RESEARCH ARTICLE

Triggered Crosslinking of Main-Chain Enediyne Polyurethanes via Bergman Cyclization

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Crosslinking chemistries occupy an important position in polymer modification with a particular importance when triggered in response to external stimuli. Enediyne (EDY) moieties are used as functional entities in this work, known to undergo a pericyclic Bergman cyclization (BC) to induce a triggered crosslinking of polyurethanes (PU) via the intermediately formed diradicals. Diamino-EDYs, where the distance between the enyne-moieties is known to be critical to induce a BC, are placed repetitively as main-chain structural elements in isophorone-based PUs to induce reinforcement upon heating, compression, or stretching. A 7-day compression under room temperature results in a ≈69% activation of the BC, together with the observation of an increase in tensile strength by 62% after 25 stretching cycles. The occurrence of BC is further proven by the decreased exothermic values in differential scanning calorimetry, together with characteristic peaks of the formed benzene moieties via IR spectroscopy. Purely heat-induced crosslinking contributes to 191% of the maximum tensile strength in comparison to the virgin PU. The BC herein forms an excellent crosslinking strategy, triggered by heat or force in PU materials.

1. Introduction

Activation of chemical bonds to induce crosslinking in polymers is a common strategy to modify and obtain polymer networks. Similar to conventional thermal, photo, and redo-x methodologies, activating chemical bonds by strain is attractive.[1,2] Thus chemical bonds and bonding entities termed mechanophores can be activated by molecular forces, representing a promising technique for responsivity in materials by directing specific strain-dependent reaction pathways.[2–7] Since the first observation of mechanically-induced bond-rupture by Staudinger[8] in

the 1930s, tremendous efforts have been accomplished in developing specific mechanophores,[9,10] wherein an applied strain is correlated to an effective geometry, chemistry, or location of a bond. Major factors to tune the efficiency of force on a chemical reaction are the position of the applied force on the specific bond[11] in view of its regiochemistry,[12,13] the position,[14] type,[15,16] and length[17] of attached polymer chains, and also the material morphology such as in semicrystalline[18] polymers or microphase-segregated block copolymers.[19] The use of such chemistries allows to induce chemical reactions, such as crosslinking, to form permanent networks in materials at positions where either stress or heat has been applied.

Pericyclic reactions have been investigated intensely as potential mechanophores as the geometry of bonding arrangements and the resulting molecular strain can be well predicted therein.[3,20–29] To this end, cyclo-reversion-chemistries, such as in 1,2,3-triazoles,[30,31] cyclobutanes,[32–34] dimeric anthracenes,[35] anthracene–maleimide adduct,[36,37] coumarin dimer,[38] methanone-tethered cinnamate dimer,[39] or dihalocyclopropanes,[40] can be induced mechanically, addressing even forbidden reaction pathways not accessible via purely thermal or photochemical reactions.[29] The activation in solution via ultrasound, in embedded materials, such as thermoplastic polymers or networks, and of single molecules (via single-force molecules spectroscopy, SFMS) have been accomplished.

In our search for stress-induced crosslinking chemistries in solid polymers we came across novel pericyclic reaction chemistries, such as the Bergman cyclization (BC), as a potential target. In Bergman cyclization, enediynes (EDYs) undergo a cycloaromatization to generate a 1,4-phenyl-diradical[41] mainly influenced by proximity effects,[42–44] namely the distance between the acetylenic carbon atoms (d) (**Scheme 1**). Additionally, the electronic effects brought by substituents[45] and molecular-strain differences[46–48] allow an excellent tuning of the EDY's reactivity on a molecular basis.[49] Conventionally, the BC is induced thermally,[41] by photochemistry,[50–53] or by metal catalysis.[54,55] Inspired by these unique properties, we herein report on the crosslinking of a polyurethane (PU) polymer embedded with EDYs as the active element embedded therein. We highlight the function of EDYs as the resource of diradicals via Bergman cyclization, which undergoes coupling partially to induce covalent

