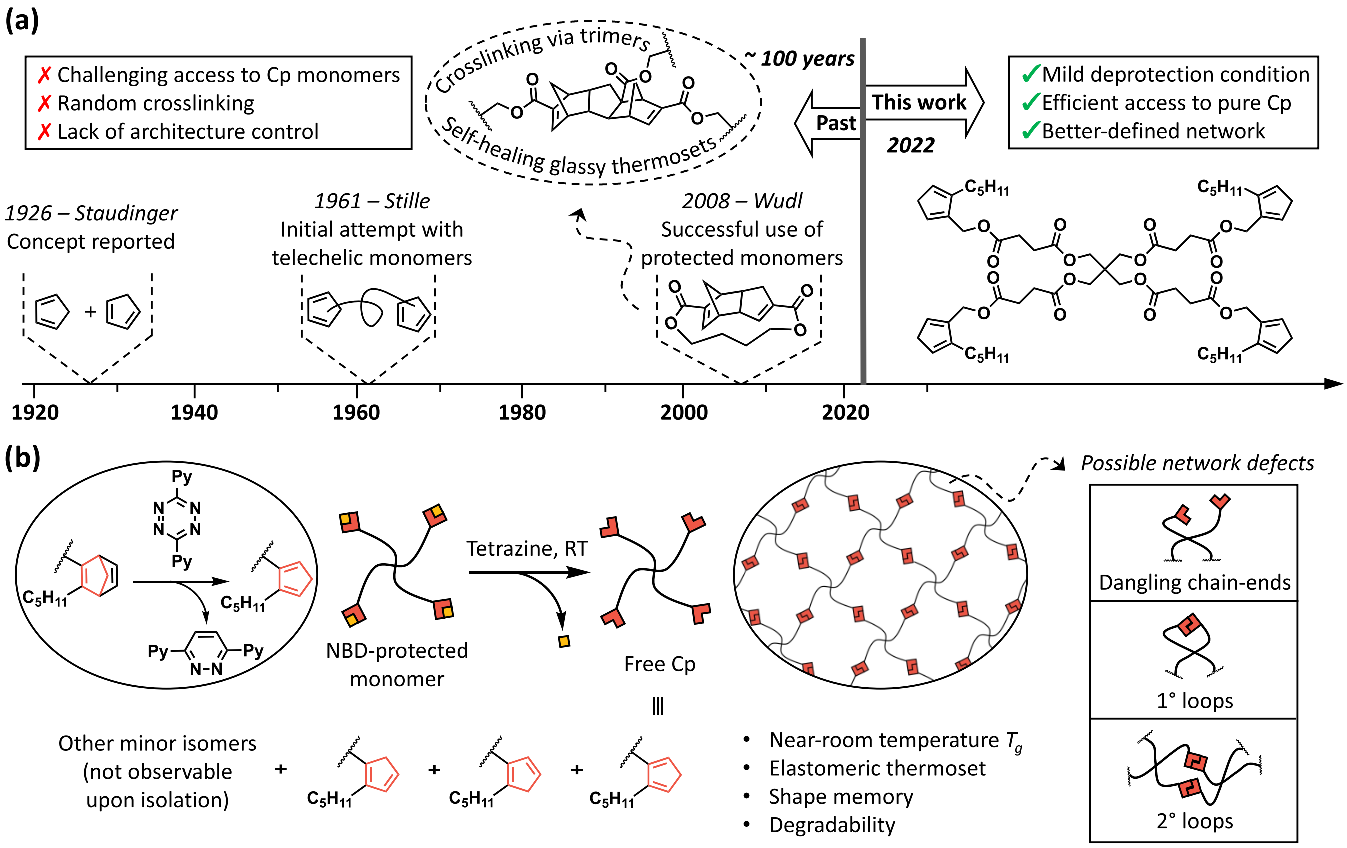

Figure 1. (a) Time series of the synthesis of Cp homopolymer (past works remain uncontrolled and challenging). (b) Norbornadiene−tetrazine cascade reaction reveals free Cp for dimerization. Efficient access to a 4-arm Cp monomer with minimal trimer leads to the formation of a better-defined network with appealing characteristics. Of note, 1,5-H shift of Cp monomers at RT and formation of *endo*/*exo* Diels−Alder adduct (not shown) generate a mixture of different diastereomers, leading to topological diversity. Also, the network scheme does not exclude unavoidable defects, composed of dangling chain ends and primary and secondary loops.

