Title

Efficient Cross-Linking through C-H Bond Insertion of Unfunctionalized Commodity Materials Using Diazirine-Containing Polymers.

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Efficient Cross-Linking through C−H Bond Insertion of Unfunctionalized Commodity Materials Using Diazirine-Containing Polymers

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ABSTRACT: The synthesis and application of multifunctional diazirine-containing polymers for on-demand cross-linking of unfunctionalized commodity polymers through C−H bond insertion is demonstrated. While small-molecule diazirine cross-linkers have seen important applications such as plastic compatibilization and photopatterning, the high degree of functionalization of polymer-based diazirine cross-linkers offers promise for enhanced compatibility based on polymer blending and increased efficiency due to controllable multivalency. As a demonstrative example, unfunctionalized linear poly(n-butyl acrylate) (PnBA) can be cross-linked using various polymeric cross-linkers with diazirine contents as low as 0.8 wt % in 1 min under photochemical conditions. With gel fractions up to 95%, tunable rheological behavior is observed with increasing cross-linker loadings, consistent with a transition from entangled branched polymers to a cross-linked network. Moreover, the synthetic stability of the diazirine units can be exploited to prepare diazirine-containing polymers based on a variety of different backbones, from vinyl copolymers to poly(dimethylsiloxane) (PDMS), which allows successful photopatterning using a commercial 3D printer.
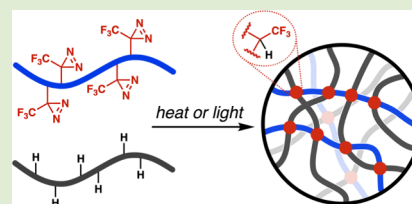
Cross-linking is a critical process in enhancing the mechanical properties and stability of polymeric materials.[1−4] By introducing cross-links along the backbone of linear polymer chains, thermoplastics could be converted into elastomers or thermosets, resulting in increased impact resistance, tensile strength, and high-temperature performance. This transformation also enhances resistance to chemical or biological degradation, with these properties being crucial for applications spanning from adhesives to medical devices.

Traditionally, unfunctionalized polymers can be cross-linked through e-beam irradiation or by thermal treatment in the presence of organic peroxides.[5] These radical-based methods, however, pose significant challenges, including undesired cleavage of the polymer backbone and limited control over the nature and number of cross-linking sites, ultimately compromising the integrity of the material.[6] Alternatively, cross-linking methods that leverage specific functional groups face challenges when applied to commodity polymers that are difficult to functionalize or have only C−C and C−H bonds such as polyethylene and polypropylene.[7−10]

Recent advances in C−H functionalization chemistry have facilitated the development of more efficient and controlled cross-linking techniques.[11,12] Specifically, the use of carbenes for direct C−H insertion into the polymer backbone has emerged as a promising strategy. Under mild thermal or photochemical conditions, singlet carbenes can be generated from diazirine or diazo precursors, enabling efficient functionalization and cross-linking.[13−17] These carbene-medi-

ated cross-linking strategies have found a diverse array of applications, including plastic compatibilization,[18] LED processing,[19,20] photopatterning,[21−25] and as adhesives.[26−29]

Despite the potential of small-molecule diazirine and diazo compounds, their application is often hindered by challenges, such as limited structural variability, the need for relatively high loading levels due to their difunctional nature, and potential leaching of unattached cross-linkers. To address the limitations of small-molecule cross-linkers, incorporation of diazirine groups into polymeric structures offers a versatile platform for enhancing cross-linking efficiency and fine-tuning material properties (Figure 1A). In particular, we have recently demonstrated the facile synthesis of diazirine-containing polymers via controlled radical (co)plymerization, which allows the preparation of vinyl polymers with up to ∼50 diazirine units per chain.[30]

