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Degradable Cross-Linkers and Strippable Imaging Materials for Step-and-Flash Imprint Lithography

William H. Heath,[†] Frank Palmieri,[†] Jacob R. Adams,[†] Brian K. Long,[†] Jerred Chute,[†] Thomas W. Holcombe,[†] Shelley Zieren,[†] Matthew J. Truitt,[‡] Jeffery L. White,[‡] and C. Grant Willson*,[†]

Departments of Chemistry and Chemical Engineering, The University of Texas at Austin, Austin, Texas 78712, and Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

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ABSTRACT: The ability to produce tough, cross-linked networks that can, if necessary, be rendered soluble by an external stimulus such as acid or heat is highly desirable for a number of applications. An acetal containing diacrylate, 2,2-di(acryloyloxy-1-ethoxy)propane (ADA) (**1**), was synthesized by transketalization with 2-hydroxyethyl acrylate. Its photopolymerization kinetics were measured by real-time FT-IR and its degradation in acidic organic solvents was evaluated. Additionally, a diacrylate cross-linker containing a thermally labile Diels−Alder (DA) linkage (**2**) was synthesized and its reversibility was evaluated using solid-state NMR spectroscopy. The DA cross-linker (**2**) and ADA (**1**) were evaluated for use in Step-and-Flash Imprint Lithography (S-FIL). Finally, a dimethacrylate cross-linker containing a thermally labile urethane-oxime linkage (**10**) was synthesized. Its copolymerization with methyl methacrylate and reversibility were evaluated by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy.

Introduction

The exponential increase in device density predicted by Moore's law and made a reality by the microelectronics industry has been accompanied by an overwhelming increase in production costs. The exposure tools utilized to produce the integrated circuits of microprocessors and memory chips have become increasingly sophisticated and expensive over the past 40 years. Current exposure tools cost as much as $25 million and next generation tools are expected to cost up to $50 million.[1] Imprint lithography has emerged as a less expensive alternative to print features smaller than 45 nm.[2,3] Step and flash imprint lithography (S-FIL) shows great promise as a low-cost, high-resolution alternative to traditional photolithography.

S-FIL replaces the mask used in optical lithography with a transparent template that molds the resist into the desired features (Figure 1). A low viscosity photocurable prepolymer resist consisting of acrylate based monomers, siloxane containing monomers (for etch resistance), diacrylate cross-linkers, and radical photoinitiator is dispensed onto a silicon wafer. The template is then brought into contact with the wafer filling the recessed features on the template with resist. Subsequent irradiation through the template cures the prepolymer to produce a cross-linked material. The template is then removed leaving an inverse relief image of the mold. The image is finally transferred into the underlying substrate by traditional anisotropic reactive ion etch processes.

Using S-FIL, researchers have printed 20 nm features with tools that cost less than $8 million.[4] This low cost is possible because exposure is performed with an inexpensive mercury arc lamp through relatively simple optics.[4] The intimate contact between the resist and template, however, pose challenges not encountered with traditional optical lithography. The template is susceptible to contamination from debris and/or from residual resist left in its recesses. The templates for S-FIL produce an exact inverse image of themselves; therefore, they are 1:1 templates for the desired features to be printed. Production of these templates requires the use of a very slow, precise e-beam writer causing the templates to cost as much as $70 000.[5] If these expensive templates cannot be cleaned in the event of contamination, S-FIL could become a cost prohibitive technology.

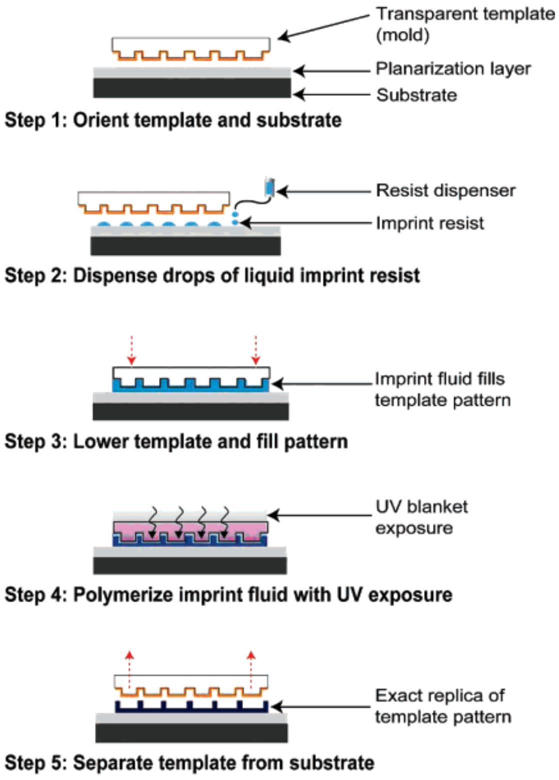

Figure 1. Step and flash imprint lithography (S-FIL) process.