pioneering, the uncontrolled nature of cross-linking resulted in a macromolecule with a high decomposition temperature and poor polymer processability.[19−21] Expanding upon this work, Stille explored the use of bis(cyclopentadienyl)alkane derivative as a telechelic monomer, however, due to the high reactivity of Cp—at room temperature, Cp is unstable, readily dimerizes, and undergoes a fast 1,5-sigmatropic hydride (1,5-H) shift—the monomer could not be purified prior to polymerization. As a result, the formed polymeric materials were contaminated with impurities and the cross-linking process was presumably attributed to random oxidative cross-linking.[22]

Building on the implementation of DA-based thermally remendable polymer materials,[23] Wudl developed an innovative strategy using cyclic Cp dimers derived from Thiele's acid as a premonomer[24] (Figure 1a). The basis of this approach lies in the thermally reversible DA cycloaddition. Upon heating to 120−150 °C, the cyclic Cp dimer undergoes the retro-DA (rDA) reaction to reveal telechelic Cp monomers that subsequently underwent DA polyaddition to form self-healable cross-linked polymer networks. By providing access to a well-defined monomer using the rDA reaction, Wudl elegantly demonstrated that the cross-linking occurred via an uncontrolled trimer formation between the alkene on the polymer backbone from the Cp dimer and another reactive Cp. This approach realized the feasible processability of Cp-based homopolymers, subsequently enabling characterization studies and post-damage (i.e., self-healing) repair strategies. Besides the prominent reports of homopolymer networks, more strategies have been applied to generate Cp groups *in situ* via postfunctionalization[25] or pair it with a highly reactive dienophile, such as cyanodithioester (CDTE).[17,26,27] For example, Kennedy and Castner reported the incorporation of pendant Cp units by cyclopentadienylation with chlorinated butyl rubber polymers. *In situ* dimerization of Cp leads to the formation of reversible networks.[25] More recently, Barner-Kowollik and co-workers exploited the fast hetero-DA reaction between Cp and CDTE to prepare a highly efficient self-healing polymer network with tunable properties.[26] Despite the pioneering ideas of using Cp derivatives as the sole component to form homopolymer networks or prepare new materials with other dienophiles, the practice of controlling the Cp reactivity to prepare tailored advanced materials remains in infancy.[21,28]

One key synthetic challenge that remains is addressing the high reactivity of Cp and minimizing uncontrolled branch functionality in the polymer network. Given that many properties (e.g., elasticity, shape memory, and fracture toughness) have topology origins, providing controlled access to well-defined Cp-based monomers can result in design of remarkable new polymer networks with tunable advanced properties. For example, the DA self-reactions of Cp, including its 1,5-H shift isomers, can lead to several diastereomers that increase the number of possible DA cycloadducts at the cross-linking points, each with its own "bite angle" and topological shape (see Supporting Figure S1 and Table S1 for detailed