This study explores the synthesis and application of multifunctional diazirine-containing polymers for on-demand cross-linking of various unfunctionalized polymers (Figure 1B). Facile access to multifunctional diazirine copolymers enables
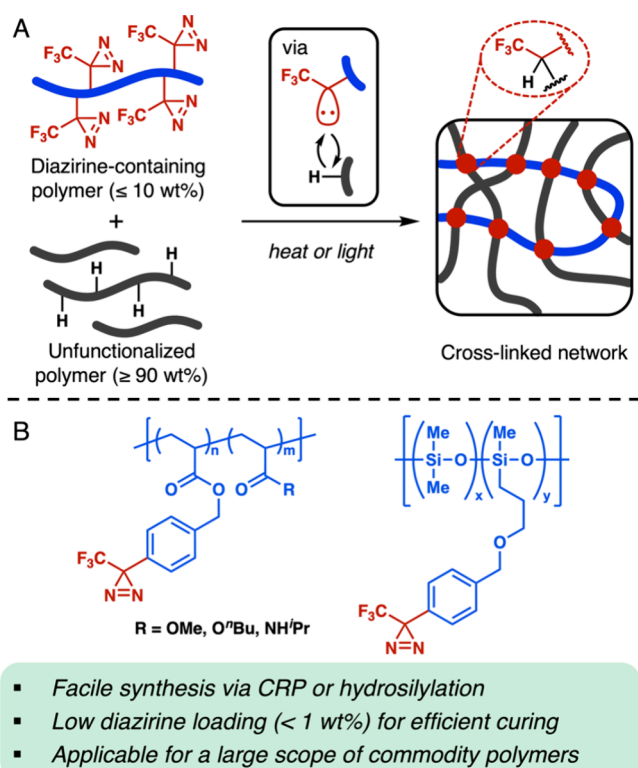
Figure 1. (A) Unfunctionalized commodity polymers can be efficiently cross-linked by diazirine-containing polymers via direct C–H insertion of singlet carbenes. (B) Variable backbone structures of polymeric cross-linkers.

Figure 2. (A) UV or thermal curing of P*n*BA blends with different loadings of cross-linker **P1**. Photos showing the blend with 0.8 wt % of **CF₃Dz** after UV-curing (left) and thermal-curing (right). (B) Gel fractions of cured P*n*BA blends with varied loadings of **CF₃Dz** show enhanced curing efficiency with higher cross-linker loadings.

curing studies on a wide variety of commodity acrylic and siloxane polymers. Analysis of the structure and properties before and after cross-linking demonstrates that a high degree of cross-linking and gel formation could be achieved at minimal diazirine loadings, with oscillatory rheology providing insight into the evolution of a network structure as the diazirine loading is increased. The versatility of this approach is further emphasized by demonstrating the effective cross-linking and photopatterning of commercially relevant acrylate, acrylamide, methacrylate, and siloxane-based systems.

The cross-linking performance of diazirine-containing polymers was initially explored using a blend system comprising an unfunctionalized P*n*BA as the bulk matrix with varying amounts of poly(*n*-butyl acrylate-diazirine acrylate) copolymer (P*n*BA-*co*-PDzA) added as a cross-linker. Through reversible addition–fragmentation chain-transfer (RAFT) copolymerization, a P*n*BA-*co*-PDzA (**P1**) cross-linker was synthesized containing 10 mol % diazirine acrylate repeating units with a M_n of 52 kDa. Clear blends with a light-yellow color were prepared in a mold by mixing 90−99 wt % of unfunctionalized P*n*BA (105 kDa) with varied loadings of **P1** at 1, 3, 5, and 10 wt % (Figure 2A). Notably, these cross-linker loadings correlated to low contents of the trifluoromethyl diazirinyl group (**CF₃Dz**, highlighted in red in Figure 2A) in the entire blends. **CF₃Dz** contents of 0.1, 0.2, 0.4, and 0.8 wt % were estimated for the four blends, respectively. For consistency in the following discussions, the **CF₃Dz** wt % content in the entire blend will be used primarily to quantify diazirine loadings (see Supporting Information for calculation details). The prepared P*n*BA blends were then cured either by exposure to 370 nm UV light for 1 min or by heating at 110 °C
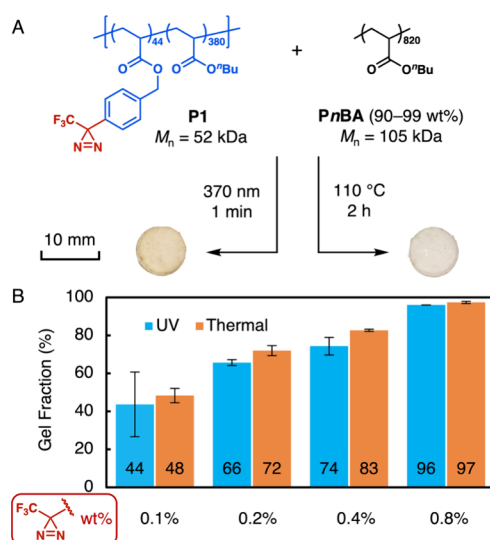
for 2 h. Homogeneous, solidified samples were observed, suggesting successful cross-linking.

