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Reactive, Multifunctional Polymer Films through Thermal Cross-linking of Orthogonal Click Groups

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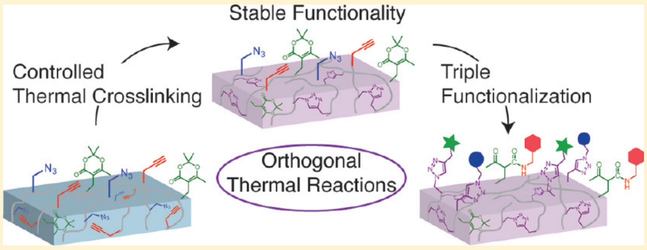
Ⓢ *Supporting Information*



ABSTRACT: The ability to produce robust and functional cross-linked materials from soluble and processable organic polymers is dependent upon facile chemistries for both reinforcing the structure through cross-linking and for subsequent decoration with active functional groups. Generally, covalent cross-linking of polymeric assemblies is brought about by the application of heat or light to generate highly reactive groups from stable precursors placed along the chains that undergo coupling or grafting reactions. Typically, these strategies suffer from a general lack of control of the cross-linking chemistry as well as the fleeting nature of the reactive species that precludes secondary chemistry. We have addressed both of these issues using orthogonal chemistries to effect both cross-linking and subsequent functionalization of polymer films by mild heating, which results in exacting control of the cross-link density as well as the density of the residual stable functional groups available for subsequent, stepwise functionalization. This methodology is exploited to develop a strategy for the independent and orthogonal triple-functionalization of cross-linked polymer thin-films through microcontact printing.

■ INTRODUCTION

Cross-linking is of crucial importance to endow enhanced thermal stability, mechanical properties, and solvent resistance to commodity materials.[1−9] Two general strategies include (1) the preparation of cross-linked materials directly through the polymerization of multifunctional monomer units and (2) the induced covalent cross-linking of preformed polymer chains in a secondary step.[10] The latter method allows facile processing and may be brought about through reaction along the polymer chain with difunctional small molecule cross-linkers, a process which generally proceeds through mild and well-defined chemistry but results in material that must be further purified to remove either catalyst or unreacted small molecules. Alternatively, cross-linking may be externally triggered by the application of heat, light, or pressure to generate highly reactive intermediates that undergo nonselective bond formation in an uncontrolled and ill-defined manner.[11−14] While many commodity materials are processed in this way, such as the vulcanization of rubber at high temperatures[15] or the cross-linking of polyethylene through strong ionizing γ-ray irradiation,[16] these conditions are often too harsh to combine cross-linking with secondary functionalization. Therefore, an approach combining the best of each established strategy is necessary, where *well-defined chemistry* induced under *mild conditions* without any small molecule additives is employed to produce cross-linked materials. An additional advantage of using such an approach is that residual functional handles remaining following cross-linking are active for subsequent functionalization steps.

Examples of controlled, externally triggered cross-linking strategies include the photolytic generation of reactive nitrenes,[17] the thermal activation of benzocyclobutene[3,18] and the thermolytic generation of ketenes from Meldrum's acid derivatives.[19] While these approaches have been used advantageously to prepare polymer coatings[3] for surface energy neutralization, to trap assembled polymer domains,[20−27] or prepare monofunctionalized surfaces,[19] the harsh conditions used to generate the active cross-linking species often limit the functional group tolerance of these processes and therefore the end-use of the resulting materials. One such application is as a general platform for functional surface coatings, especially those bearing diverse orthogonal reactive chemical functionalities available for covalent patterning.

The ability to selectively pattern multiple ligands within the bulk of a material or at the surface enables many applications such as differential surface wetting,[3] site-specific biomolecule or cell affinity,[28] and multicomponent catalytic systems.[29] A number of elegant techniques have been developed to achieve spatial surface patterning of orthogonal functionalities, including electron-beam lithography,[30] inkjet printing of reactive ligands,[28] reactive imprinting,[31] dip-pen[32] and direct-write nanolithography,[33] as well as microcontact printing (μCP).[19,34] Such patterning is usually

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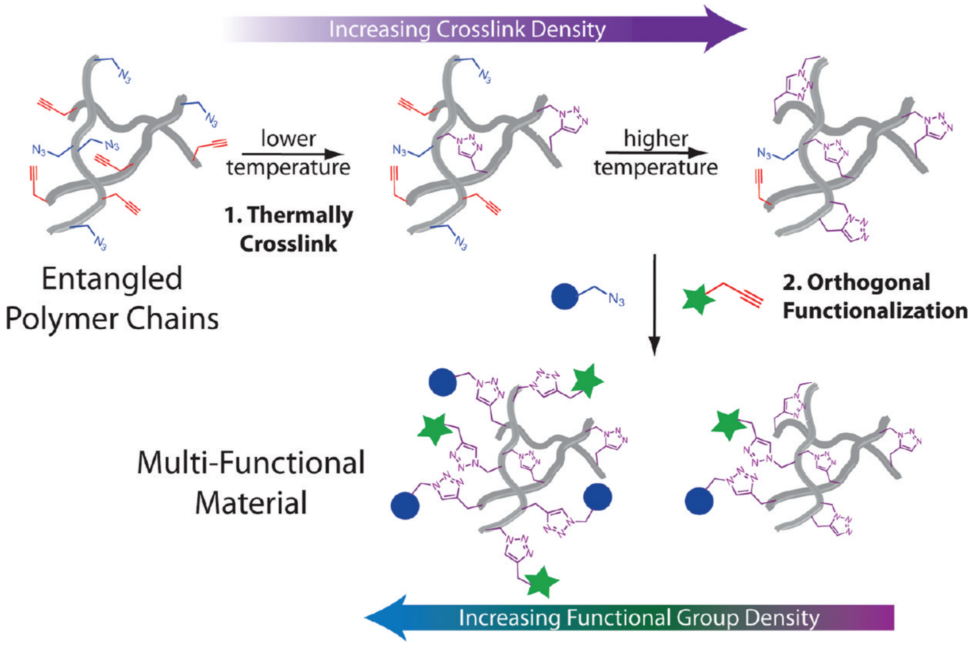