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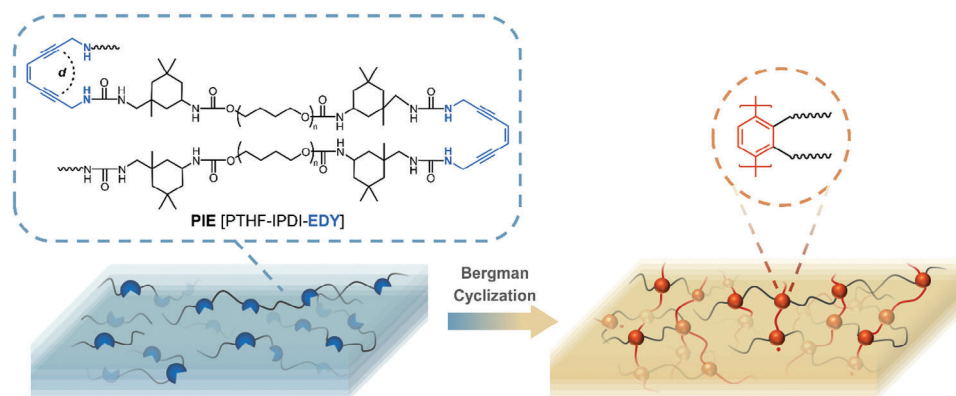
Scheme 1. Schematic illustration of the designed enediyne (EDY)-embedded polyurethane (PU) and the triggered crosslinking via Bergman cyclization.

Table 1. Overview of the composition of PUs containing enediynes (EDY) (samples **PIE**, **PME**) and the PU without EDYs (**PIC**).

| Sample	Compositions			$M_{n, GPC}$ [kDa]
	Prepolymer 1 equiv.	Diisocyanate 2 equiv.	Diamine 1 equiv.	
PIE	PTHF	IPDI		10.6
PME		MDI		25.3
PIC		IPDI		8.6

crosslinking, in turn leading to an efficient hardening of the PU material. The activation used here varied from conventional heat to force observing hardening phenomenona which leads to novel types of responsive materials.

2. Results and Discussion

We recently reported the BC of EDYs embedded into the main chain of polyimines in solution to tune a chain-length dependent Bergman cyclization with different structural elements.[56] The potential of EDYs as latent crosslinking agents was first considered in the 1990s,[2] expected to activate upon swelling a network equipped with embedded EDY's by triggering a BC via changing the distance of the terminal acetylen-units.[57] Despite significant experimental and theoretical efforts[57,58] this behavior has not been proven in materials, neither by temperature nor strain. Based on the known theoretical background[30] we designed EDYs embedded into linear PUs, where we expected that activation of a BC would lead to a subsequent crosslinking via the intermediate biradicals. Due to the presence of hydrogen bonds at the joiningurea groups, we expected facilitstion of the

BC, as BC is accelerated using metal-coordination close to the EDY-moieties,[59] and thus the chance to promote subsequent crosslinking chemistries in the PUs. EDYs embedded directly into the main chains of the linear PUs could display an enhanced activation, in turn inducing measurable and observable evidence of a BC in the formed PU network, although BC in acrylate-based networks could not be observed previously.[57]

Based on an amine-functional EDY, (Z)-octa-4-en-2,6-diyne-1,8-diamine (**Figure 1**A),[60] we were able to introduce EDY into the main chain of a PU, resulting in the polymer **PIE** containing ≈3 EDY-groups per chain in average (**Table 1**). We first generated an isocyanate-terminated polytetrahydrofuran (PTHF, 2.9 kDa) with isophorone diisocyanate (IPDI, molar ratio PTHF/IPDI = 1/2), followed by polyaddition with an equimolar amount of the (Z)-octa-4-en-2,6-diyne-1,8-diamine. The choice of IPDI was motivated by generating PUs of appropriate hardness, able for subsequent testing via the available rheology/stress–strain testing methods. Results from NMR spectroscopy (Figure 1B, assigning chemical shifts of the double bond (δ = 5.79 ppm, red dot) and the methylene group (δ = 4.14 ppm, purple dot)), gel permeation chromatography (Figure 1C) and