Subsequently, gel fraction measurements were conducted on the cured P*n*BA samples to quantify the cross-linking efficiency after either thermal or photochemical generation of the reactive carbene units from the starting diazirine groups.[3,31] Soluble polymer chains unconnected to the cross-linked network were removed by repeated swelling of cured samples in dichloromethane (DCM) and collection of the soluble fractions. This allows for comparison of gel content across various cross-linker loadings and curing procedures (Figure 2B). When the blend containing a **CF₃Dz** content of 0.1 wt % was subjected to curing conditions, gel fractions of 44% for UV-cured samples and 48% for thermally cured samples were achieved, respectively. The observed gel fractions suggest that at a diazirine loading of 0.1 wt % only partial cross-linking occurred, leaving approximately half of the P*n*BA as linear or branched architectures. Higher gel fractions were observed for increased **P1** loadings, with **CF₃Dz** contents of 0.2 and 0.4 wt %. For the blend with a **CF₃Dz** loading of 0.8 wt %, nearly quantitative cross-linking of the starting linear unfunctionalized P*n*BA was achieved, resulting in gel fractions of 96% and 97% for UV or thermally cured samples, respectively (Figure 2B). This low **CF₃Dz** loading of 0.8 wt % underscores the advantage of employing a multifunctional polymer containing on average 4−50 diazirine units along the backbone as a cross-linker. These results also suggest that thermal curing typically results in slightly higher gel fractions when compared to UV curing across different cross-linker loadings, presumably due to a higher conversion of the diazirine moiety into carbene intermediates at elevated temperatures and extended curing times (2 h versus 1 min).

It is noteworthy that attempted cross-linking of the same unfunctionalized linear P*n*BA with a small-molecule, bisdiazirine derivative failed to form a network at the same **CF₃Dz** loading of 0.8 wt % , under either photochemical or thermal conditions (see Supporting Information for details). Only after increasing the bisdiazirine cross-linker to 10 wt %, equivalent

to a **CF$_3$Dz** content of 4.2 wt %, was cross-linking observed in the cured samples. At these high loading levels of small-molecule diazirines, however, a heterogeneous sample was observed under UV conditions, likely due to the rapid and extensive nitrogen evolution and phase separation during the curing process (Figure S10). These findings highlight the advantages of using low loadings of polymer-based diazirine cross-linkers.

Following the determination of gel fractions for cured blends containing varying amounts of diazirine cross-linkers, the impact of curing on mechanical properties was then investigated by photorheology. For experiments with a UV intensity of 25 mW/cm^2, a rapid sol−gel transition was observed after ∼1 min of UV irradiation, as indicated by a significant increase in storage modulus (G') that surpassed loss modulus (G'') (Figure 3). This fast solidification process is fully consistent with the efficient carbene formation from diazirine groups and subsequent cross-linking during photochemical curing.
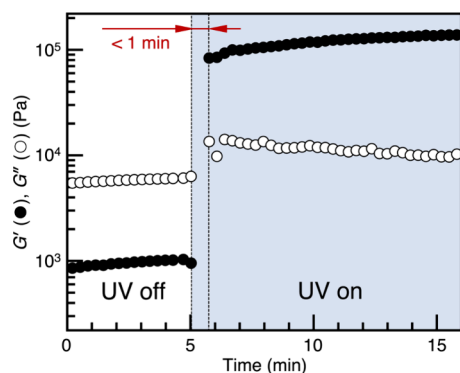
Figure 3. Photorheology (at 1% strain and 1 rad/s frequency) shows rapid cross-linking of the PnBA blend with 0.8 wt % of **CF$_3$Dz** under UV light (25 mW/cm^2).