Figure 1. Schematic representation of the thermal azide−alkyne cycloaddition chemistry used to prepare cross-linked material with the residual azide and alkyne groups being stable after cross-linking and amenable to secondary functionalization. The temperature used for cross-linking provides accurate control of the cross-link density as well as the density of remaining functional groups.

achieved through the serial application[35−38] of the same ligation chemistry to append different molecular species in nonoverlapping areas with little control over the extent of functionalization. While orthogonal chemistries have been explored recently for the multifunctionalization of surfaces,[39−42] appending different molecular functions to the same regions of a surface remains a significant challenge.

Herein, we report a system that employs mild, orthogonal chemistries to both cross-link and functionalize polymer structures in a controlled manner (Figure 1). We first describe the thermal azide−alkyne cycloaddition (TAAC) chemistry[43] (Figure 2a) to cross-link polymer films at low temperatures with fine control over the extent of cross-linking and residual functionality. The classical TAAC reaction was employed for a number of reasons, including the ability to conduct the reaction under normal atmospheric conditions without the use of additional reagents, solvents, or catalysts. Both van Hest and co-workers[41] as well as Gonzaga and co-workers[44] utilized these features to covalently cross-link side-chain functional azide polymers using small difunctional alkyne molecules, where effective cross-linking was achieved at temperatures above 125 °C when unactivated alkyne groups were employed. By placing both reactive groups along the same polymer backbone, the need to use small molecule cross-linkers is removed and, more importantly, effective cross-linking of unactivated azide and alkyne moieties can be achieved at lower temperatures. The resulting, mild conditions for TAAC cross-linking also enable the incorporation of diverse residual functional groups, active for subsequent ligation. To demonstrate the potential of this strategy, the spatial surface ligation of small molecules to these residual surface functionalities on the cross-linked polymer films was performed using TAAC chemistry as well as an orthogonal acyl ketene functional handle[45] (Figure 2b). This enables the patterning of independent and overlapping regions of three unique functionalities.

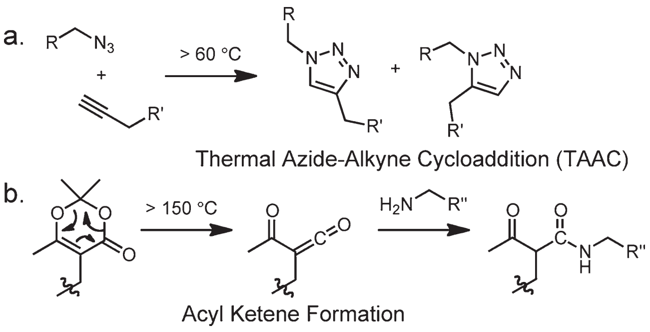
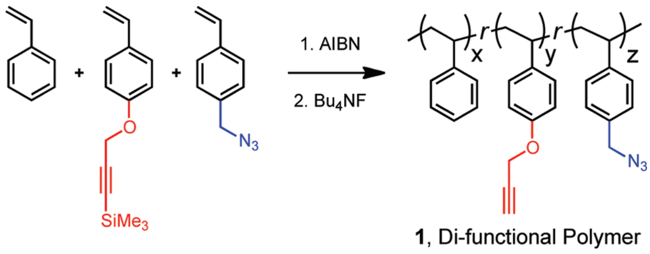


Figure 2. Representative examples of mild and orthogonal covalent bond forming chemistries, (a) thermal azide−alkyne cycloaddition (TAAC) and (b) thermolytic retrocyclization generation of acyl ketenes followed by nucleophilic trapping.

RESULTS AND DISCUSSION

Polymer Synthesis and Cross-linking. Polymers containing both azides and alkynes randomly incorporated along the backbone were prepared utilizing free radical copolymerization of a three component mixture of styrene, TMS-protected propargyloxy-styrene,[46] and vinylbenzyl azide (Scheme 1). Both the azide and protected alkyne monomers have been used previously[47−49] to provide macromolecules with functional azide and alkyne moieties enabling efficient chain functionalization using Cu-based click chemistries. Less commonly applied is the incorporation of both azide and alkyne functionalities along the same polymer backbone; these approaches have enabled intramolecular cross-linking to afford single chain polymer nanoparticles.[50−52] We prepared a single macromolecule bearing both the azide and alkyne functionalities in order to prevent possible phase separation and thus ensure the availability of both reactive partners for

Scheme 1. Synthesis of Di-functional Linear Polymer Building Block 1



cross-linking. The ratio of azide to alkyne and the total incorporation were easily controlled by the feed ratio of the three monomers with the terminal alkyne being obtained after deprotection with tetrabutylammonium fluoride (TBAF).[46] Through radical polymerization, we prepared difunctional polymer **1** with a number average molecular weight of 17 kg/mol and bearing 5 mol percent each of azide and terminal alkyne repeat units along the backbone (Scheme 1).[53]

