

Initiator-Free Synthesis of Semi-Interpenetrating Polymer Networks via Bergman Cyclization

Yue Cai, Florian Lehmann, Justus F. Thümmeler, Dariush Hinderberger, and Wolfgang H. Binder*

Semi-interpenetrating polymer networks (semi-IPNs), composed of two or more polymers, forming intertwined network-architectures, represent a significant type of polymer combination in modern industry, especially in automotive and medical devices. Diverse synthesis techniques and plentiful raw materials highlight semi-IPNs in providing facile modifications of properties to meet specific needs. An initiator-free synthesis of semi-interpenetrating polymer networks via Bergman cyclization (BC) is reported here, acting as a trigger to embed a second polymer via its reactive enediyne (EDY) moiety, then embedded into the first network. (Z)-oct-4-ene-2,6-diyne-1,8-diol (diol-EDY) is targeted as the precursor of the second polymer, swollen into the first polyurethane network (PU), followed by a radical polymerization induced by the radicals formed by the BC. The formation of the semi-IPN is monitored via electron paramagnetic resonance (EPR) spectroscopy, infrared-spectroscopy (FT-IR), and thermal methods (DSC), proving the activation of the EDY-moiety and its subsequent polymerization to form the second polymer. Stress–strain characterization and cyclic stress–strain investigations, together with TGA and DTG analysis, illustrate improved mechanical properties and thermal stability of the formed semi-IPN compared to the initial PU-network. The method presented here is a novel and broadly applicable approach to generate semi-IPNs, triggered by the EDY-activation via Bergman cyclization.

1. Introduction

Interpenetrating polymer networks (IPNs) are defined as the combination of two or more chemically independent polymers.^[1,2] Among the coexisting networks, at least one network is synthesized and/or crosslinked in the presence of the other. Since the profound combination of phenol-formaldehyde resins with vulcanized natural rubber by Aylsworth in 1914 and the discussion from Millar^[3] in 1960, IPNs have occupied a significant role in macromolecular topologies.^[4] The unique properties of swelling capacity and mechanical strength of IPNs have enabled them to be widely applied in automotive parts,^[5] engineering plastics,^[6] damping compounds,^[7–9] biomedical devices,^[10–13] or as structural concepts in molding materials. Depending on the synthetic routes and the combined patterns of the two polymers,^[1,14] IPNs could be classified as sequential, semi-, and simultaneous IPNs, displaying various topologies and chemical bonding.^[15–19] Among them, semi interpenetrating networks (semi-IPNs) are built from two or more polymers, one of

which is crosslinked, the other embedded into the first one, either with a linear or branched architecture, but in itself not crosslinked.^[20–22] Tremendous efforts have been focused on the synthesis, morphology, physical/chemical properties, and applications of various ingeniously designed semi-IPNs. Represented by hydrogels,^[23–25] which are derived from bio-friendly and hydrophilic raw materials, recently semi-IPNs have been particularly empowered in the field of stimuli-responsive sensors and pharmaceutical devices. Via sequential synthesis methods, (semi-)IPNs are prepared by firstly polymerizing monomer I with crosslinker I to produce the first network, followed by the swelling of monomer II and a subsequent polymerization to generate the second polymer.^[26,27] The first generated network thus plays a fundamental role in the mechanical or thermal properties of the finally formed (semi-)IPN products. Owing to its versatile properties (elastomeric to rigid polymers) and facile synthesis, polyurethanes (PU) are identified as one of the most privileged network components.^[28–30] Among the corresponding IPNs constituted from PU, various polymeric components such as epoxy resins,^[31] vinyl ester resins,^[7] unsaturated polyester resins,^[32]

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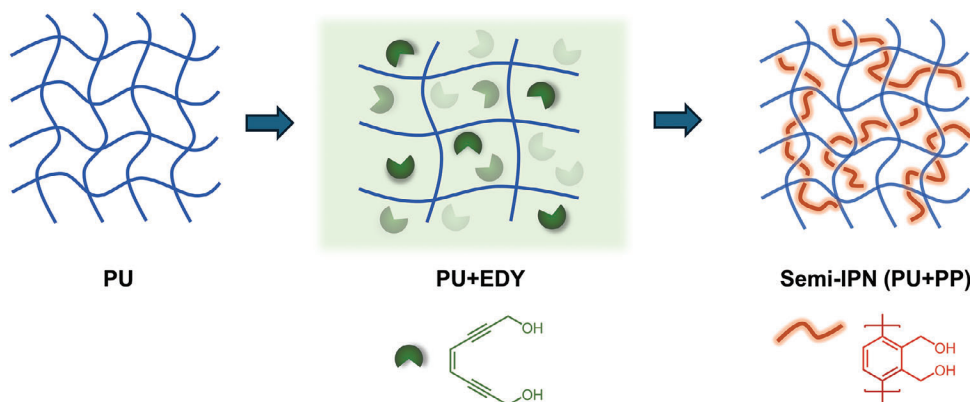