Because the cured resist is a highly cross-linked polymer, stripping it with traditional organic solvents is impossible.[6]

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* To whom correspondence should be addressed. E-mail: Willson@che.utexas.edu.

[†] The University of Texas at Austin.

[‡] Oklahoma State University.

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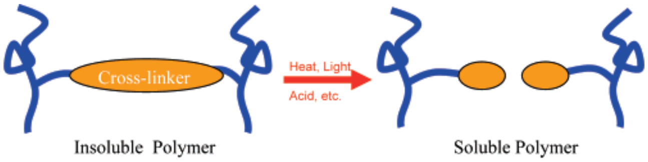


Figure 2. Schematic for processing degradable cross-linked resist.

Additionally, the inclusion of siloxane derived monomers in the formulation produces a material with etch characteristics similar to that of the quartz template, meaning that any etch process capable of stripping the resist would also damage the template. For these reasons, a resist that can be removed under conditions other than anisotropic etching is highly desired and practically requisite for S-FIL to find a place in the microelectronics industry.

Design of Strippable Resist. It is well-known that the solubility of a polymeric material in organic solvents is dependent upon the molecular weight and degree of cross-linking. We sought to design a system using a diacrylate cross-linker with a degradable linkage. As shown in Figure 2, upon degradation of this linkage the degree of cross-linking and molecular weight of the polymer will decrease thereby rendering it soluble in an organic solvent. Linkages that can be either thermally or hydrolytically degraded below the boiling point of common organic solvents yet are stable to ambient conditions are particularly attractive.

Acetals are stable under neutral and alkaline conditions but readily undergo hydrolysis in aqueous acidic solutions. Dimethacrylate acetals have been successfully incorporated into polymer networks, and these networks have been shown to undergo acid-catalyzed hydrolysis to produce linear polymers that are soluble in organic solvents.[7−9] Acrylates show increased photopolymerization rates compared to their methacrylate analogues and are thus more attractive for S-FIL where photospeed is critical to maintain high throughput. Traditional reaction conditions which favor acetal formation result in thermally induced polymerization due to the high temperature required for water removal. In the current work a facile synthesis of a hydrolyzable acetal diacrylate, 2,2-di(acryloyloxy-1-ethoxy)propane (ADA) (**1**), will be presented.

Covalent linkages that are in thermodynamic equilibrium with their precursors are also attractive for inclusion in a thermally strippable resist system. Diels−Alder adducts have been used in so-called dynamic or remendable polymer systems.[10,11] Diels−Alder adducts degrade to their diene and dienophile precursors upon heating above their cycloreversion temperatures. Additionally, urethanes derived from isocyanates decompose to their precursors upon heating to elevated temperatures. These latent isocyanates, known as blocked isocyanates, have found use in polymer coating applications because of their ability, when heated, to be cross-linked with hydroxyl or amino groups present on the polymer chain. The acetal based cross-linker referenced above forms useful diacrylate cross-links in polymer systems that can be degraded to produce a linear polymer; however, this requires acid catalysis to effect degradation. We sought to expand the useful options of degradable diacrylate cross-linkers to ones that can be decross-linked at low temperatures (<150 °C) and without the need for added catalyst. The synthesis of diacrylate cross-linkers containing Diels−Alder and urethane linkages will be described herein.

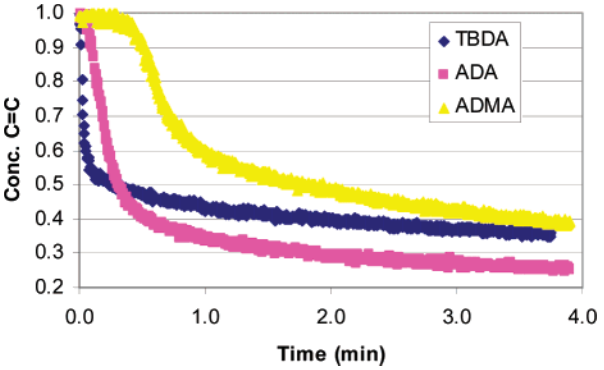


Figure 3. Alkene conversion monitored by FT-IR as a function of exposure time.