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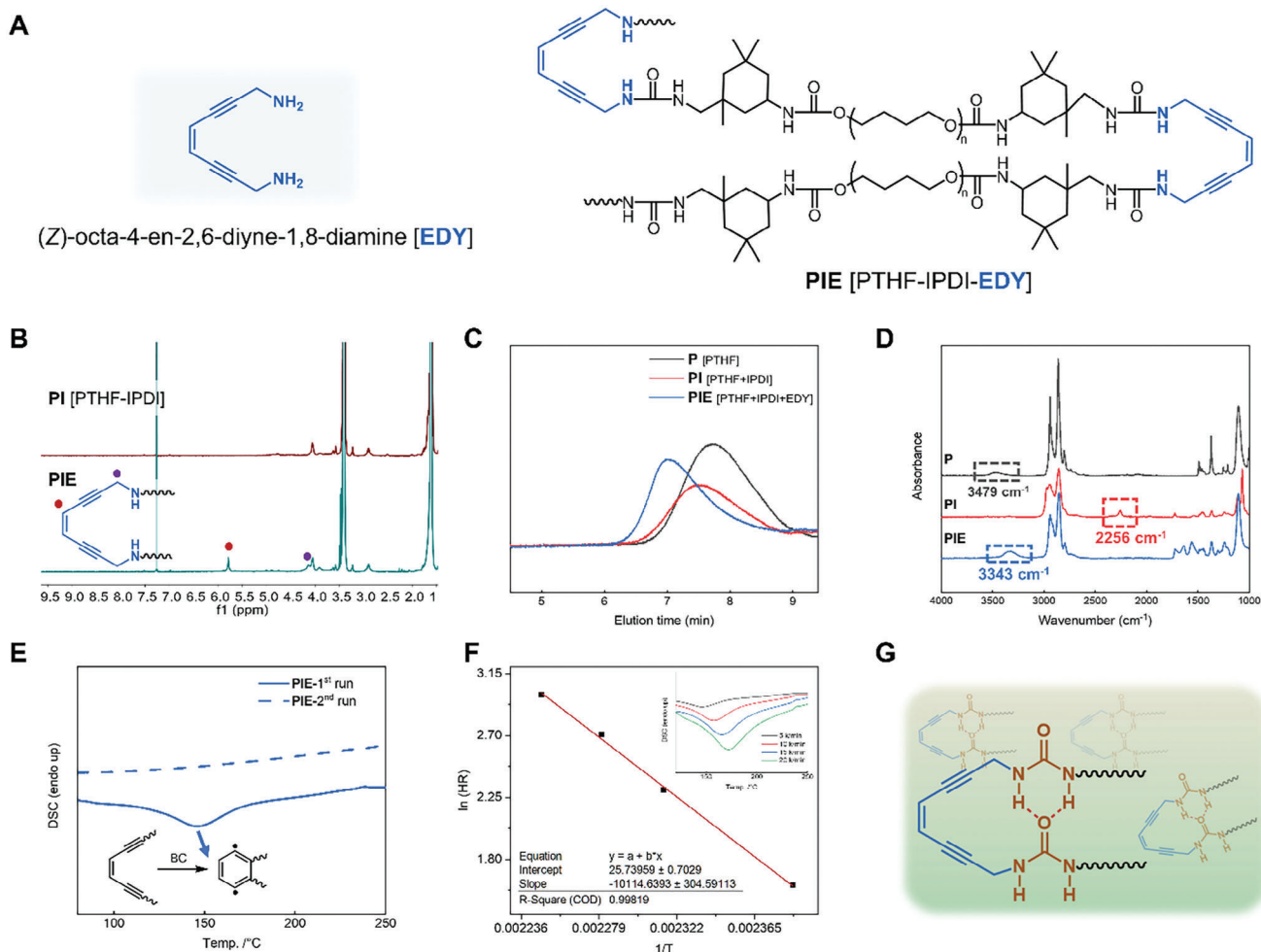
Figure 1. Synthesis and characterization of the main chain enediyne elastomeric PU polymer **PIE**. A) Chemical structure and compositions of **PIE**. B) Comparison of the ^{1}H NMR between the isocyanate-terminated PTHF and **PIE**. C) GPC of the initial PTHF, the isocyanate-terminated PTHF, and **PIE**. D) FT-IR. E) Two-cycle DSC curves under heating condition, N$_2$ atmosphere, 5 K min^{-1}: the first cycle (lower solid line) and the second cycle (upper dashed line). F) Arrhenius plot for the Bergman cyclization of **PIE** in neat conditions obtained by DSC measurements using ASTM E698 standard procedure. Inset: DSC thermograms at four heating rates (HR) of 5, 10, 15, and 20 K min^{-1}. G) The hydrogen bonds between the urea groups in the joint of the enediyne moieties.

FT-IR spectroscopy (Figure 1D) gave evidence of the successful synthesis of the targeted polymer **PIE** and the successful incorporation of the EDY-moieties with a molecular weight of ≈10.6 kDa. As depicted in Figure 1D, a full conversion of all NCO groups after the second reaction step was proven by FT-IR spectroscopy with the disappearance of the characteristic —NCO group at 2256 cm^{-1} and the emergence of the —NH stretching band at 3343 cm^{-1}. Increasing peaks (around ≈1600 cm^{-1}) showed the appearance of the urea group (Figure S5, Supporting Information). Similar to literature,[61] the bulky chain elements between the EDYs impeded the detection of the alkynyl group in IR-spectroscopy. In a similar procedure, we also prepared **PME** (containing EDY, methylene diphenyl diisocyanate (MDI, instead of IPDI)), and a sample devoid of EDY as control (**PIC**) (Table 1).