The TAAC cross-linking was initially evaluated with the difunctional polymer. Polymer films of **1** were prepared with an average thickness of 160 nm through spin-coating onto hydrophobic *n*-octane functionalized silicon substrates; matching the polarity of the surface and polymer allowed greater reproducibility in the preparation of uniform polymer films. The resulting thin films of **1** were heated under air across a range of temperatures and lengths of time to induce TAAC-mediated cross-linking, followed by washing with tetrahydrofuran to remove un-cross-linked polymer chains. The ratio of final to initial film thickness provides a metric of cross-linking efficiency. Examination of the film thickness ratio versus cross-linking temperature (Figure 3a), reveals that critical cross-linking can be achieved at temperatures below 100 °C and that a plateau in cross-linking occurs after progressively longer times as the cross-linking temperature is lowered. Appreciable cross-linking was achieved following heating at 60 °C for 20 h or 110 °C for 30 min, which demonstrates the mild nature of the process (Figure 3b). In control experiments, no cross-linking was observed for films of monofunctional azide or alkyne polymers (see Supporting Information, Figure S2) at even the highest temperatures effective for cross-linking the difunctional polymer. This confirms that the presence of both species is necessary and is indicative of the TAAC reaction.

Spectroscopic techniques provided valuable insights into the chemical and physical nature of the cross-linking process. Fourier transform infrared (FT-IR) spectroscopy of bulk samples of polymer heated at 90 °C for various times (see Supporting Information, Figure S3) reveal a progressive and coupled attenuation of absorbances attributed to both the azide (N═N═N) and alkyne (≡C−H) functional groups with heating, suggesting coreaction to form the desired triazole. However, to provide a more detailed and quantitative picture of the chemistry occurring during the cross-linking process, we employed solid-state nuclear magnetic resonance (NMR) spectroscopy. The cross-polarization magic angle spinning ^{13}C NMR spectrum of polymer **1** was unsurprisingly dominated by resonances due to the polystyrene backbone, providing little information even after prolonged acquisition times. To achieve adequate signal-to-noise for the specific resonances arising from the alkyne moieties, a difunctional polymer bearing ^{13}C-labeled alkyne carbons was prepared from $^{13}C_3$-propargyl alcohol (see Supporting Information). An added advantage of using this labeled polymer was that high signal-to-noise spectra could be recorded in less than 15 min, a feature which allowed real-time *in situ* analysis of the cross-linking reaction occurring in the solid state.

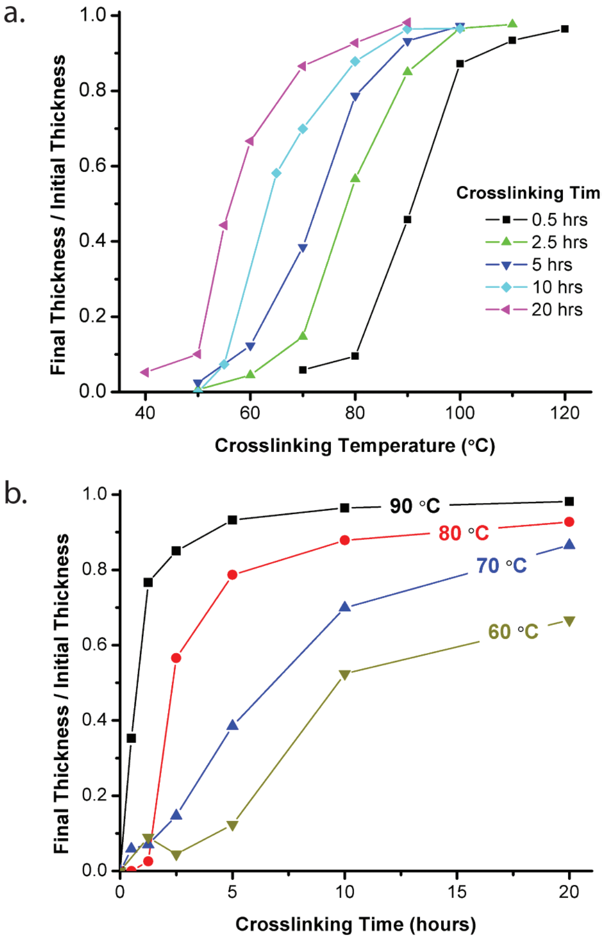


Figure 3. Relationship between cross-linking (a) temperature and (b) time and the extent of cross-linking for difunctional linear polymer **1**.

Bulk samples of the ^{13}C-labeled polymer were loaded into 4 mm bore sample rotors and heated within the NMR spectrometer while recording ^{13}C NMR spectra every 20 min. Initially, as displayed in Figure 4b, two dominant resonances appear attributed to the overlapping signals of both alkyne carbons, occurring around 77 ppm, as well as the propargyl methylene carbon at *ca.* 55 ppm. Additional signals also appear due to the natural abundance ^{13}C resonances for both the backbone aromatic and aliphatic positions. After heating for extended periods, dramatic changes are evident in the NMR spectra with a significant attenuation occurring in the resonance intensity of the alkyne carbons and a correlated growth in aromatic signals. The appearance of the three aromatic signals correlate with the formation of both 1,4- and 1,5-triazole rings, as expected.[54] A shift in the propargyl methylene also correlates with its transformation into a methylene neighboring the newly formed triazole ring. By performing the cross-linking reaction within the rotor itself, while recording spectra every 20 min, a wealth of kinetic data was obtained. Quantitative data was extracted by calculating the percentage change of any one resonance across time. The comparison of the normalized changes in intensities of both the alkyne carbons