Oscillatory shear rheology measurements were then conducted to evaluate the mechanical properties of cured samples with varying diazirine contents. For cured blends with **CF$_3$Dz** contents of 0.2, 0.4, and 0.8 wt %, frequency sweeps conducted at 1% strain shed light onto the structural differences resulting from different cross-linking densities (Figure 4A). For UV-cured blends with **CF$_3$Dz** contents of 0.2 and 0.4 wt %, slightly higher values of G' than G'' at low frequencies (<1 rad/s) suggest the existence of highly branched or entangled polymer chains. In contrast, the frequency sweep of a UV-cured blend with a **CF$_3$Dz** content of 0.8 wt % showed minimal change in G' across different angular frequencies. These findings, coupled with gel fractions exceeding 95%, indicated near-complete cross-linking with 0.8 wt % loading of diazirine. Similar trends were observed in thermally cured samples (Figure S13). Overall, unfunctionalized PnBA materials could be cross-linked with the formation of a viscoelastic solid in both UV and thermally cured samples through blending with diazirine-containing linear polymers. In these systems, G' dominates over G'' throughout the examined angular frequency range. It should be noted that the mechanical fragility of cured blends with a **CF$_3$Dz** content of 0.1 wt % prevented further rheological measurements, likely resulting from insufficient cross-linking at this low loading level.
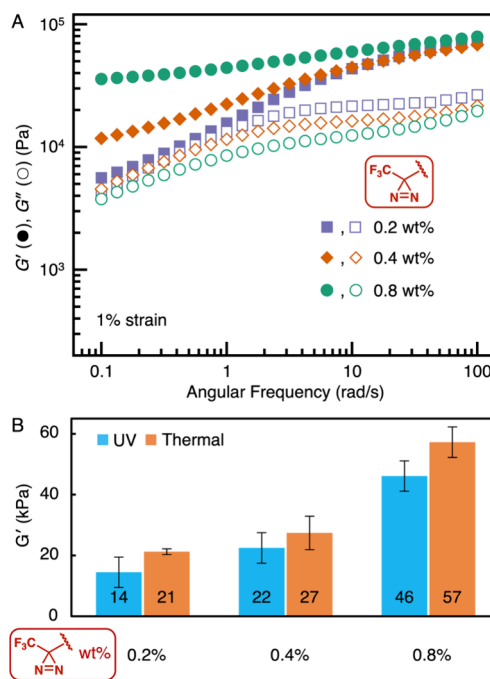
Figure 4. (A) Frequency sweep at 1% strain of UV-cured blends shows increased degree of cross-linking with higher **CF$_3$Dz** loading. (B) Storage modulus values obtained at 1% strain and 1 rad/s frequency of UV- or thermally cured blends show increased modulus with higher **CF$_3$Dz** loadings.

To further understand the impact of curing conditions on mechanical properties, the moduli of these cured PnBA samples were compared at a 1 rad/s frequency and 1% strain. A gradual increase in G' was noted within the series of UV- or thermally cured samples with increasing diazirine loadings (Figure 4B). Notably, a higher storage modulus (G') was consistently observed in thermally cured samples compared to their UV-cured counterparts at equivalent cross-linker loadings. This higher modulus correlates with the increased gel fraction observed for the thermally cured samples. It is proposed that this small but consistent increase in gel fraction between UV- and thermally cured samples is due to both longer reaction times and enhanced chain mobility at elevated temperatures. Additionally, the initial formation of a yellow color for the UV-cured samples is noteworthy. This color is consistent with a minor side reaction involving the formation of a diazo isomer from the starting diazirine units. The inability of these diazo isomers to generate carbene intermediates may decrease overall carbene content upon irradiation, contributing to the observed differences in properties between UV- and thermally cured samples.[14] Upon heating, the yellow color disappears presumably due to the conversion of diazo groups to the desired carbene species, leading to a higher degree of cross-linking.

With the efficient curing of unfunctionalized PnBA being established, the molecular weight impact of the PnBA-co-PDzA cross-linker was then investigated. In addition to **P1** (M_n = 52 kDa, 10 mol % functionalization), two PnBA-co-PDzA cross-linkers with M_n = 22 and 11 kDa containing 10 mol % diazirine acrylate units were also prepared. With the same feed ratio of 10 mol % diazirine, these molecular weights correspond to approximately 44, 18, and 9 diazirine groups per chain, respectively. Despite the significant variation in molecular weight, all of these cross-linkers were fully miscible with high

molecular weight, unfunctionalized PnBA and could lead to successful curing at a **CF$_3$Dz** content of 0.8 wt % (10 wt % loading of the polymeric cross-linkers). In each case, high gel fractions exceeding 95% were achieved under both UV and thermal curing conditions (Tables S6 and S7; Figure S14).

While cross-linkers with varied molecular weights afford equally high gel content, the molecular weight of the unfunctionalized PnBA homopolymer was also shown to significantly influence the efficiency of network formation. For example, a blend consisting of an unfunctionalized PnBA with a lower molecular weight (M_n = 25 kDa) yields a gel fraction of 44% when subjected to UV curing (Table S8; Figure S15). This reduction in cross-linking can be attributed to two factors: (1) compared to the PnBA with M_n of 105 kDa, the lower M_n of 25 kDa correlates to an approximately 4-time increase in the number of chains in this blend, leading to less efficient cross-linking, and (2) the chain entanglement is significantly reduced with the lower M_n of 25 kDa, resulting in fewer entanglements being trapped as cross-links after curing.