The so-formed **PIE** was then checked for a thermally induced BC reaction: considering that BC is an exothermic reaction, the existence of the EDYs was verified with two cycles of differential scanning calorimetry (DSC) as shown in Figure 1E (and Figures

S6 and S7, Supporting Information). Under an atmosphere of N$_2$, **PIE** was heated to 250 °C, followed by cooling to 25 °C and a second heating process. The exothermic peak ($T_{peak} = 145.96$ °C) in the first cycle (solid line), which was attributed to the completion of a thermally triggered BC of the EDY moieties, did not appear in the second heating process (dashed line). The calculated exothermic value ($\Delta H = 63.9$ kcal mol^{-1} EDY) is within expectations for the exothermic EDY cyclization.[62] With the method of the ASTM E698 standard procedure,[63] DSC thermograms of neat **PIE** at four heating rates (HR) of 5, 10, 15, and 20 K min^{-1} yielded an Arrhenius plot for its BC with calculated activation energy as 20.1 kcal mol^{-1} (Figure 1F and Table S2, Supporting Information). According to the literature,[65] the ASTM E698 method is reliable for comparing the reactivities of BC in structurally similar compounds, leading to verified and justifiable amounts of BC in our series of PU materials. Therefore this method was utilized specifically to compare the reactivities of **PIE** and **PME**. For a pericyclic reaction like BC, the hydrogen bonds, present not only be-
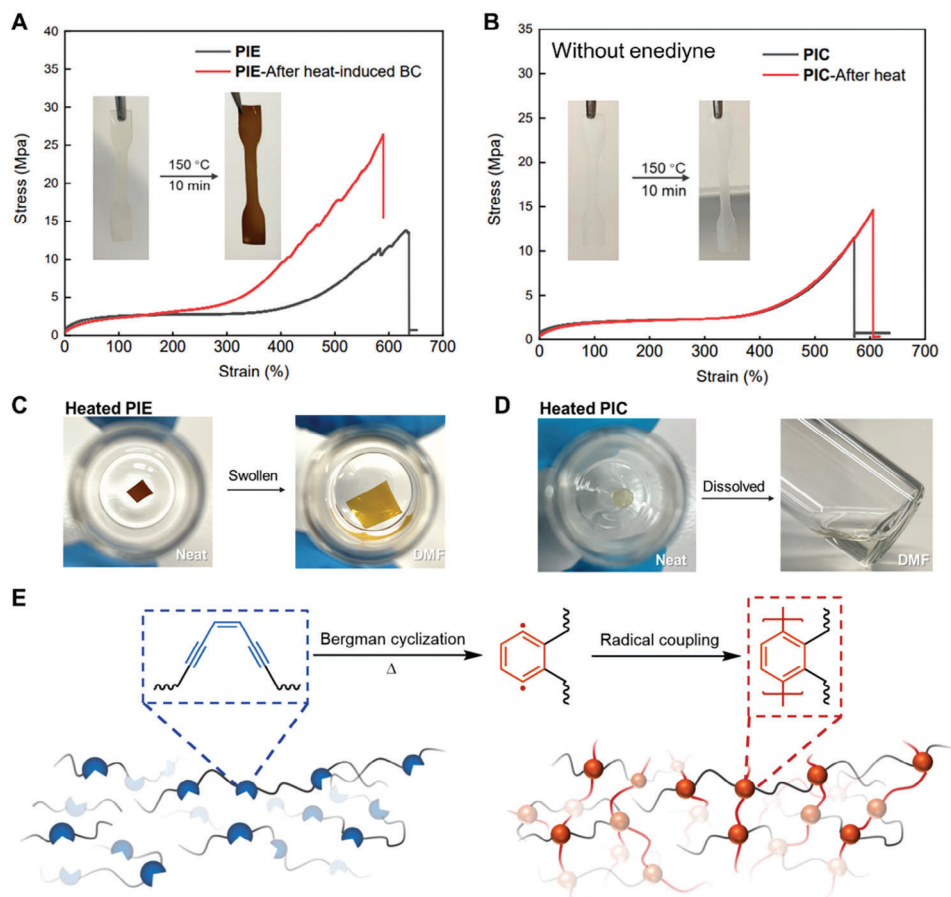
Figure 2. Changes in material properties induced by Bergman cyclization by comparing EDY-PU of **PIE** and the negative control **PIC** without EDY. A) Tensile tests of **PIE** before and after heat. B) Tensile tests of **PIC** before and after heat. C) Swelling test of heated **PIE** in DMF. D) Dissolution of heated **PIC** in DMF. E) Proposed mechanism of the generation of crosslinks induced by Bergman cyclization in the enediyne-embedded chains.