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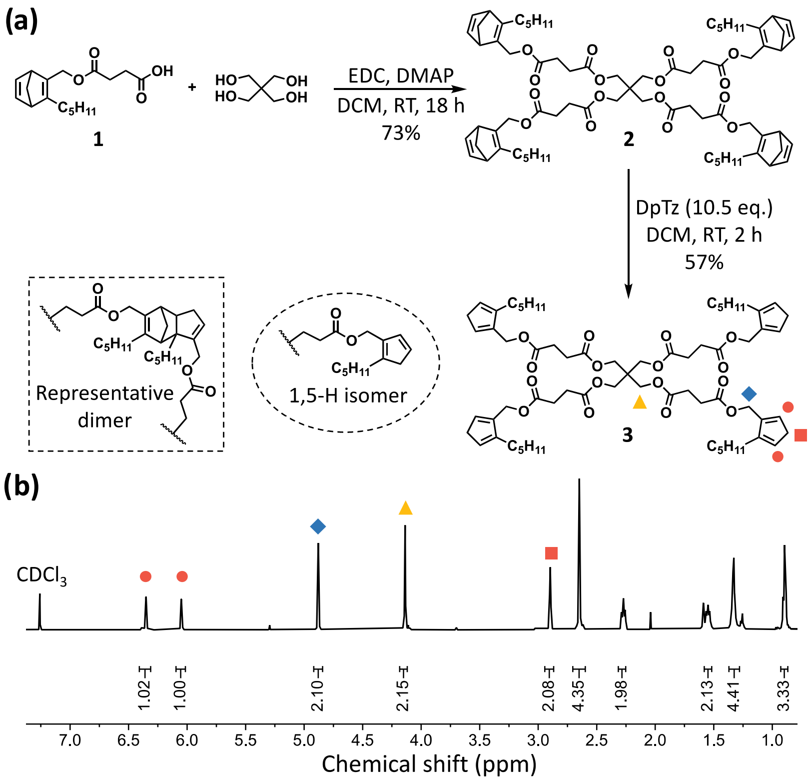

Figure 2. (a) Synthetic route to NBD-protected 4-arm monomer, followed by deprotection with tetrazine to reveal the pure, unmasked Cp derivative. (b) ^{1}H-NMR shows the clean formation of the free Cp units with negligible appearance of Cp dimers or 1,5-H shift isomers.

description and calculation). Furthermore, at high temperatures, an equilibrium between forward and retro-DA reactions provides a pathway to equilibrate the system to the thermodynamically most stable network. Even though these attributes potentially complicate the preparation of ideal networks, they raise new opportunities to study and tune polymer network properties. Here, we identify three important factors to access better-defined Cp cross-linked homopolymer networks (Figure 1b): (1) efficient and scalable access to a well-defined Cp monomer; (2) modifying the substitution pattern of the Cp chain ends to suppress the 1,5-sigmatropic hydride (1,5-H) shift and minimize uncontrolled trimer cross-linking; and (3) utilizing a tetrafunctional monomer (A_4) to control the end-linked network branch functionality primarily through dimerization rather than uncontrolled trimerization. The realization of these goals, including the isolation of a well-defined pentaerythritol-based Cp monomer, is described. Contrary to previously uncontrolled preparation of Cp-based polymers, the resulting network has a near-room-temperature glass transition temperature (T_g), elastomeric tensile behavior, and cold shape memory effect. Moreover, the material is degradable because it is formed in its entirety by reversible cross-linked covalent bonds. The strategy provides a new general platform, based on step-growth polymerization of A_4 + A_4, to access single-component Cp-based polymer materials with better-defined and tunable properties.

■ RESULTS AND DISCUSSION

Monomer Synthesis and Stability. While exploring the use of norbornadiene (NBD) as a "masked" Cp group,[29,30] we envisioned that access to a pentaerythritol core, substituted with four NBD units (**2**), could serve as an ideal precursor to synthesize and isolate a 4-arm Cp monomer **3**. The NBD adduct can be efficiently prepared on a 10 g scale and deprotected under mild reaction conditions at room temperature, thus enabling the isolation of this notoriously challenging monomer (Figure 1b). The highly efficient deprotection proceeds through an inverse electron demand DA (IEDDA) reaction in the presence of dipyridyl tetrazine (DpTz) to afford a reactive intermediate that subsequently undergoes an rDA reaction that results in the formation of the desired Cp derivative and the corresponding dipyridyl pyridazine (DpPz) byproduct (Supporting Figure S12). Due to the known effects of substitution patterns on the reactivity of Cp derivatives,[31−38] we also postulated that the previously reported utilization of the pentyl-substituted Cp derivative[29,30] could help minimize premature dimerization and 1,5-H shift.