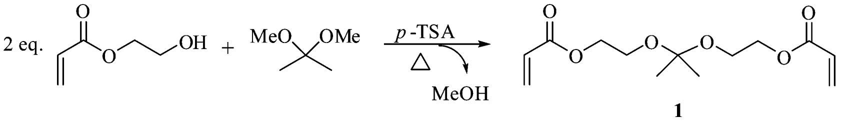
Results and Discussion

Preparation of ADA Cross-Linker. ADA was synthesized through transketalization of 2,2-dimethoxypropanone with 2-hydroxyethylacrylate in the presence of *p*-TSA catalyst in benzene.[12] Methanol was continuously removed by distillation of the benzene−methanol azeotrope (58 °C), and the crude product was purified by flash column chromatography (Scheme 1). It is important to obtain a high degree of cross-linking in the cured film to ensure high fidelity image transfer to the wafer with minimal distortion upon template removal. For this reason, the cross-linker must be soluble in the monofunctional acrylate in the range of 10−20% (wt/wt). The ADA cross-linker was obtained as a colorless liquid and was freely soluble in various alkyl acrylates.

Photopolymerization. The rate and extent of photopolymerization of the ADA cross-linker was investigated by real-time FT-IR spectroscopy. A neat solution of **1** was irradiated, and monomer conversion was determined by monitoring the decrease in the C=C stretch at ~1680 cm^{-1}. The extent of conversion for the ADA (~70% @ 2 min) was greater than that for commercially available 2,5-di(acryloyloxy-1-ethoxy)-2,5-dimethylhexane (TBDA) (~60% @ 2 min) under identical exposure conditions and initiator formulations (Figure 3). Ober observed a similar phenomena when photopolymerizing diacrylates with differing linker lengths.[13] He found that the extent of polymerization increased with the number of methylene spacers and attributed this to increased accesibility of the propagating radical. The diethyl acetal spacer of the ADA is seven units long whereas the TBDA spacer is only four methylene units long, agreeing with Ober's findings. Additionally, 2,2-di(methacryloyloxy-1-ethoxy)propane (ADMA) was synthesized as described for ADA above and its polymerization rate compared to ADA. As was expected, ADA provides a substantial increase in reactivity relative to ADMA.

Patterning and Stripping. Patterning with ADA was performed using a solution of the monomer diluted with isobornyl acrylate and formulated with a photoinitiator (Daracure). Patterns to be used for stripping experiments were produced by hand, whereas those for SEM analysis were produced with an Imprio 55 imprint tool from Molecular Imprints, Inc. The cross-linker

Scheme 1. Synthesis of ADA Cross-Linker (1)



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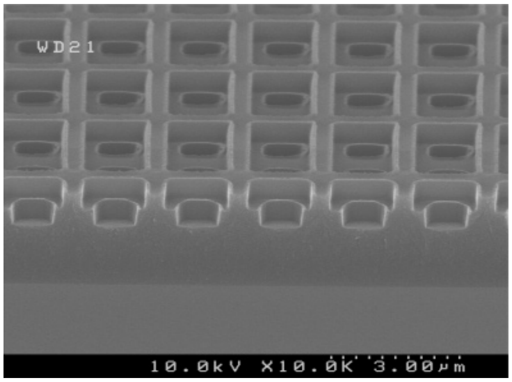


Figure 4. SEM image of 500 nm vias patterned on an Imprio 55 S-FIL imprint tool with ADA formulation.

produced patterns with good profile properties as shown in Figure 4 when formulated with 20% (wt/wt) cross-linker.

The ADA patterns were stripped by submerging the wafer in acidic aqueous THF. The patterns dissolved slowly at room temperature, but it was found that refluxing the THF solution provided clean wafers in less than 5 min (Figure 5). Polymer films containing up to 40% (wt/wt) cross-linker swelled immediately upon submerging in the solution and then dissolved completely to produce a homogeneous solution. Films prepared with ethylene glycol diacrylate (EGDA) were used to confirm that hydrolysis of the acetal, not the ester, was responsible for dissolution of the cross-linked film. EGDA cross-linked films remained insoluble after refluxing for 18 h in both acidic THF and NMP.

Synthesis of DA Cross-Linker. The synthesis of DA adduct linked diacrylate **2** began with the Diels−Alder reaction between furan and maleic anhydride followed by amine insertion into DA adduct **3**.[14] The resultant maleimide (**4**) was deprotected via a retro-DA reaction by refluxing open to air in toluene to provide *N*-(hydroxyethyl)maleimide. Furfuryl alcohol was reacted with maleimide **5** in refluxing benzene to provide exclusively the exo isomer of DA adduct **6** (Scheme 2). It should be noted that upon scaleup, extended reaction times were required to obtain the isomerically pure exo product. However, there is in principle no need to separate isomers for this application. The diacrylate was obtained by reaction with excess acryloyl chloride under standard reaction conditions and purified via silica gel flash column chromatography.