Figure 1. Schematic illustration of the designed construction of semi-interpenetrating polymer networks via a Bergman cyclization (BC).

acrylates,^[33] and styrene^[34] have been extensively used as the precursors of existing networks. However, for many of those networks, residues from the initiators used for the often free radical initiation processes are difficult to avoid, often hampering the broad use of those networks. Thus many reactive initiators such as peroxides,^[35] azo-initiators,^[36] or phosphine oxides,^[37] together with the crosslinking agents or monomers^[38] as well as their residues after activation and crosslinking have been widely recognized as detrimental in the final IPNs which often prevents application due to their inherent biological toxicity. Thus there is a critical need to avoid residues of the used cross-linking (re)-agents in the final IPNs.

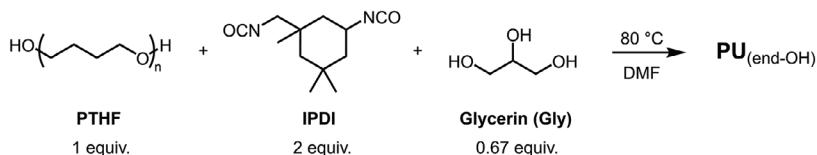
We here report on a novel method to generate semi-IPNs, using an initiator-free approach for a radical-polymerization via a thermally triggered Bergman-cyclization (BC). In our search for initiator-free coupling chemistries, we came across a pericyclic reaction such as the Bergman cyclization (BC) as a potential target, which was first reported in 1972.^[39] 3-Ene-1,5-diyne (EDYs) can undergo exothermic cycloaromatization by thermal or photochemical activation in the presence of suitable hydrogen donors to generate benzene derivatives via a diradical intermediate, generated by a pericyclic reaction in a distance-dependent (1,6)-reaction. The intermediately formed 2,5-diradicals can serve as a source for a radical polymerization to form functional polymers, such as conjugated polymers, polymeric nanoparticles, or carbon nanomembranes via a direct coupling of the radicals to generate a polymer.^[40,41] Inspired by the excellent properties of the BC and our own previous work,^[42,43] we herein report an initiator-free construction of a novel interpenetrating polymer network consisting of an elastic polyurethane and a rigid polyphenylene (see **Figure 1**). We highlight the function of EDY as one of the precursors to be swollen into the existing crosslinked polyurethane and subsequently to be initiated thermally to obtain semi-IPN. The diradicals formed via BC undergo radical-coupling to induce covalent coupling via radical polymerization, in turn leading to an efficient hardening of the original PU material. Induced changes in the physical and mechanical properties lead to a novel type of construction of semi-IPN and a promising post-modification of polyurethanes.

2. Results and Discussion

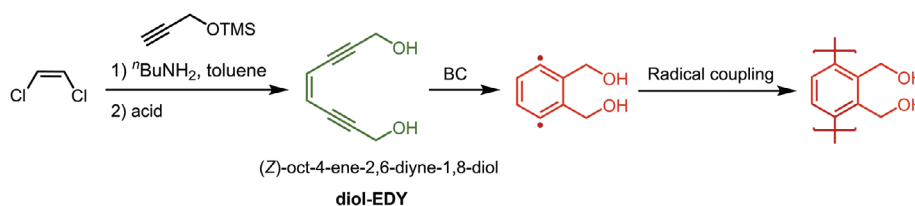
As depicted in **Scheme 1**, we initiated our studies by synthesizing a polyurethane (PU) network as the basis for the first network, allowing to tune its rigidity and composition. A mixture of polytetrahydrofuran (PTHF, 650 Da, 40 mmol), isophorone diisocyanate (IPDI), and glycerol (Gly) (molar ratio of PTHF/IPDI/Gly:1/2/0.67) was heated to obtain the crosslinked PU with dimethyl formamide as solvent.^[44] Subsequently, the reaction mixture was cast into a mold, followed by intensive drying under vacuum and heat to remove all solvent residues. It is worth emphasizing that the synthetic procedure herein of crosslinked polyurethane is mature and the scalability is adjustable depending on practical requirements. In parallel, the precursor enediyne (EDY) of the semi-interpenetrating network was prepared, representing the basis for the second polymer. (*Z*)-oct-4-ene-2,6-diyne-1,8-diol (**diol-EDY**),^[45] up to now only scarcely used for BC processes,^[46–51] was selected, and deemed useful due to its stability at ambient conditions, combined with its ease of preparation and the triggerable activation of the BC. For synthesis, the trimethylsilyl (TMS) group was added as a protective moiety on propargyl alcohol, followed by a classical Sonogashira coupling reaction with (*Z*)-1,2-dichloroethene and subsequent acid-catalyzed deprotection, in turn yielding the diol EDY (Figure S1, Supporting Information, all data are inline with the data reported from literature).^[46] It should be noted that similar to our recent results focusing on diamine EDY ((*Z*)-octa-4-en-2,6-diyne-1,8-diamine), the final **diol-EDY**, (*Z*)-oct-4-ene-2,6-diyne-1,8-diol, is stable in solution with the required concentration owing to its primary alcohol groups inducing intramolecular hydrogen bonding, thus allowing its integration into the first PU-network without primordial polymerized reactions.