Following the straightforward synthetic route in Figure 2a, 4-arm NBD substrate **2** was prepared by reacting the carboxylic NBD derivative **1** with pentaerythritol via carbodiimide EDC coupling. The isolation of tetratelechelic Cp (TCp) monomer **3** was subsequently tested on a 6 mg scale using our deprotection approach with DpTz.[29] Heating **3** at 50 °C for 18 h in a vacuum oven resulted in a cross-linked polymer as confirmed via its insolubility in dichloromethane. Despite the encouraging preliminary results, we noted a small yellowish byproduct during the isolation of compound **3** (~2%). Therefore, optimization of the deprotection conditions, such as concentration, stoichiometry of tetrazine, and reaction time (Supporting Table S2), was necessary to isolate the pure single Cp isomer, as shown by ^{1}H-NMR spectroscopy (Figure 2b). We found that the treatment of **2** with 10.5 equiv of tetrazine at RT for 2 h, followed by chromatography, afforded **3** in 57% isolated yield on a gram scale. With access to the pure TCp monomer, we next studied the stability of **3** toward 1,5-H shift and dimerization at room temperature. To our gratification, we

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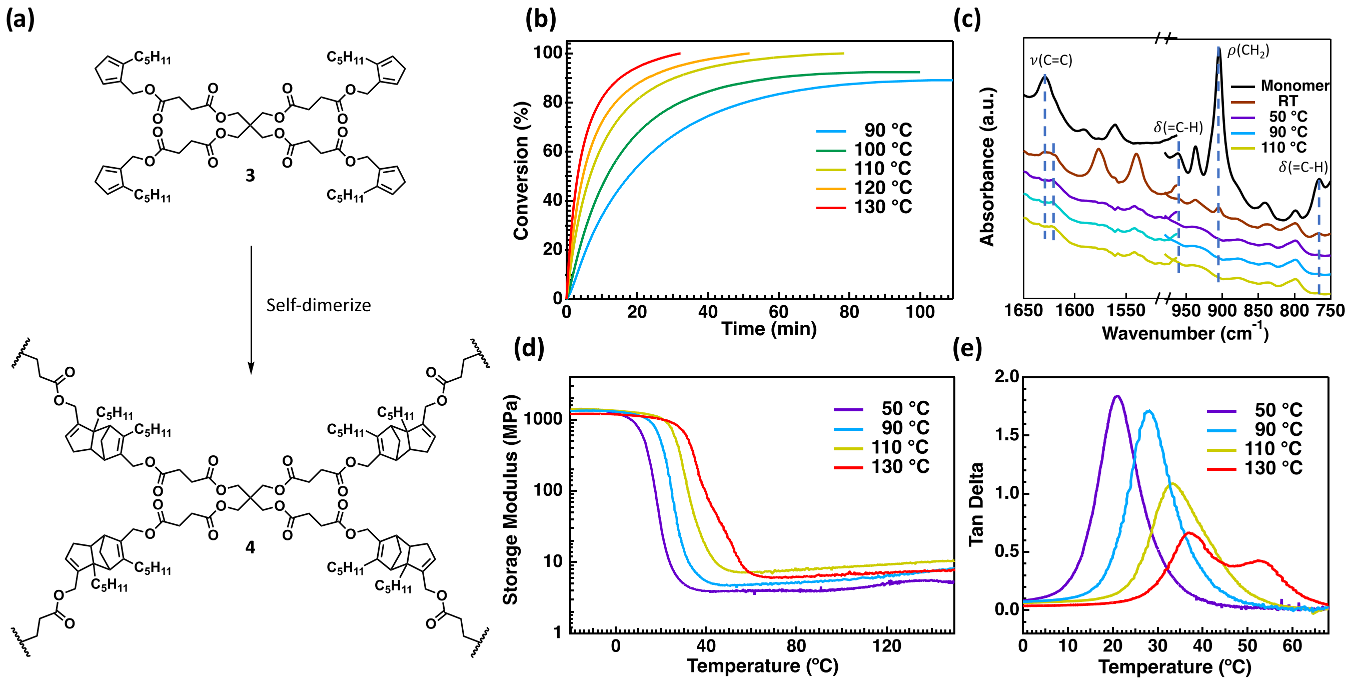