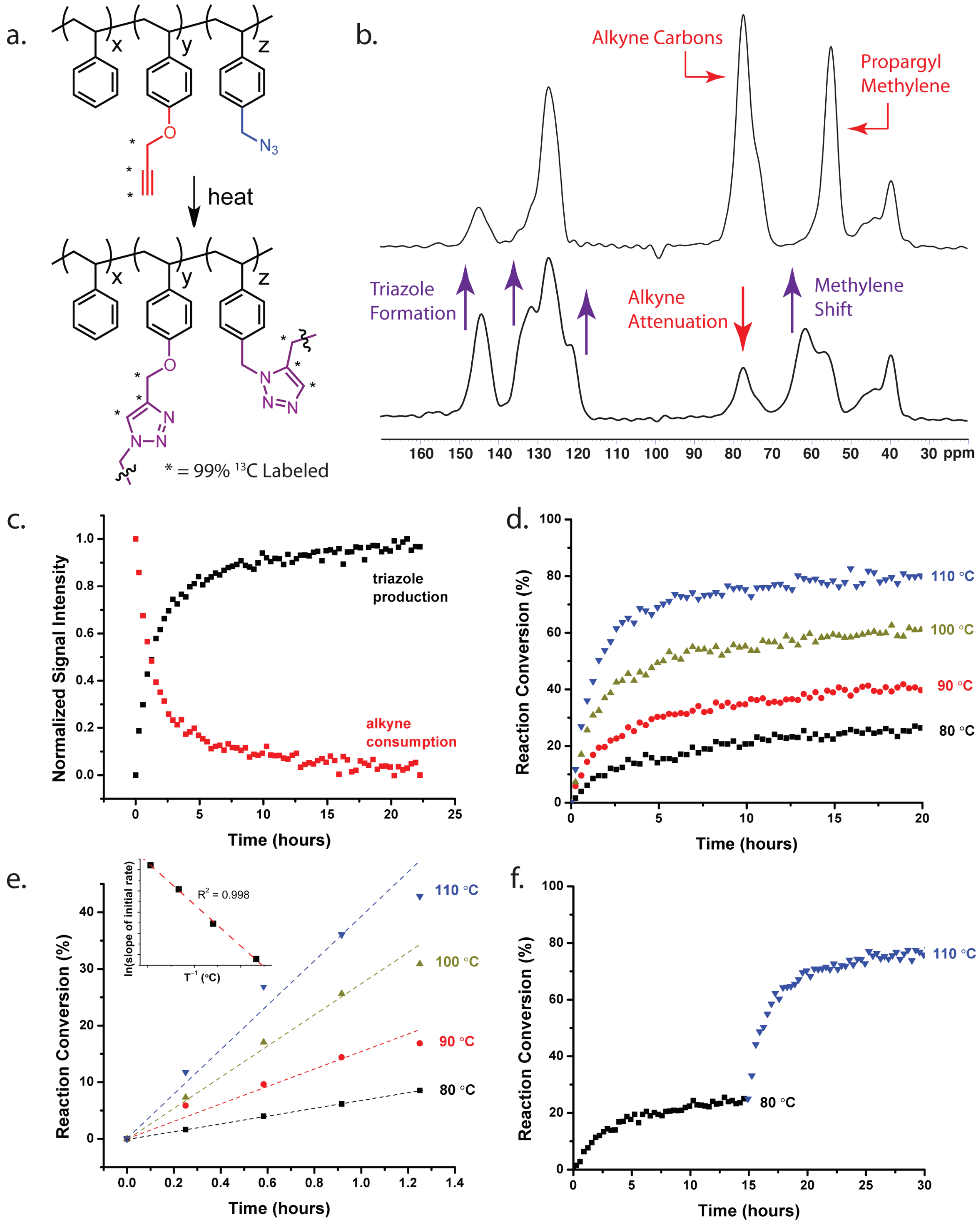


Figure 4. Solid-state ^{13}C NMR spectroscopy of (a) isotopically labeled cross-linkable polymer **1** provides (b) good signal-to-noise spectra detailing the initial (top) and final (bottom) state of the material where the alkyne peak is attenuated and triazole signals arise after heating. (c) Alkyne consumption and triazole production are observed in real time and are perfectly correlated, data shown collected at 110 °C; (d) the alkyne signal attenuation is used to calculate the reaction conversion as a function of time. (e) Initial rate kinetics follow Arrhenius behavior (an enlargement of the Arrhenius plot insert is displayed in the Supporting Information, Figure S8). (f) Two-stage heating experiment displays two distinct plateau regions.

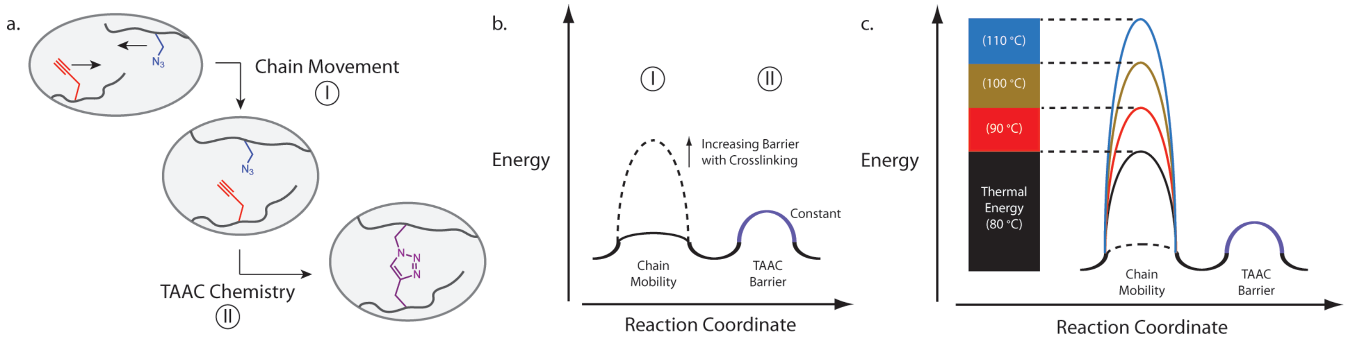


Figure 5. Proposed mechanism to polymer cross-linking in which (a) two basic steps are the important parameters, chain movement and cycloaddition chemistry. Initially, the barrier to TAAC is the largest such that the reaction may be described as an activated process. (b) Over time chain mobility becomes the most important term such that the extent of cross-linking may be tuned actively with temperature (and mobility of the chains). (c) Barrier to chain movement increases until the available thermal energy disallows any further cross-linking.