A major advantage of the polymeric diazirine strategy is the ability to tune the nature of the backbone to allow blending with a wide variety of unfunctionalized linear polymers. Having demonstrated the efficient cross-linking of PnBA, curing studies were then conducted on other commercially important polymers, including poly(methyl acrylate) (PMA), poly-(methyl methacrylate) (PMMA), poly(N-isopropylacrylamide) (PNIPAM), and polydimethylsiloxane (PDMS). For the vinyl-based systems, facile RAFT copolymerization of diazirine-containing acrylate or methacrylate monomers with the desired vinyl monomers successfully produced polymeric cross-linkers with 10 mol % of diazirine content and varied backbone structures (Table 1, **P2**−**P4**).

In all cases, homogeneous blending of the diazirine-containing copolymer with the corresponding unfunctionalized systems proved to be successful. For example, the PMA copolymer (**P2**) was blended with linear unfunctionalized

Table 1. Gel Fractions of Cross-Linked PMA, PMMA, and PNIPAM

Polymer Cross-Linker	Linear Polymer	Gel Fraction[a]	
		UV[b]	Thermal[c]
P2		56% ± 9%	91 ± 1%
P3		51% ± 6%	87% ± 1%
P4		78% ± 1%	81% ± 2%

[a]Average values of triplicate experiments. [b]Exposed to 370 nm light for 1 min (PMA) or 5 min (PMMA and PNIPAM). [c]Heating at 110 °C for 2 h.

PMA at a 10 wt % loading (1.0 wt % of **CF$_3$Dz**), and the blend was subjected to curing conditions. A moderate gel fraction of 56% and a high gel fraction of 91% were achieved through UV and thermal curing, respectively (Table 1). Similar to the results with PnBA, superior cross-linking efficiency was observed with thermal curing, supporting the hypothesis that increased chain mobility and a higher amount of carbene intermediate upon heating also contributed to enhanced cross-linking efficiency. Notably, the discrepancy between UV and thermal curing is particularly pronounced in the case of PMA compared with PnBA, likely due to the higher glass transition temperature for PMA (T_g = 10 °C). To further investigate the influence of T_g on the curing process, a blend of PMMA with the corresponding cross-linker **P3** at a 10 wt % loading (1.0 wt % of **CF$_3$Dz**) was cured (Table 1). Gel fractions of 51% and 87% were observed after UV and thermal curing, respectively, consistent with the lower cross-linking efficiency of the glassy PMMA blend at room temperature, which limits polymer chain mobility (T_g = 110 °C). Additionally, the cross-linking of PNIPAM was examined, owing to its versatile biomedical applications.[32,33] Unfunctionalized PNIPAM could be blended with a diazirine-containing PNIPAM copolymer (**P4**) at a 10 wt % loading (0.8 wt % of **CF$_3$Dz**) and successfully cured under both UV and thermal conditions, yielding high gel fractions of 78% and 81%, respectively (Table 1). Collectively, these findings illustrate the versatility of diazirine-containing polymers in cross-linking a diverse range of acrylic polymers.

To further expand the scope of polymer backbones, the cross-linking of PDMS systems with diazirine chemistry was examined. Unlike acrylic-based polymeric cross-linkers prepared from radical copolymerization, the required PDMS-based diazirine-containing cross-linkers can be synthesized through the modification of commercially available polysiloxanes. Specifically, a hydrosilylation reaction between the Si−H groups of a commercial PDMS copolymer and an allyl-containing diazirine derivative (**1**) was employed to produce the desired cross-linker, with nearly quantitative conversion of the Si−H groups to the desired diazirine units (**P5**, Figure 5A).[34,35] Significantly, the compatibility of the diazirine units with hydrosilylation chemistry further demonstrates the synthetic versatility of diazirine building blocks in polymer science. Photo-cross-linking of commercial polysiloxane derivatives was then examined with a view to the growing range of applications for PDMS systems in the fabrication of elastomers and coating materials.[36−39]

The PDMS-based cross-linker **P5** was first blended with an unfunctionalized PDMS and subjected to typical UV-curing conditions. However, no cross-linking was observed, likely due to the high bond dissociation energy of the C−H bond in the Si−CH$_3$ groups (Table S12).[40] To test this hypothesis, two commercial PDMS copolymers containing more reactive silane groups (Si−H, 4−8%) or thiol groups (S−H, 4−6%) were then blended with **P5** and cured by UV irradiation. It is noteworthy that gel fractions of 46% and 58% were achieved for these two blends (Table S12). Compared to unfunctionalized PDMS, the introduction of cross-linkable silane or thiol groups into the PDMS backbone significantly enhanced the ability to cross-link polysiloxane materials.