Figure 3. (a) TCp monomer was cured under different conditions: at RT for 9 days, 50 °C for 24 h, 90 °C for 120 min, 110 °C for 100 min, or 130 °C for 80 min. (b) Isothermal conversion plot demonstrates the curing efficiency of the TCp monomer at different temperatures. (c) FTIR spectrum shows full consumption of Cp chain ends for samples cured at high temperatures (>90 °C). (d) Storage modulus from the rubbery plateau region of the DMA spectrum is correlated to molecular weight between cross-links (M_c). (e) Comparison of tan delta curves for different samples reveals molecularly heterogeneous cross-linking at high temperatures (e.g., 130 °C).

observed that on short timescales (1-5 h), the dialkylated substitution of the Cp units resulted in minimal dimerization and 1,5-H shift. The isolated Cp chain ends were monitored at ambient atmosphere via ^{1}H-NMR spectroscopy (both neat and in solution) to observe the course of 1,5-H shift and dimer formation. The amount of dimers and constitutional isomers generated within 5 h is negligible (<10% dimers and 3% isomers), establishing a working timeline for the isolation and polymerization of the TCp monomer. Of note, the dimers form more readily than the 1,5-H shift isomers; the latter were not observed until after 1 h (Supporting Figure S14). These results demonstrate the ability to isolate a pure single Cp isomer, potentially allowing the construction of a better-defined homopolymer network, polytetracyclopentadiene (PTCp, **4**, Figure 3a). Furthermore, the TCp monomer is stable when stored in a freezer up to 1.5 months (<0 °C); thus, successful polymerization is not required immediately after isolation. We also tested the possibility of uncontrolled cross-linking, presumably due to trimer formation, by polymerizing a two-arm Cp model compound (Supporting Figures S15 and S16). Despite the structural analogy to Wudl's two-arm Cp adduct,[24] the sol−gel test showed minimal gel formation (approximately <25%) (Supporting Figure S16). This suggests that the substitution pattern, including the pentyl side chain, helps suppress uncontrolled trimer formation. There are also other factors that can induce the aforementioned gelation in the model system, such as the possible entanglement of the long linear chains or radical-mediated cross-linking. We investigated these possible hypotheses and discovered that the addition of a radical inhibitor (5 mol % BHT) to the polymerization of the two-arm Cp model at 90 °C completely inhibits gelation (Supporting Figure S17). We also further confirmed the absence of trimer by analyzing the mass spectrum of a monofunctional Cp model after heating it neat for 25 h at 90 °C (Supporting Figure S18b). Current studies are ongoing to evaluate if further modification of the sterics and electronics of the substituents will enable access to high-molecular-weight linear polymers.

Polymer Synthesis and Monitoring. With access to the desired TCp monomer, the kinetics of the step-growth A_4 polymer network formation was investigated. The homogeneous nature of the monomer enabled the efficient bulk polymerization of **3**, and its behavior was monitored at different curing temperatures via differential scanning calorimetry (DSC) (Supporting Figure S21). As seen by the conversion plot in Figure 3b, after 100 min, the sample heated at 90 °C can reach up to 89% conversion of the Cp chain ends. The quantitative conversion of chain ends includes those at 110, 120, and 130 °C with the timescales of 80, 50, and 30 min, respectively. Of note, we refrain from curing at higher than 130 °C due to the increased rate of side reactions at an elevated temperature (e.g., radical process) and to avoid accessing a monomer−dimer equilibrium via the dynamic rDA/DA reaction. Based on the conversion plot, the Cp monomer was cured at 50, 90, 110, and 130 °C, and the resulting polymer samples were monitored via Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). The intensity of C═C stretching at 1628 cm^{-1} from the monomer was diminished and red-shifted to 1620 cm^{-1} for all samples that are cured at 50 °C or higher. The sample cured at RT for 9 days still shows a broad peak across 1628−1620 cm^{-1}, showing incomplete consumption of Cp chain ends. The bands at 960, 904, and 765 cm^{-1}, which are characteristics of Cp cyclic C−H and CH_2 bending,[39] completely disappear for samples cured at or higher than 50 °C. Again, the room temperature sample still shows retention of peak intensity, compared to full peak disappearance from other samples (Figure 3c).