signals and the sum of triazole carbon signals with time (Figure 4c) reveals a clean transformation of the alkyne species into triazole products—clearly demonstrating that the TAAC reaction is the sole process occurring upon heating.

Accurate control over the cross-linking process was also apparent by observing the differences in reaction conversion as a function of time for samples heated at different temperatures (Figure 4d). In each case, the reaction conversion plateaued and a distinct trend was observed linking the plateau conversion with cross-linking. Closer examination of these data show that the initial rates of the reactions (Figure 4e) are constant at each temperature; an Arrhenius plot of the natural logarithm of the slope of the initial rates versus the inverse of the temperature provided a straight line, with no discontinuities, as might be expected, around the glass transition temperature of polystyrene (around 100 °C).[55] From these data it is apparent that the cross-linking reaction proceeds as a thermally activated process; over time, however, the reaction progress halts at a unique conversion, the position of which is dictated by the cross-linking temperature. To better understand the nature of these plateau regions, specifically to determine if a trajectory effect determines the plateau position, we performed a two part heating experiment, where a sample heated to well within its plateau region at 80 °C was then subsequently heated higher to 110 °C. Interestingly, it was found that upon higher heating, the reaction resumed at a rapid rate, plateauing at *ca.* 80% conversion (identical to the single heat treatment experiment) free of any trajectory effects (Figure 4f).

The kinetic data together describe an interesting cross-linking mechanism (Figure 5) where the cycloaddition proceeds as a thermally activated process to a critical reaction conversion when chain mobility begins to hinder reaction progress. Such behavior has been studied in the thermosetting of bulk epoxy resins[56,57] where the interplay of T_g and degree of cross-linking are aligned. In the case of the TAAC cross-linking that occurs efficiently at low temperatures (significantly below the T_g of polystyrene), the mobility of reaction partners becomes an extremely important parameter. This is best described using a reaction coordinate diagram where we reduce the complexity to two simple barriers, the first being a chain movement step and the second the actual bond formation (Figure 5b). As bond formation progresses, the forming cross-linked network increasingly hinders the movement of chains. Hence, the barrier of movement necessary for reactive alkyne and azide partners to find one another becomes larger over time. This self-limiting mechanism is supported by the fact that the T_g of a bulk polymer sample steadily increased with progressive heating at 80, 90, 100, and 110 °C (see Supporting Information, Figure S4) such that the cross-linking reaction is always performed at a temperature below the T_g of the resulting cross-linked network. Eventually, the chain mobility barrier becomes dominant and the reaction stops. By heating the sample to higher temperatures, the necessary thermal energy is introduced to allow more chain mobility and hence further cross-linking to occur (Figure 5c). The implications of this self-limiting mechanism are that the cross-link density and concentration of remaining functional groups may be accurately tuned by selection of the curing temperature (Figure 2). We further speculate that conditions in which the lowering of T_g at interfaces and/or in nanoconfinement[58] may be devised to affect the degree of cross-linking and residual functionality in those regions; perhaps such effects could allow cross-linking at even lower temperatures or could be exploited to produce materials with a gradient of cross-linking density/secondary reactive groups.

Interestingly, the trimethylsilyl (TMS)-protected alkyne difunctional polymer (polymer **S1**, see Supporting Information) demonstrates efficient thermal cross-linking. However, the efficiency is greatly reduced at lower temperatures (around 60 °C), but approaches comparable values at temperatures above 80 °C (see Supporting Information, Figure S5). Solid-state ^{13}C NMR analysis of the ^{13}C-labeled polymer **S1** clearly demonstrates that the TMS protecting group, rather than first being thermally hydrolyzed to then allow the TAAC of the resulting terminal alkyne and the azide moieties, remains in place throughout the course of the TAAC reaction (see Supporting Information, Figure S5). These data lend further support to our cross-linking mechanism—the TAAC barrier is dominant at lower temperatures such that drastic rate differences exist between the TMS-protected and terminal alkyne difunctional polymers. At higher temperatures, however, chain mobility becomes the rate-limiting factor and the two different polymers cross-link at comparable rates.[59]

Cross-linked Polymer Film Functionalization. The availability and controllable density of the reactive azide and alkyne functionalities within cross-linked polymer films presents many attractive possibilities for preparing multifunctional materials, especially when considering the powerful click chemistry paradigms that have developed recently.[48,49] These groups, when presented within cross-linked films at temperatures below those used for initial cross-linking, are isolated from one another such that they are only