With the original PU material and the precursor enediyne (**diol-EDY**) of the second polymer in hand, the preparation of various samples was conducted as shown in **Figure 2A**. After casting and drying as described above, a transparent and colorless film was obtained. To remove possibly unreacted monomers, the film was immersed in tetrahydrofuran for 24 h, whereafter all adsorbed initial components for the PU were removed as proven

I. Synthesis of the 1st network polyurethane (PU):



II. Synthesis of enediyne (EDY) and the 2nd polymer polyphenylene (PP) via BC:



Scheme 1. Synthesis of the first network polyurethane (PU), enediyne monomer (Z)-oct-4-ene-2,6-diyne-1,8-diol (**diol-EDY**), and the second polyphenylene (PP) via BC.

by NMR of the solvent. The so purified PU material was then soaked in the solution of the **diol-EDY** with ethyl acetate as the solvent ($c = 50 \text{ mmol L}^{-1}$). With a swelling time of 48 h, **diol-EDY** was swollen into the network of PU as expected, together with the solvent ethyl acetate without reaction with the PU-endgroups (targeted as OH), thus allowing a homogeneous distribution of the diol-EDY inside the PU-network. After probing different concentrations of the EDY-solution, the chosen concentration of 2.5 mmol mL^{-1} was identified as the optimum to reach a successful embedding of the EDY inside the PU. Higher concentrations

or the application of neat EDY lead to primordial BC, as probed separately in solution.^[43] After swelling, the film was removed from the solution and dried, the sample PU + EDY was collected and ready for characterization. During the process of drying the samples, a high vacuum with a pressure of 0.01 mbar was applied for 24 h, and a continued monitoring of the mass was conducted to ensure that the solvent, ethyl acetate, was completely removed. The gained weight of PU + EDY compared with the original PU sample was attributed to the embedded **diol-EDY** and showed its content as 4 wt% through calculation. After a thermally-induced