tween the PU chains but also between the urea groups in the joint of the EDY moieties as shown in Figure 1G, assist to reach this comparably low Ea value. Replacement of MDI by IPDI (**PME**) favoring hydrogen bonding between the PU chains[64] gave an even lower Ea value of 14.1 kcal mol^{-1} (Figures S12–S18, Supporting Information), which was considered too low, also taking into account the possibility of an underestimation in solid polymers as stated in literature[65] (Figure S18, Supporting Information).
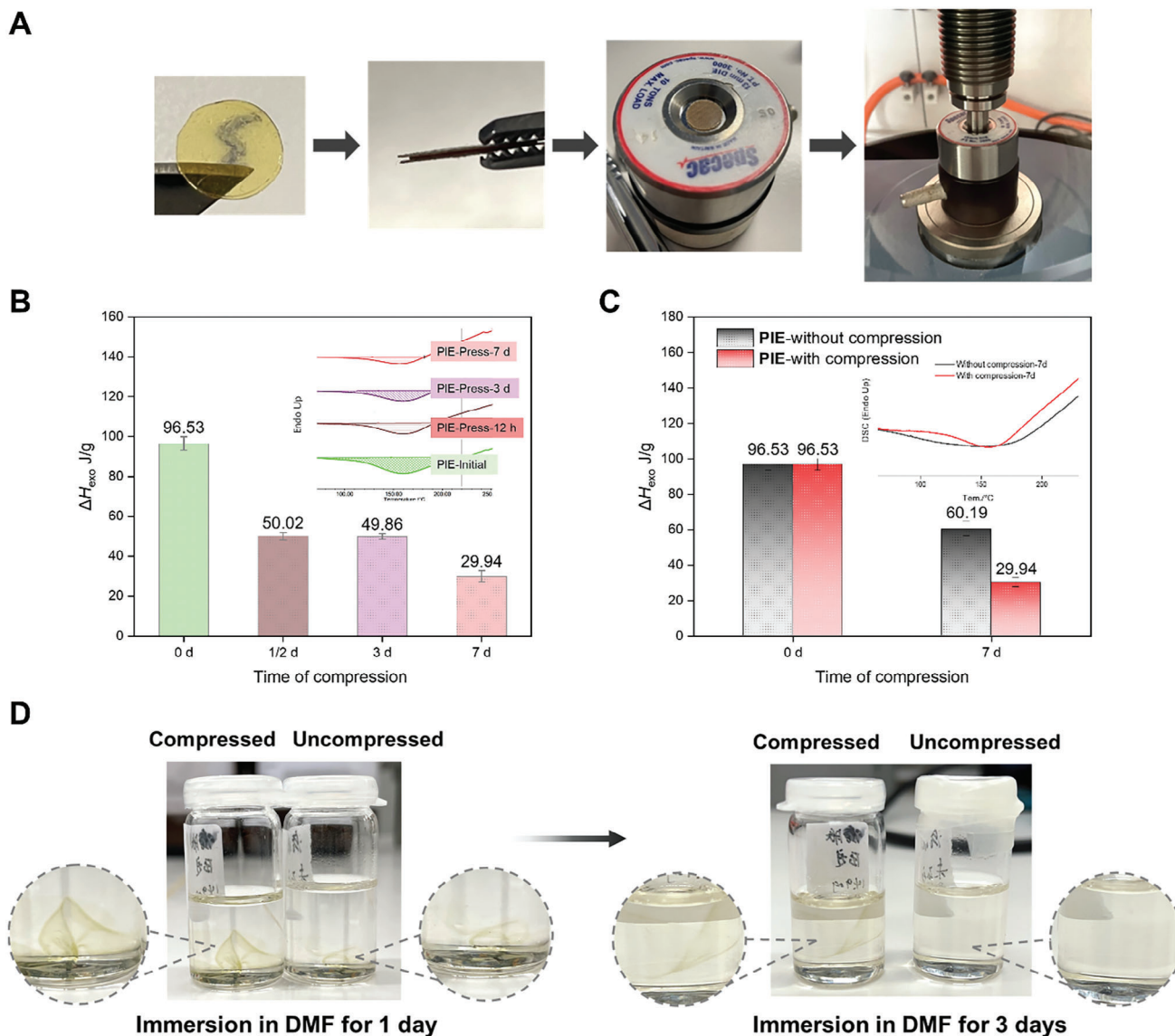
For comparison the polyurethane **PIC** (devoid of EDY-moieties) was synthesized as a negative control, derived from the polyaddition between the initially used isocyanate-terminated PTHF and octane-1,8-diamine, which possesses the same length of the carbon chain with EDY ($M_{n, GPC}$ = 8.6 kDa, Figures S19–S22, Supporting Information). To verify the crosslinking potential brought by the embedded EDYs, conventional heat induction with **PIE** (containing EDY) and **PIC** (devoid of EDY-unit) were first attempted, followed by stress–strain tests to prove the formation of additional covalent crosslinks during the dimerization of the diradicals formed via BC. Freshly made **PIE** and **PIC** were thus placed at 150 °C for 10 min, followed by tensile tests after cooling. As shown in **Figure 2**A, for **PIE** before and after heating, a significant improvement of the tensile strength was observed, increasing to a maximum value of 26.4 MPa (191% of the maxi-