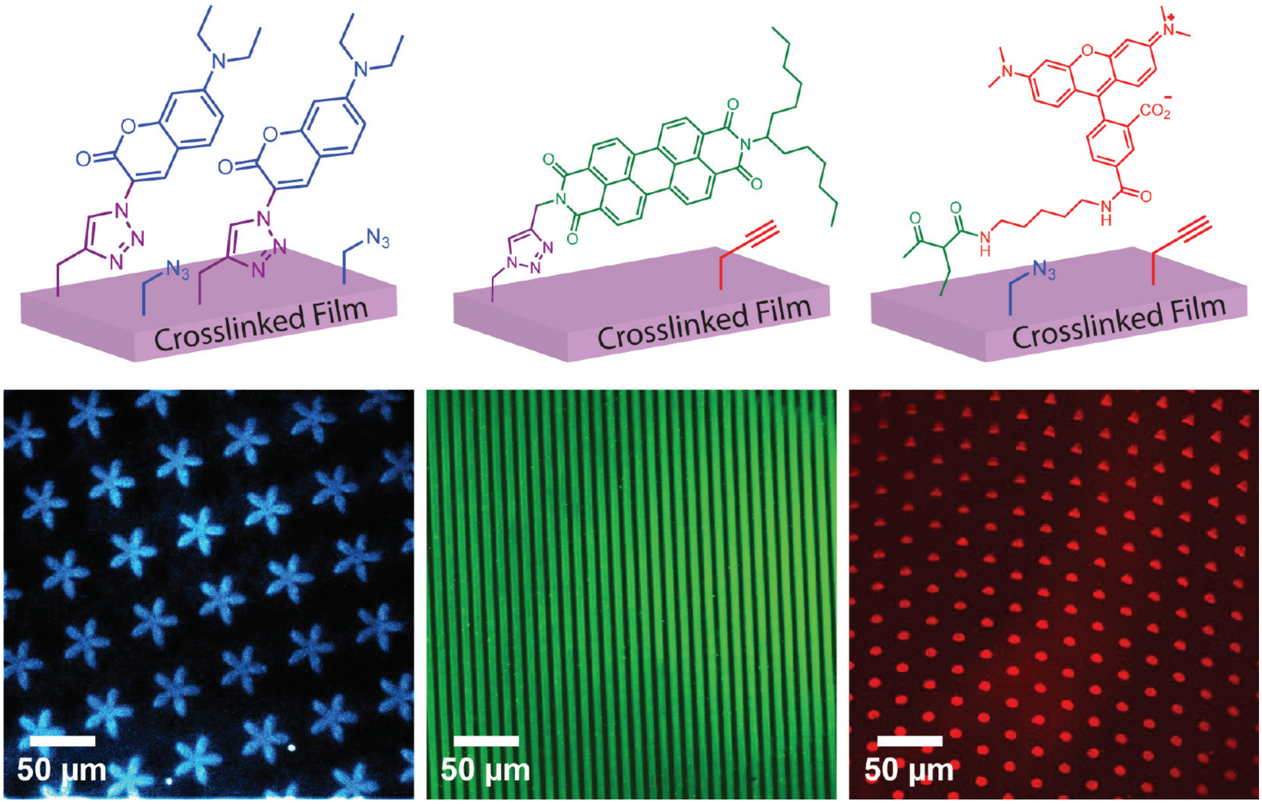


Figure 6. Confocal fluorescence images of different polymer films each patterned with either (left) azide-, (center) alkyne-, or (right) amine-bearing fluorescent dyes using thermal microcontact printing mediated covalent bond formation. The two left images utilized the difunctional polymer **1**, while the right image was recorded from a trifunctional polymer **2** substrate.

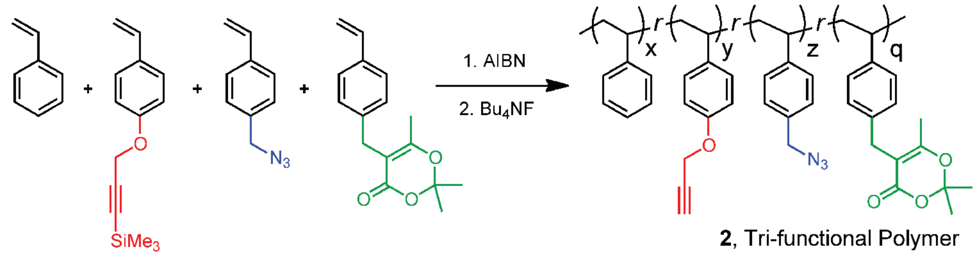
accessible for reaction with mobile complementary reactive partners, typically small molecules. Taking advantage of these unique features, we chose to decorate both the alkyne and azide moieties at the surface of the cross-linked films by independent, covalent patterning of the corresponding azide- and alkyne-bearing fluorescent probes through TAAC chemistry directed by microcontact printing.

Patterned elastomeric stamps of poly(dimethylsiloxane) (PDMS), inked with solutions of either an azido-coumarin dye[60] or an alkynyl-perylene derivative[61] were pressed onto films of polymer **1** that had previously been cross-linked at 90 °C for 12 h. This prior cross-linking at 90 °C consumes roughly 35% of the total azide and alkyne groups, leaving the remaining 65% isolated from one another and available for functionalization. The “inks” were transferred to the cross-linked polymer surface through direct contact with the stamp which was pressed onto the substrates during heat treatment at 90 °C for 30 min to induce covalent ligation. To remove any absorbed dye, the surfaces were then washed extensively with dichloromethane, toluene, and ethanol. The resulting 2-dimensional covalent patterns on the cross-linked polymer surface were imaged using confocal fluorescence microscopy (Figure 6). The blue fluorescence pattern observed for printed azido-coumarin features indicates the formation of the triazole linkage with the residual alkyne units within the cross-linked polymer network, as the coumarin azide dye precursor was developed as a turn-on dye, only becoming fluorescent upon reaction.[60] The bright green features observed for printed alkyne-functional perylene probe demonstrate that the complementary azide units are also accessible.[62] The faithful reproduction of the pattern in each case indicates that the thermal printing process occurs efficiently and without significant lateral diffusion of the probe molecules throughout the film.