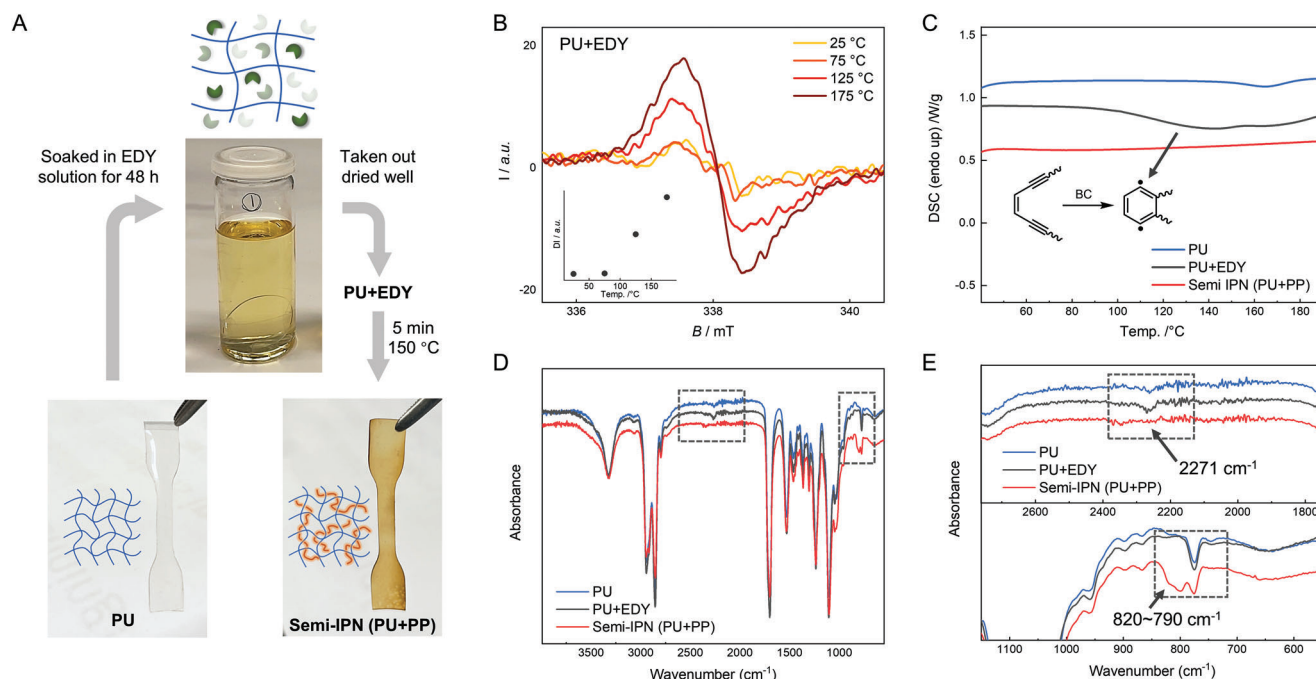


Figure 2. A) Digital photographs of the preparation of sample PU, PU + EDY, and semi-IPN (PU + PP). B) EPR spectra of PU + EDY after 20 min at each temperature (legend). C) DSC curves of PU, PU + EDY, and semi-IPN (PU + PP) under heating conditions, N₂ atmosphere, 5 K min⁻¹. D,E) Comparison and enlargement of FT-IR spectra of the samples PU, PU + EDY, and the semi-IPN (PU + PP).

Table 1. Overview of dissipated energy of sample PU and semi-IPN (PU + PP) at a maximum strain of 50%, 100%, 150%, and 200%, together with strain at break, stress at break of each sample, and swelling degree of two samples in toluene.

Sample	Dissipated energy [MJ m ⁻³]				Fracture strain [%]	Fracture stress [MPa]	Swelling [%] (toluene)
	Strain 50%	Strain 100%	Strain 150%	Strain 200%			
PU	16.3	35.0	55.7	80.0	679 (± 58)	13.9 (± 5.1)	131
Semi-IPN (PU + PP)	27.6	53.4	77.9	102.0	672 (± 73)	15.0 (± 4.4)	119

BC (150 °C for 5 min), the semi-IPN (PU + PP) was obtained, wherein the formed 2,5-diradicals form the second polymer via radical coupling. It is worth mentioning that the temperature chosen for the thermal initiation was according to the detected peak temperature of the reaction curve in DSC, referring to previous work on the polymerization of enediynes.^[52]

To prove the successful Bergman-cyclization-chemistry and the formation of the second polymer, various analyses were conducted. First, the verification of the presence of EDY in the network was probed with electron paramagnetic resonance (EPR) spectroscopy as illustrated in Figure 2B. Thermally-induced formation of the radicals was proven by the increasing intensity of the carbon-centered radical signals when gradually heating the sample in situ from 25 to 175 °C in steps of 25 °C, revealing the progressive initiation of BC and generation of radical moieties. The double integral (DI) calculated from the EPR spectra at each temperature (25, 75, 125, and 175 °C) is directly correlated to the radical concentration in the sample. The DI was plotted against the temperature, which is shown in the inset of Figure 2B, clearly proving the formation of radicals inside the semi-IPN by thermal initiation of the embedded EDYs.