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Cross-Linking Assessment. Dynamic mechanical analysis (DMA) was then utilized to measure the experimental molecular weight between cross-links (M_c) (Supporting Table S3), which was then compared to the theoretically ideal value (Supporting Figure S28). Figure 3d shows that with increasing curing temperatures, the rubber plateau modulus E'_p increases, and correspondingly, M_c decreases. This trend reflects the increasing amount of cross-link density as a function of curing temperatures. The tan delta peak intensity reasonably becomes lower and broader with increasing T_g values. However, the 130 °C cured sample exhibits lower E'_p (or higher M_c) compared to the 110 °C cured sample (Supporting Table S3). The tan delta peak of this sample is also bimodal compared to a single peak from other samples (Figure 3e). This might result from the heterogeneity of cross-link density due to the difference in segmental mobility, thermal lag,[40] or possible competing rDA reaction while curing at 130 °C. From the experiment with the two-arm model system, we postulated that the radical process likely occurred at a high curing temperature and could contribute to the appearance of the bimodal tan delta curve. Therefore, we repeated the curing of the sample at 130 °C with and without BHT (5 mol %) and observed that the bimodal appearance was completely suppressed with BHT addition (Supporting Figure S29b), which further supports our hypothesis. Even though higher curing temperatures normally lead to higher cross-link density, other factors can be involved (e.g., vitrification, side reactions, decomposition, etc.).[41,42] Hence, the optimal curing condition for this system was determined to be at 110 °C for 100 min. Under these conditions, the calculated M_c is 875 g/mol, compared to the theoretically ideal value of 558 g/mol (Supporting eq S3, Table S3). Of note, the calculated value is an estimate because it neglects the coefficient of thermal expansion, which is essential to determine the temperature-corrected density. Due to the limited mobility in the gel state, especially with a multifunctional cross-linker, the presence of network imperfections (i.e., loops, chain entanglement, and dangling chains)[9,11,43,44] is normal, and therefore, it is not surprising that the experimental M_c is larger than the theoretically ideal value (Supporting Figure S28). Since the unavoidable network imperfections can possibly influence the property of our material (e.g., T_g values), we further studied the controlled defect materials by reacting Cp chain ends with substoichiometric amount of maleimides (5−15 mol %). We attributed these capped chain ends analogous to dangling chain ends and to some extent, loop defects. We used *N*-phenyl maleimide (*N*-PhM) as our initial candidate. However, we surprisingly observed a large counter-effect of crystallinity in our material. T_g values increased by more than ∼10 °C, despite a supposedly lower amount of cross-linking in our system (Supporting Figure S30a). We then switched to *N*-methyl maleimide (*N*-MM) and observed that T_g values reasonably decreased with an increasing amount of added *N*-MM. However, the variation was insignificant (∼5 °C with 15 mol % capped Cp, as shown in Figure S30b). As reflected in the control experiments, to a first approximation, we assume that the properties of our materials were not affected significantly by chain-end network defects, but further studies are warranted.

Physical and Mechanical Properties. The homopolymer network **4** is faintly yellow, fully transparent, and flexible with a density of 0.88 ± 0.05 g/cm^3. The sample, cured at 110 °C for 100 min, shows a T_g of 33 °C (from tan delta max) with a storage modulus before glass transition of 1.4 GPa (at T = −15 °C). The storage modulus remains in the sufficient value of ∼9−10 MPa during the plateau region of up to 160 °C (Supporting Figure S31), which indicates minimal effects from the dynamic rDA/DA reactions at these temperatures and suggests that physical aspects of chain flexibility and mobility also hold significant importance to the thermal stability of the material. Uniaxial tensile tests were also performed, revealing an ultimate tensile strength of 11.8 ± 1.3 MPa and elongation at break of 101.6 ± 3.51% (Supporting Figure S33). The Young's modulus was determined to be 221.4 ± 23.9 MPa (Table S4). The tensile behavior reflects a tough and elastic material, which is comparable to rubber and thermoset elastomers[45−48] (Figure 4). Of note, by controlling the molecular weight between cross-links via structural designs and curing conditions, we were able to lower the T_g to near room temperature. In contrast, previous Cp materials appear as glassy and brittle thermosets with high T_gs, due to the uncontrolled cross-link density, which resulted from the extensive formation of trimers and oligomers.[18−22,24] For example, the only report of a processable Cp cross-linked homopolymer from Wudl has the lowest T_g of 89 °C.[24] These results demonstrate that the viability of controlled cross-linking, via dimerization of well-defined Cp monomers, enables access to new compelling Cp-based materials.