mum tensile strength of the virgin sample), an effect which was not observed for **PIC** (devoid of EDYs) (Figure 2B).

Subsequently, pieces of the two heated samples (**PIE**, **PIC**) were soaked in DMF as shown in Figure 2C,D to probe the crosslinking density. The **PIE**-sample immediately swelled in the solvent, reaching 157% of swelling degree after swelling for 72 h (equilibrium), indicative of permanent crosslinks with a calculated density v_c as 5.50×10^{-4} mol cm^{-3} according to the Flory–Rehner equation,[66] Table S4, Supporting Information. In comparison, **PIC**, which remained unchanged in its tensile strength and appearance, completely dissolved in the solvent. As illustrated in Figure 2E, triggered by heating, EDYs embedded in the PU chains underwent Bergman cyclization and were transformed into the diradical species which could recombine randomly resulting in covalent crosslinking to form a permanent network. The resulting conjugated system of benzene rings shifted the absorption to a longer wavelength in line with previous observations in literature[67] made from BC-cyclization and subsequent aromatization. Monitoring with UV–vis under heated conditions (Figure S8, Supporting Information) supported this assumption.

After using heat as an external trigger we then tested a pressure-induced activation of the BC as a further trigger to in-

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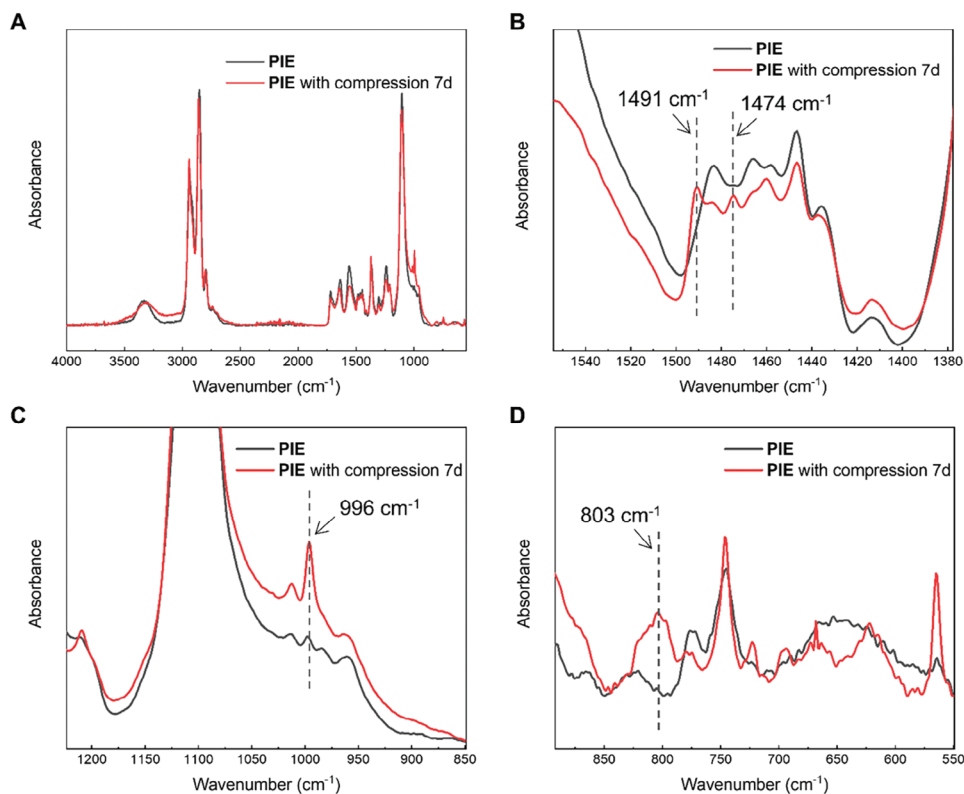
A