As BC is an exothermic reaction, differential scanning calorimetry (DSC) was measured with the samples PU, PU + EDY, and the semi-IPN (PU + PP) to probe the progress of the BC, indicated by a decreasing exothermic profile as the reaction proceeded. All samples were heated to 250 °C, followed by cooling to 25 °C under an atmosphere of N₂. As shown in Figure 2C, for the intermediate sample PU + EDY (black line), the broad exothermic peak (≈140 °C) was attributed to a thermally triggered BC of the enediyne moiety, which did not appear for sample PU. For the formed interpenetrating sample semi-IPN (PU + PP), the flat curve (red line) during heating further proved the completion of BC of the gained enediyne inside the network. Furthermore, BC was proven by IR-spectroscopy, indicating the chemical changes occurring during BC, changing from the EDY-moieties to the poly(aromatic) polymers formed after BC (see Figure 2D/E). Comparison of the spectra of the samples PU (blue line), PU + EDY (black line), and the semi-IPN (PU + PP) (red line) showed that an increase stretching band of the ene (C≡C) at 2271 cm⁻¹ appeared first along with the embedding of the enediyne monomers, followed by a decrease at the same position during the formation of the semi-IPN, providing solid evidence about the process of incorporation first and consumption of the subsequently added enediyne monomers in the preparation of semi-IPN sample. Besides, a characteristic absorption at ≈810 cm⁻¹ in the sample semi-IPN could be attributed to the CH bending of the conjugated benzene ring system. It is worth mentioning that, compared to the CH bending on the 1,2-substituted benzene, the absorption

presented here at a higher wavenumber (810 cm⁻¹) revealed the formation of the 1,2,3,4-substituted benzene moieties as a result of free radical polymerization in the presence of diradical intermediates, which was consistent with the previous work^[53] on the polymerization of enediynes published in 1994. In addition, as shown in Table 1, swelling experiments proved the formation of a second polymer by BC: the presence of the interpenetrating composition decreased the swelling degree of the network, from 131% for PU to 119% semi-IPN (PU + PP). Therefore, the presence of EDY swollen into the PU network, together with the formed skeleton of semi-IPN (PU + PP) via BC, was verified.

With the semi-IPN (PU + PP) in hand, the difference in the mechanical properties compared to the original PU was examined, as the formation of a second polymer inside the first PU-network was expected to yield changes in the mechanical properties. To avoid eventual errors caused by the soaking process of sample semi-IPN (PU + PP) in EDY/ethyl acetate solution, PU used in this paper was treated precisely with the same soaking process in a blank solvent (ethyl acetate) without EDY. Correspondingly, rectangular specimens with a length of 40 mm, a width of 4 mm, and a thickness between 0.2 and 0.4 mm were prepared. Three specimens for each sample were measured on average with a uniform stretching speed of 20 mm min⁻¹. As illustrated in Figure 3, the mechanical properties of both samples were studied by stress–strain characterization and cyclic stress–strain investigations. Their determined strain at break, stress at break, and dissipated energy values at each strain are depicted in Table 1. For the two elastomer samples, an increase of the tensile stress was observed from 13.9 MPa for PU to 15.0 MPa for semi-IPN (PU + PP), while the extensibility slightly decreased from 679% to 672%. The slightly improved mechanical properties could be attributed to the existence of the second polymer polyphenylene, inducing structurally physical entanglement, thus boosting its rigidity.^[54,55] In the research of IPNs, higher tensile strength and lower elongation are common.^[56] Besides, cyclic stress–strain investigations of both samples were performed at room temperature to study the energy dissipation capacity related to the bonding interactions. Therefore, cyclic loading and unloading at a maximum strain of 50%, 100%, 150%, and 200%, far below the strain at break, were performed continuously without rest. The area between the load and unload stress–strain curves equals the dissipated energy. Compared to PU, the integral area of the corresponding hysteresis loop of semi-IPN (PU + PP) was increased ≈48 times on average, indicating the impact of the entanglement on the mechanical properties in its semi-interpenetrating form. Furthermore, a similar native PU* was synthesized by lowering mole ratio of the crosslinker glycerol (Gly), and corresponding semi-IPNs (PU*+ PP) were obtained. The cyclic stress–strain investigations also verified the improved