The mild nature of the TAAC cross-linking and functionalization enables other orthogonal, reactive groups to be easily introduced into these cross-linked systems. To demonstrate this inherent versatility, trifunctional polymer, **2**, incorporating 5 mol percent each of azide, alkyne, and acyl ketene precursor, was prepared through copolymerization of an acyl ketene styrenic precursor with styrene, vinylbenzyl azide, and TMS-protected propargyloxy-styrene (Scheme 2). The resulting polymer **2** provided easy access to a triply functional material, where the orthogonal chemistries of the azide, alkyne, and acyl ketene handles could be used to tailor the properties of any cross-linked polymer material with three distinct and individually addressable reactive handles. We have discovered significant opportunities[19,26] for the ketene functional group in polymer chemistry, including polymer cross-linking and functionalization. Acyl ketenes, as opposed to the alkyl derivatives previously studied, are generated at significantly lower temperatures, do not participate in [2 + 2] dimerizations, and are potent electrophiles. These features make the acyl ketene an ideal orthogonal and complementary thermally activated reactive group to the azide/alkyne chemistry used for both cross-linking and functionalization.

Spin-coated films of the trifunctional polymer **2** were therefore cross-linked by heating at 90 °C for 12 h in an analogous manner to polymer **1**. The acyl ketene precursor was shown to be stable at temperatures below 150 °C and is thus fully compatible with and orthogonal to the azide–alkyne thermal cross-linking and

Scheme 2. Synthesis of Tri-functional Linear Polymer Building Block 2



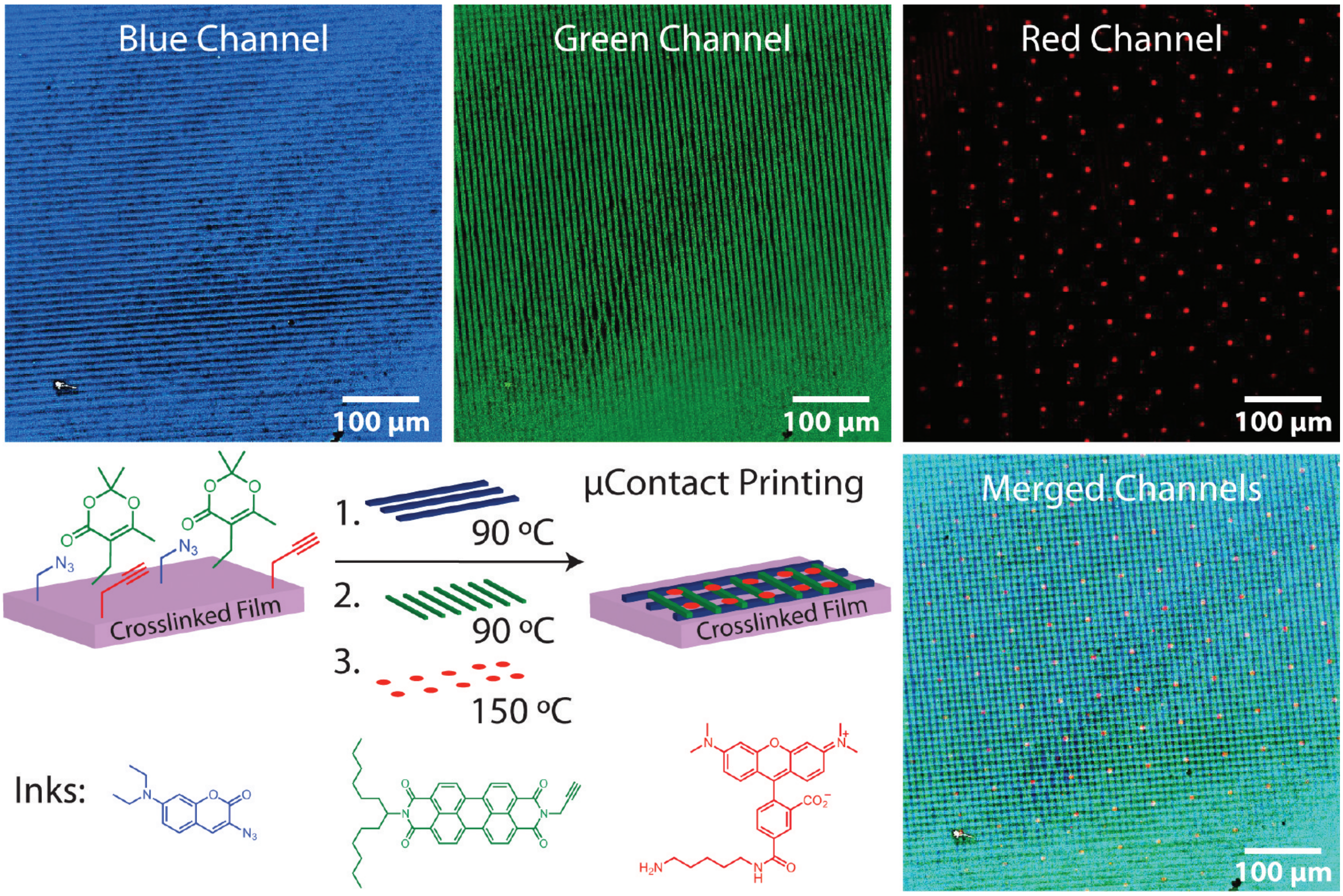


Figure 7. Single trifunctional polymer **2** film having been functionalized in a three-step process with blue, green, and red features orthogonally through thermal microcontact printing mediated covalent bond formation. Imaging in separate color channels reveals the trifunctional pattern that is based upon orthogonal chemistry and regions of double and triple functionality coexist with singly functionalized domains are easily identified by merging the three channels.