B

C

D

Figure 3. Compression test applied to the elastomeric enediyne PU polymer **PIE**. A) Compression device and operations taken during the compression. B) Monitoring with DSC during the 7-day compression of **PIE**. C) Comparison of ΔH calculated by DSC between **PIE** with or without compression for 7 days. D) Comparison of solubilities in DMF between PIE with or without compression.

duce crosslinking chemistry (**Figure 3**A).[16,20] Thus a combination of compression tests of **PIE** and DSC was utilized to monitor BC owing to its exothermal feature. With the transparent and elastomeric **PIE** in hand, the compression test proceeded by covering the well-shaped sample with two PTFE films and placing it in a press with a force of 10 tons ranging from 12 h to 7 days. As it is expected that after BC activation the materials should display a lower heat-of-conversion in an thereafter conducted DSC analysis, the decline in reaction heat can be correlated to the fraction of BC achieved during the compression cycles. As shown in Figure 3B, in neat samples that had experienced compression of various durations (up to 7 days), the exothermic values of each sample decreased gradually with time. Compared to the initial sample, 12 h of compression brought a ≈48% decrease in the exothermic value, which dropped by ≈69% after 7 days.

In parallel samples without compression were studied under the same conditions, but without compression and in the dark, to avoid eventual photoactivation of the BC. With an activation energy of ≈20.1 kcal mol^{-1} Ea, **PIE** experienced a small decrease in the exothermic (≈38%), as shown in Figure 3C. The exothermic values of **PIE** without compression after 12 h and 3 days are shown in Supporting Information (Figure S11, Supporting Information).

To prove that BC had formed additional crosslinks during the pressing cycles, we again conducted swelling experiments to verify the formation of a covalently linked network (Figure 3D). Two samples of **PIE** (one compressed for 7 days, one uncompressed) were placed in DMF. After 3 days, the uncompressed sample was dissolved completely, whereas the compressed sample was just swollen with a considerable volume expansion owing to a cova-

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Figure 4. A) Comparison of IR spectra of fresh sample **PIE** and the sample after 7-days compression with 10 tons. B) Enlargement of IR spectra (wavenumber: 1600–1380 cm^{-1}). C) Enlargement of IR spectra (wavenumber: 1200–850 cm^{-1}). D) Enlargement of IR spectra (wavenumber: 900–550 cm^{-1}).

lently linked network (swelling degree 693%). By employing the equilibrium swelling method, the crosslink density (v_c) was estimated as 9.59×10^{-5} mol cm^{-3} using the equations, introduced by Flory and Rhener[66] (Table S4, Supporting Information). This result proves that covalent networks were formed during compressing the EDY-containing sample, **PIE**.

To further prove that radical coupling after cyclization took place in at least one of the primary reaction pathways, FT-IR spectroscopy was used focusing especially on the fingerprint region. If the diradical benzene intermediates were coupled together partially, a multi-phenylene system consisting of 1,2,3,4-substituted benzene moieties would be obtained. Correspondingly some changes in the fingerprint region could be expected and used to distinguish. As illustrated in **Figure 4**, the absorption peaks around ≈1500 cm^{-1} (1491 and 1474 cm^{-1}) are important characteristic peaks of the C=C stretching vibration of the conjugated benzene ring system. More importantly, the absorption at 996 and 803 cm^{-1} can be attributed to the CH bending. Compared to the normal CH bending on the 1,2-substituted benzene, the absorption at a relatively higher wavenumber (803 cm^{-1}) demonstrated the existence of 1,2,3,4-substituted benzene moieties.

In addition to compression tensile stress was probed to probe crosslinking of EDY-PU polymer. With the two elastomeric materials **PIE** and **PIC** in hand and the induced crosslinking brought by heat or compression in mind, cyclic stress–strain investigations were applied to each sample under room temperature in the dark to study the possible effect induced by external stretching. Cyclic loading and unloading from 0% strain to 300% strain,

far below the strain at break, were performed continuously without rest. As depicted in **Figure 5**A, similar to Mullin's effect,[68,69] a notable hysteresis, together with a softening and a decreased maximum tensile stress value was detected for both samples (**PIE** and **PIC**) during the first cycles.[64] However, continuously enhanced toughness and growing maximum-tensile stress values (up to 4 MPa, 162.1% of the virgin maximum-tensile stress value) were observed for **PIE** as shown in Figure 5B. On the contrary, nonsignificant changes except a slight strain hardening were found for **PIC** (111.2% of the virgin maximum-tensile stress value), in line with effects known for other PU-polymers.[70,71] Strain-hardening of **PIE** is, therefore, a clear consequence of and at least partial crosslinking of the diradicals formed during the strain induction (Figure 5C), thus proving its potential activation by stress and its activity as a mechanophore.