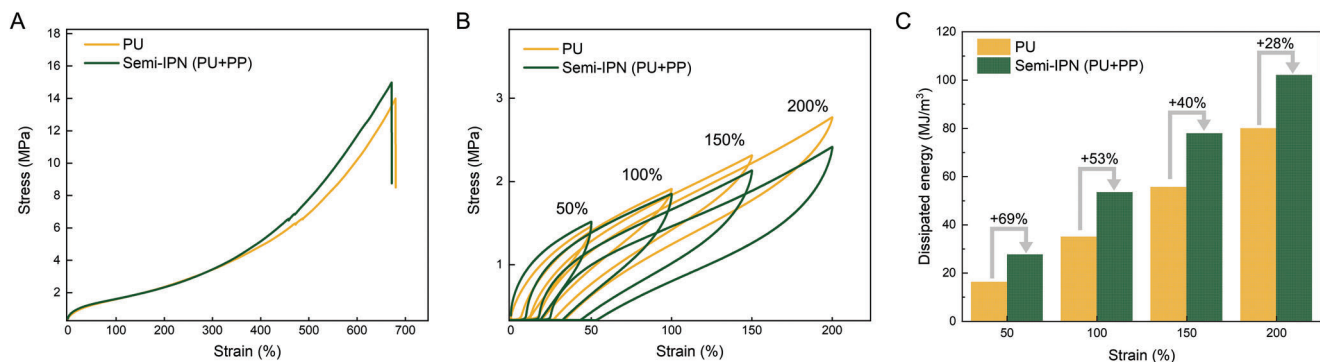


Figure 3. A) Tensile curves of PU and semi-IPN (PU + PP). B) Cyclic stress-strain curves of sample PU and semi-IPN (PU + PP). Cyclic loading and unloading were performed continuously without rest at 50%, 100%, 150%, and 200% strain. C) Dissipated energy values at each strain.

Table 2. Thermal properties of the PU and the semi-IPN (PU + PP).

Sample	$T_{5wt.}/^{\circ}\text{C}$	$T_{15wt.}/^{\circ}\text{C}$	1st decomposition		2nd decomposition		Residue (600 °C)/wt.%
			Mass loss/ wt.%	$T_{max}/^{\circ}\text{C}$	Mass loss/ wt.%	$T_{max}/^{\circ}\text{C}$	
PU	281	305	62.2	338	35.9	397	0.1
Semi-IPN (PU + PP)	286	309	61.9	338	32.9	398	3.3

mechanical strength (Figure S4 and Table S2, Supporting Information). An enhancement of the mechanical properties was detected in the study, underscoring the use of the Bergman cyclization to form the semi-IPN.

As illustrated in Figure 4, thermogravimetric analyses (TGA) were applied further to probe the thermal stabilities of this series of samples. Along with continuous heating conditions up to 800 °C, the EDY moieties inside sample PU + EDY were supposed to undergo Bergman cyclization (according to the DSC curve in Figure 2C). Therefore, in terms of the thermal stabilities, the original PU and the obtained semi-IPN (PU + PP) were analyzed here. The determined temperature and mass loss at different stages of the decomposition, together with the residue

percentages at 600 °C are depicted in Table 2. The decomposition processes of both samples were quite comparable. The 5% decomposition of PU ($T_{5wt.}$) happened at ≈ 281 °C, but for the semi-IPN (PU + PP), the temperature required for the same 5% decomposition was increased to 286 °C. Additionally, two stages of degradation were recorded for both samples with similar maximum degradation temperatures (for T_{max1} : 338 °C, for T_{max2} : 397 °C) as shown in the corresponding DTG curves (blue line), but with respectively different proportions of mass loss in each of the two stages. During the first stage (the peak shown between 230 and 380 °C in the blue line), both samples were thermally degraded, which could be attributed to the decomposition of the urethane bonds taking place through the dissociation to