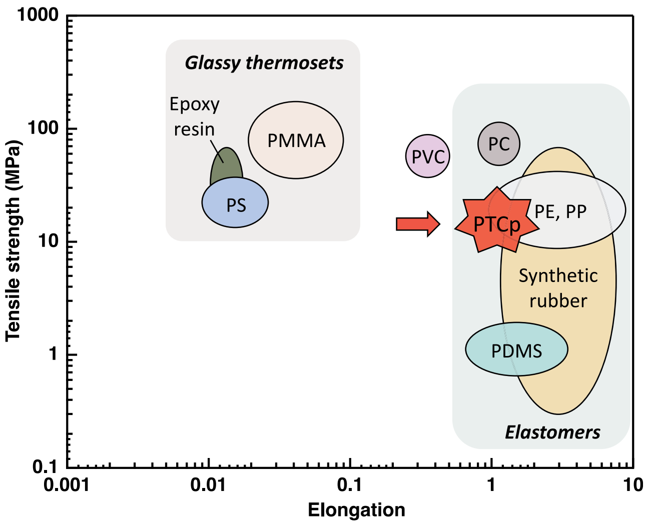

Figure 4. Ashby plot of tensile behaviors of common thermoset elastomers versus strong and glassy thermosets. The plot shows that PTCp can be categorized as a thermoset elastomer.

Shape Memory and De-cross-linking. After confirming the rubber elasticity of the homopolymerized material, the viscoelastic behavior of **4** was studied by creep−recovery experiments. High elastic recovery was observed below the yield stress of 0.62 MPa at 0.2% strain (Figure 5a). Based on the shape-recovery ability and sufficient storage modulus difference during glass transition, a cold-programming shape memory behavior was also demonstrated, taking advantage of the T_g in the range of 10−30 °C.[49,50] The desired shapes can be fixed at 0 °C (below T_g) and the original shape can recover at room temperature (or higher than T_g). This process is illustrated in Figure 5b, where the original rectangular shaped material can be reconfigured into a U- or S-shape at RT. The new shapes were then "locked" by immersing in an ice bath at 0 °C. Upon warming to RT at ambient atmosphere, the

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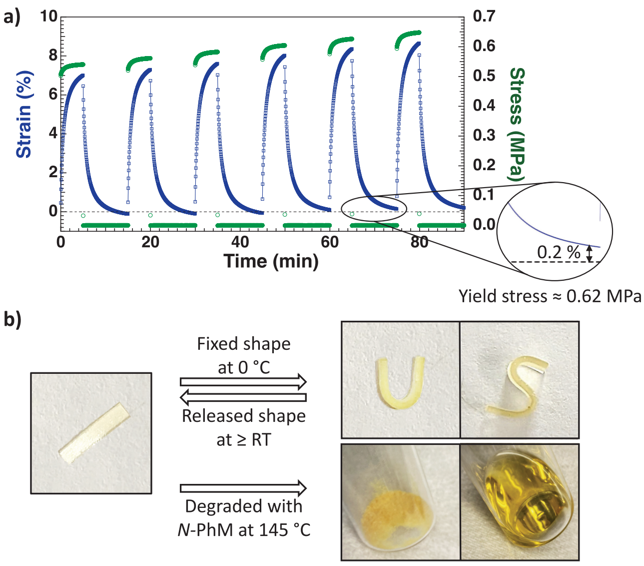

Figure 5. (a) Creep−recovery experiments demonstrate high elasticity below the yield stress. (b) Shape memory was cold-programmed due to the near-room-temperature T_g; polymer degradation with *N*-PhM at 145 °C results in a yellow solid (left picture) that is soluble in DCM (right picture).