functionalization strategy presented. Its thermolysis at higher temperature activates it to the corresponding ketene, an excellent electrophile for the attachment of a wide variety of nucleophiles in a secondary step. In the case of a homopolymer of the acyl ketene precursor monomer (see Supporting Information, Figure S6), a mass loss of 20% corresponding to the liberation of acetone (and generation of the acyl ketene species) was observed by thermal gravimetric analysis (TGA) beginning around 170 °C for the polymer in the solid-state. An analogous small molecule study was conducted (see Supporting Information), in which heating an acyl ketene precursor in the presence of benzyl amine at 150 °C for 45 min resulted in the clean and near quantitative conversion to the amide product. It is known[63,64] that the environment affects the kinetics of retrocyclic formation of acyl ketenes and that the presence of an electron donating species during the heating process could account for the lower temperature of ketene formation in the small molecule case.

To probe the presence of the acyl ketene functionality at the surface of the cross-linked networks of trifunctional polymer **2**, we chose to thermally microcontact print a commercially available red fluorescent amine-containing dye, TAMRA-cadaverine, as the "ink" onto the cross-linked film. Heating a substrate in contact with the amino-functional red dye patterned stamp at 150 °C for 30 min resulted in the thermolytic generation of the acyl ketene as well as its rapid nucleophilic trapping by the amino-functional dye, as evidenced by the faithful fluorescence pattern replication (Figure 6, right). No dye transfer or covalent attachment was observed when temperatures less than 130 °C were employed for thermal microcontact printing, indicating that acyl ketene generation occurs only at higher temperatures and is an ideal orthogonal handle to complement the azide−alkyne chemistry occurring at lower temperatures. Similarly, no dye transfer was observed when **1** was employed in the 150 °C thermal printing because this polymer lacks the orthogonal acyl ketene precursor unit. Additionally, we confirmed that the benzyl azide moieties were stable toward the 150 °C thermal treatment, only thermolyzing at even higher temperatures[17] to form highly reactive nitrene functions, as evidenced by FT-IR measurements (see Supporting Information, Figure S9).

While we were encouraged by the ability to separately address each of the alkyne, azide, and acyl ketene functions within cross-linked films of **2**, the orthogonality of these chemistries is best demonstrated through a multistep printing process onto a single polymer film. Overlapping patterns were produced by successive thermal printings onto the same substrate. Line features of both blue and green dyes were printed in a perpendicular direction, first printing the azido-coumarin dye in a horizontal line pattern at 90 °C followed by printing of alkyne-perylene dye in the same line pattern in the perpendicular direction with a second thermal treatment. To this substrate was then printed the red amine dye in a dot pattern by heating to 150 °C for 30 min. The resulting film was rinsed with good solvents for the respective dye molecules in between thermal treatments and again following the final thermal patterning. Confocal fluorescence of the substrate (Figure 7), simultaneously collecting data across all three channels for blue, green, and red, allowed the separate imaging of features patterned in the same area on the substrate. The interplay of the three distinct probes, indicating three orthogonal reactions, is revealed by merging the color channels. Significantly, regions of colocalization of two and three dyes, as well as regions where only one dye were observed, indicating the accessibility and orthogonality of each functional unit. These features allow multifunctional surfaces to be produced using two distinct chemistries, enabling first a controlled materials cross-linking and then orthogonal materials functionalization utilizing three independent and stable functional handles to provide overlapping and/or separate chemical patterns.

■ CONCLUSION

The thermal cycloadition of azides and terminal alkynes in polymer films was exploited in the design of effective thermal cross-linking strategies that are operationally simple and occur under very mild reaction conditions. The thermal process occurring within the polymer matrix allows control over cross-linking density and the level of unreacted, stable azide and alkyne functionality. By exploiting the site isolation and orthogonality of these residual azide and alkyne functional groups, as well as additional reactive groups in the form of the acyl ketene, each individual functional group can be addressed in select or overlapping regions at the surface of the cross-linked polymer films. Such triply functionalized surfaces represent a significant advance to the current state of the art and enable applications in such areas as catalysis, biofunctionalization, or sensors development. We are currently pursuing these and other research goals utilizing the materials and concepts reported here.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete experimental procedures along with additional supporting data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(53) Due to the differences in reactivity of trimethylsilylpropargyloxystyrene, styrene, and vinylbenzyl azide, a slight gradient incorporation rather than true random incorporation might occur through the conventional radical polymerization employed. Nevertheless, because of the very low incorporation of functional monomers, any effect of such a slight gradient on the bulk cross-linking studies should be very minimal.

(54) The presence of three new signals indicates the formation of two separate triazole isomers (having up to four possible new signals) where two of the individual resonances are overlapping yielding three new signals. No direct measure of relative ratio of the two isomers was obtained using the cross-polarization technique because signal intensity is dependent upon spin polarization transfer, a feature that prevents normal integral analysis; moreover, overlap of the growing triazole resonances with the backbone aromatic resonances further complicates the interpretation.

(55) A larger temperature range would allow a more comprehensive assessment of the influence of T_g upon the initial rate kinetics of cross-linking. The linear Arrhenius relationship could be explained because the cross-linking reaction always seems to be occurring below the T_g of the final cross-linked material(see Supporting Information, Figure S4).

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