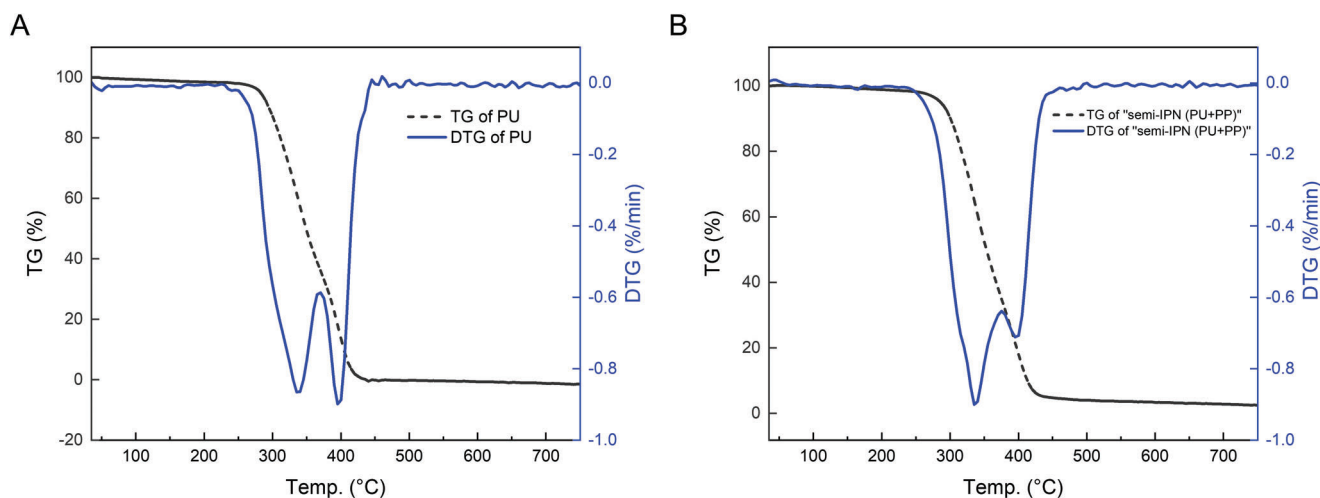


Figure 4. A) Thermal analysis of native PU (dashed line: TGA, blue line: DTG). B) Thermal analysis of semi-IPN (PU + PP) (dash line: TGA, blue line: DTG).

isocyanate and alcohol, leading to the loss of carbon dioxide from the urethane bond.^[57,58] In this stage, the semi-IPN displayed a lower mass loss compared to the native PU. A more drastic decrease in mass loss and a lower maximum weight loss rate for the semi-IPN were detected during the second stage (decomposition took place between 370 and 450 °C) involving the rupture of ester linkages and fatty acid chains of the polyurethane soft segments.^[57,58] Therefore, TGA and the corresponding DTG verified the improved thermo-stability owing to the presence of the additional PP polymer. The residual components at 600 °C for semi-IPN stemmed from the then carbonized polymers, polyphenylene, formed thermally by radical crosslinking the DEY moieties.

To investigate the surface morphologies, atomic force microscopy (AFM) analysis in the phase contrast mode was performed on three thin films prepared throughout the synthetic route: the original PU, the intermediate PU + EDY, and the final semi-IPN (PU + PP). The respective height and 3D images, together with analyzed roughness were shown in **Figure 5**. For PU, the surface morphology exhibited a surface with some non-negligible gullies. After analysis (Table S3, Supporting Information); the surface possesses a roughness average of $R_a = 2.3$ nm, which could be attributed to the incompatibility between both rigid and flexible segments in PU. For sample PU + EDY, the height image (Figure 5B) presented local accumulation with a certain height and segregated domains, with the texture providing a height of ≈ 62 nm (Figure 5E). In the meantime, a decreased roughness average (1.0 nm) was found for the surface of PU + EDY, which could be possibly attributed to the filling of EDYs in the gaps between amorphous segments of PU.^[59] When

it came to the final semi-IPN (PU + PP), the roughness was significantly reduced to 0.3 nm, together with the disappearance of the segregated domains. According to the structural changes and reactions that happened inside, it was presumed that the local clusters shown in PU + EDY were due to the introduction of EDY-OH, and the intermolecular forces of EDY-OH small molecules caused molecular stacking in the PU network. With thermal initiation, molecular diffusion in the network first occurred for locally collective EDY-OHs. When the BC temperature is reached, the EDY-OHs start to form diradical species, followed by free radical polymerization to form linear polyphenylenes in-line with the disappearance of the local clusters. As radical polymerization is normally associated with a decrease in volume due to entropic effects, the roughness average is reduced to 0.3 nm (Figure 5G). Scanning electron microscopy (SEM) was conducted further to obtain the surface morphologies of the three samples on a smaller scale (Figure S5, Supporting Information) yielding results consistent with AFM.

3. Conclusion

We have accomplished a facile construction of a semi-interpenetrating polymer network via Bergman cyclization (BC) as an initiator-free process for the second polymer. The synthesis started from a preformed, first polyurethane (PU) network comprised of polytetrahydrofuran (650 Da), isophorone diisocyanate, and glycerol with a molar ratio of 1/2/0.67. (*Z*)-oct-4-ene-2,6-diyne-1,8-diol (**diol-EDY**) was targeted as the precursor of the second polymer and swollen into PU to form the interme-