material returns to its original shape within 35 s, while it takes ~5 s in a 30 °C water bath (Supporting Videos S1, S2, and S3). To further highlight the advanced properties of this material, we sought to demonstrate the ability to convert the highly cross-linked material to small and soluble oligomers. Because **4** is comprised almost entirely of Cp cross-linking dimers, it presents unique and exciting opportunities for selective degradation upon heating above the rDA temperature (150−180 °C).[25,51] To evaluate this potential feature, the polymer was heated in refluxing xylene (~145 °C) in the presence of *N*-PhM, which served as a DA capping reagent. As expected, the degraded polymer network, yellow solid, was completely soluble in DCM upon treatment due to these conditions (Figure 5b). The soluble material was analyzed by ^{1}H-NMR and ^{13}C-NMR spectroscopy to assess de-cross-linking and capping with *N*-PhM by the presence of characteristic Cp-maleimide adduct peaks (Supporting Figure S35). We also repeated the degradation experiment with N15-labeled maleimide (i.e., *N*15-PhM) and analyzed the crude mixture via heteronuclear multiple bond correlation (HMBC) NMR spectroscopy (Supporting Figure S36). The signal at 195 ppm further confirms the capping of Cp chain ends (Supporting Figure S37). Analysis of the 50 °C cured sample after degradation (24 h in refluxing xylene) by gel permeation chromatography (GPC) indicated an oligomeric mixture of approximately 1−3 repeat units. The GPC curve of the 110 °C cured sample also showed degradation after heating in refluxing xylenes for 48 h. However, a smaller molecular weight of the original monomer was observed. One possible explanation is that the polymer might be partially degraded along the backbone upon exposure to the high temperature for an extended period. Heating the cross-linked polymer in refluxing xylene for 24 h without *N*-PhM resulted in the formation of a yellow but insoluble solid in DCM (Supporting Figure S38), presumably due to decomposition. These examples illustrate that the improved network formation of highly cross-linked Cp homopolymer leads to the near room temperature T_g, as well as elastomeric and shape memory properties. Since polymer **4** is formed entirely from dynamic DA cycloaddition, the self-healing behavior of the material was investigated. Unfortunately, the material became fragile when heated to its rDA temperature (150 °C for a few hours), preventing self-healing studies. As such, current studies are ongoing to improve the material with suitable structural modification to enhance its viscosity (i.e., incorporation of soft-linkers into the core 4-arm structure) to hopefully improve self-healing properties.

CONCLUSIONS

We have demonstrated an unprecedented and feasible protocol for the synthesis of a Cp network homopolymer, PTCp. Despite an early interest by Staudinger, the applications of DA homopolymer networks have remained in a nascent stage over the past century due to the formidably uncontrolled reactivity of Cp. Here, by efficiently accessing a pure Cp monomer, TCp, under mild conditions and through controlling the subsequent homopolymerization, we have discovered intriguing characteristics of the macromolecule, such as near-room-temperature T_g, as well as elastomeric and shape memory properties. We believe that the emergent properties and accessible methodology will encourage new syntheses and studies of Cp-based advanced materials that will take advantage of its homogeneous bulk polymerization, better-defined cross-link architecture, compelling shape flexibility, and degradability. Though the emergent property of polymer **4** is comparable to elastomeric materials with a compelling T_g and selective de-cross-linking, there are certain limitations as follows and current studies for further improvement are ongoing: (i) the tensile strength and strain of polymer **4** identify a tough material but are not on par with the current state-of-the-art polymers, such as polycarbonate or synthetic rubber; (ii) self-healing of the material was not observed, presumably due to the lack of flexible chain extenders within our structural design. Further investigation will explore the generality of the new single-component homopolymerization of Cp-based monomers, targeting the incorporation of flexible and functional units between the core and terminal Cp units to enable self-healing materials with enhanced mechanical properties, as well as access to high-molecular-weight linear polymers.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/jacs.2c11416.

- Synthetic procedures, characterization (NMR, GPC, TGA, DSC, DMA, and FTIR), and mechanical testing via a texture analyzer (PDF)
- Real-time videos of shape memory experiments, SShape_recovery (MOV)
- UShape_recovery (MOV)
- UShape_Recovery_water (MOV)
- Atomic coordinates of the optimized geometries of 9 structures (ZIP)

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Notes

The authors declare no competing financial interest.

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