3. Conclusion

We herein have accomplished a Bergman-cyclization-triggered crosslinking of polyurethane with EDYs using heat and stress, leading to an induced reinforcement in the mechanical strength of the material by generating permanent covalent crosslinks. The embedded EDY induced a Bergman cyclization as proven directly by the decreased exothermic values in DSC and the characteristic peaks of the generated benzene moieties via IR spectra, and indirectly via an increase in tensile strength and swelling of the formed network. Heat-induced crosslinking increased the tensile strength by 191% in comparison to the virgin sample. 7-
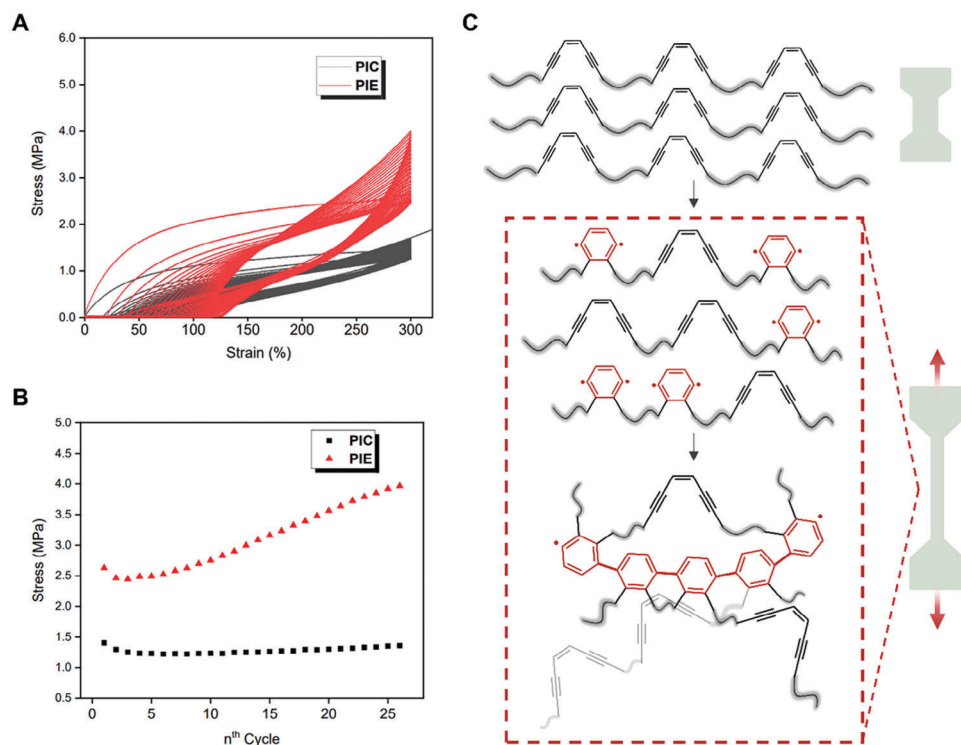
Figure 5. Stretch-induced Bergman cyclization in **PIE**. A) Cyclic stress–strain investigations of the enediyne PU chains **PIE** and the negative control **PIC**. B) The maximum tensile stress values of **PIE** and **PIC** during each stretch cycle. C) Proposed mechanism behind the increased toughness of **PIE**.

day compression resulted in a decrease of ≈69% in BC-induced exothermic values, together with the formation of permanent (covalent) crosslinks with a density of 0.96×10^{-4} mol cm^{-3} as calculated via swelling experiments, which counts to about 25% of the heat-induced crosslinks. Stretching (25 cycles) induced a significant increase (62%) in the maximum tensile stress values of **PIE**. The embedding of the EDY units as latent crosslinkers into the PU polymers is simple and yields the chance to embed a subsequent reinforcement. With the well-designed structures and simple chemistry of main chain EDY PU polymers, this work demonstrated the possibility of reviving the application of EDY as a latent crosslinker, activated either thermally or via stress, to inspire a novel type of responsive materials.

4. Experimental Section

A detailed Experimental Section can be found in the Supporting Information.

Supporting Information

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

Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Y.C. and W.H.B.: Conceptualization, methodology, investigation, and writing; W.H.B.: Supervision, project administration, and funding acquisition. Both authors have read and agreed to the published version of the manuscript.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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