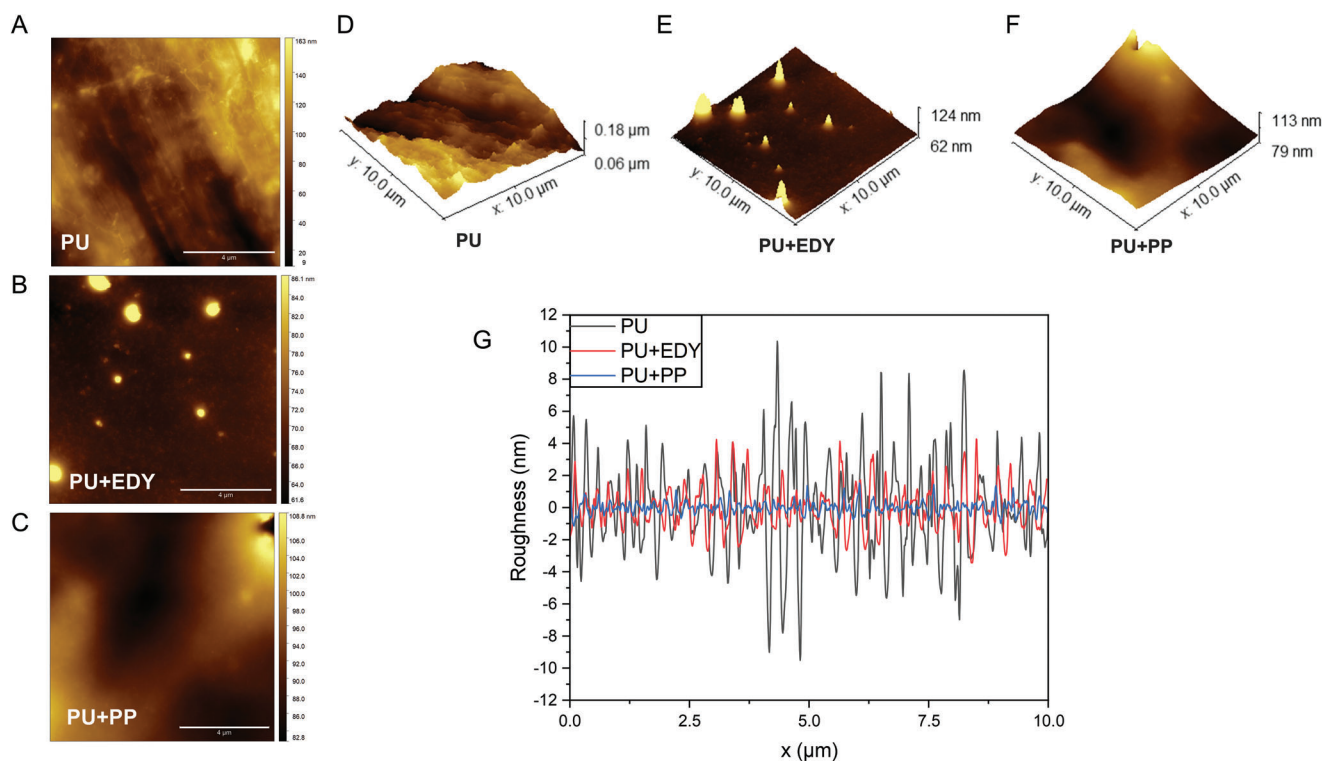


Figure 5. A–C): AFM height images of PU, PU + EDY, and semi-IPN (PU + PP). D–F): AFM 3D surface topographic images of PU, PU + EDY, and semi-IPN (PU + PP). G) Roughness analysis of three samples.

diate PU + EDY. Followed by thermal initiation to undergo BC and subsequent radical polymerization, a semi-interpenetrating polymer semi-IPN (PU + PP) was established as planned. The presence of EDY in the PU network was verified by the occurrence of carbon radicals in EPR spectroscopy during the heat-initiated BC, the disappearance of absorption of the alkyne group in FT-IR spectroscopy after the consumption of EDY, and the characteristically exothermic peak in the DSC curve arising from BC verified jointly the successful insertion of EDY. Compared to the original single network PU, the obtained sample semi-IPN (PU + PP) possesses improved mechanical properties as proven by stress–strain characterization and cyclic stress–strain measurements. Furthermore, TGA and DTG indicated an improved thermal stability of the so-formed semi-IPN. The interpenetration and physical entanglement of the elastomeric PU and rigid PP resulted in a performance-enhanced polymer. The initial crosslinked polyurethane here can be replaced by any other crosslinked network, highlighting the broad approach of the here presented method to embed a second polymer into a preformed first one, using an initiator-free monomer, further allowing a simple post-modification of crosslinked polymers via enediyne and subsequent Bergman cyclization.

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.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Conceptualization was performed by Y.C. and W.H.B.; methodology was performed Y.C. and F.L.; investigation was performed by Y.C. and F.L.; writing—original draft was prepared by Y.C. and W.H.B.; writing—review and editing was performed by Y.C., F.L., J.F.T.; D.H., and W.H.B.; supervision was performed by W.H.B.; project administration was performed by W.H.B.; funding acquisition by W.H.B. All 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.

Keywords

Bergman-cyclization, interpenetrating networks, polyurethanes, radical crosslinking

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