Next, photopatterning experiments were conducted using a low-viscosity blend based on a commercial PDMS copolymer (M_n = 7 kDa) containing 4−6% thiol groups. A clear blend was prepared by mixing 80 wt % of the commercial PDMS copolymer with 20 wt % of **P5** (1.1 wt % of **CF$_3$Dz**). Using a
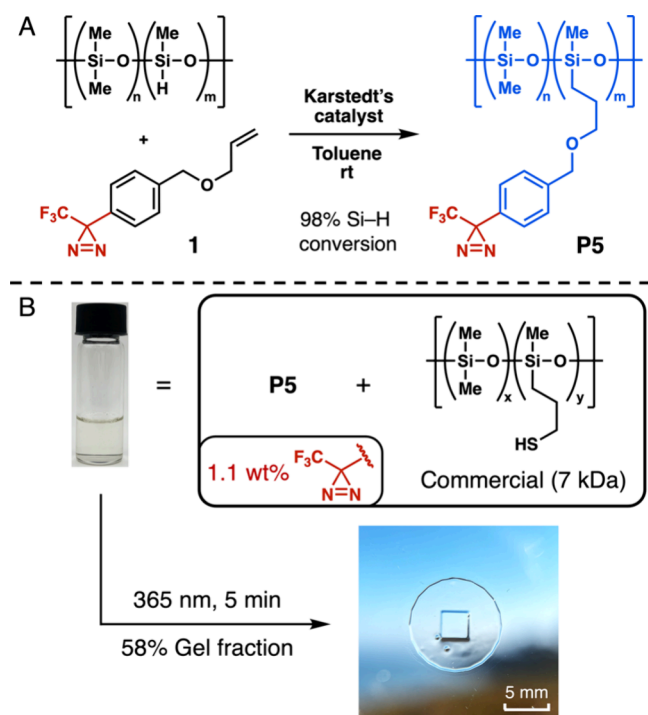
Figure 5. (A) Synthesis of diazirine-containing polysiloxane **P5** shows previously unattainable compatibility of diazirine compounds with hydrosilylation conditions. (B) Successful photopatterning of the thiol-containing resin with 20 wt % of **P5** (1.1 wt % of **CF₃Dz**). Experiments were performed on a commercial Mono3Z2 printer.

commercial Mono3Z2 3D printer, a square-void-in-circle pattern was successfully fabricated by irradiating the PDMS blend with 365 nm light for 5 min (Figure 3B). The demonstration of efficient photopatterning highlights the utility of diazirine-containing polymers in the fabrication of silicone materials, paving the way for future 3D printing applications.

In summary, this study describes the synthesis and application of diazirine-containing polymers for the efficient cross-linking of unfunctionalized vinyl- and siloxane polymers. Through the analysis of the gel content and mechanical characterization of the polymer networks, thermal and photochemical curing of a variety of blends based on commodity polymers at different cross-linker loadings was examined. Impressive gel fractions exceeding 95% are achieved with a diazirine content of 0.8 wt % upon 1 min UV irradiation for linear P*n*BA systems. Furthermore, the versatility of diazirine-containing polymers is highlighted by the effective blending and cross-linking of other vinyl polymers such as PMA, PMMA, and PNIPAM. Significantly, a diazirine-containing polysiloxane cross-linker could be synthesized via hydrosilylation, facilitating tunable cross-linking of commercially available linear silicone derivatives. The successful photopatterning of these silicone resin blends using a commercial 3D printer showcases the practicality and potential of diazirine-containing polymers in advanced materials design and fabrication.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.4c00675.

Detailed experimental procedures, characterization (NMR, SEC, rheology), and gel fraction measurements (PDF)

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#M.X. and B.H. contributed equally. CRediT: **Mizhi Xu** conceptualization, writing - original draft; **Banruo Huang** conceptualization, writing - original draft; **Haley K. Beech** investigation, writing - review & editing; **Patrick T. Getty** investigation, writing - review & editing; **Juan Manuel Urueña** investigation; **Craig J. Hawker** conceptualization, funding acquisition, supervision, writing - original draft, writing - review & editing.

Notes

The authors declare no competing financial interest.

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