Imprinting. The DA diacrylate **2** was freely soluble in methyl acrylate and imprinting was performed with 10 and 20% (wt/wt) solutions of the cross-linker formulated with 5% (wt/wt) photoinitiator. Imprinting was performed by hand as described above. Both the 10 and 20% (wt/wt) formulations provided good feature transfer (Figure 6).

Attempted Stripping and Thermal Studies. Liu recently reported the network formation of trismaleimides with trisfurans and the subsequent decross-linking through retro-Diels−Alder reactions to effect solubility in NMP.[15] However, attempts in our laboratories to thermally decross-link the polymer networks prepared as described above to achieve soluble material have failed. Polymer films were heated to various temperatures including reflux in a number of solvents such as DMSO, DMF, NMP, and toluene for extended periods with no indication of dissolution. To better understand this unexpected result, solid-state NMR was used to explore the extent of retro-Diels−Alder reaction occurring in the polymer films. Cross-linked polymer samples were formed via radical copolymerization of methyl acrylate and compound **2**. The resultant insoluble polymeric material was analyzed using both ^{1}H → ^{13}C cross-polarization/magic-angle spinning and quantitative ^{13}C Bloch decay/magic-angle spinning NMR spectroscopies. In both cases a spectrum was recorded prior to and after heating at 130 °C. As can be seen in Figure 7, the reverse Diels−Alder reaction is occurring and agrees well with the solid-state spectral data obtained by Wudl.[10,11]

It was hypothesized that although cycloreversion of the DA adduct was being realized in the solid state, the thermodynamically favored DA adduct reformed faster than solvation. To test this theory, independent experiments were performed in which cyclopentadiene or diethylacetylenedicarboxylate were added to the stripping solvent during heating in attempts to trap the retro-Diels−Alder products. This too failed and work continues in our lab to understand the differences between our system and that reported by Liu.[15]

Synthesis of Urethane Cross-Linker. Synthesis was begun by protection of 4-hydroxyacetophenone with *tert*-butyldimethylsilyl (TBDMS) chloride. The TBDMS protected 4-hydroxyacetophenone was then converted to the oxime **7** by treatment with hydroxyl amine in refluxing alkaline aqueous ethanol. The bisurethane was prepared by reaction of excess **7** with hexane diisocyanate. The crude product was purified by silica gel chromatography to provide **8** as a white powder. Removal of the TBDMS protecting group required careful selection of deprotection chemistry as hydrolysis of the urethane competes with liberation of the free alcohol. Deprotection was accomplished by stirring **8** in a solution of HF and pyridine to provide **9**, which precipitated from the reaction solution and was used without purification. The dimethacrylate was obtained by reaction with excess methacryloyl chloride under standard conditions. Purification via silica gel chromatography provided the target compound **10** (Scheme 3).

Polymerization and Decross-Linking of Lightly Cross-Linked Poly(methyl methacrylate). To demonstrate the utility of the oxime urethane di(meth)acrylate as a degradable cross-linker, lightly cross-linked poly(methyl methacrylate) was synthesized by copolymerization of methyl methacrylate with **10** by solution polymerization. A low cross-link feed ratio (∼6 mol %) was utilized to allow analysis of both the branched polymer and degraded linear polymer by GPC and ^{1}H NMR analysis. The polymerization was initiated with a relatively high ratio of AIBN to monomer to limit the molecular weight of the polymer. The resulting polymer had a M_n of 20 000 g/mol and PDI of 4.23. The incorporation of cross-linker was confirmed by the presence of aryl ^{1}H NMR resonances at 7.18 and 7.67 ppm.

Polymer Network Thermolysis. Thermolysis of the polymer network was achieved by heating to 150 °C in mesitylene for 3 h. Dibutyl amine was incorporated to trap the generated isocyanate and prevent recombination. The resulting product was precipitated into hexanes three times to remove liberated bis-1,6-(dibutylurea)hexane (subsequent precipitations were made from THF). The linear polymer was found to have a M_n of 8 800 g/mol and PDI of 1.62 as measured by GPC. The M_n is in good agreement with that predicted for the stoichiometry (8 300 g/mol). A comparison of the ^{1}H NMR spectra of the polymer before and after thermolysis indicates quantitative degradation of the urethane cross-links (Table 1). The methylene (δ 1.577 (F), 1.631 (E), and 3.298 ppm (D)) and amide (δ 6.424 ppm (C)) protons of the hexyl urethane linker are not present in the spectrum of the thermolyzed polymer (Figure 8). The absence of cross-linker resonances in the ^{1}H NMR spectrum and the reduced polydispersity of the thermolyzed polymer provide strong evidence for degradation of the urethane cross-

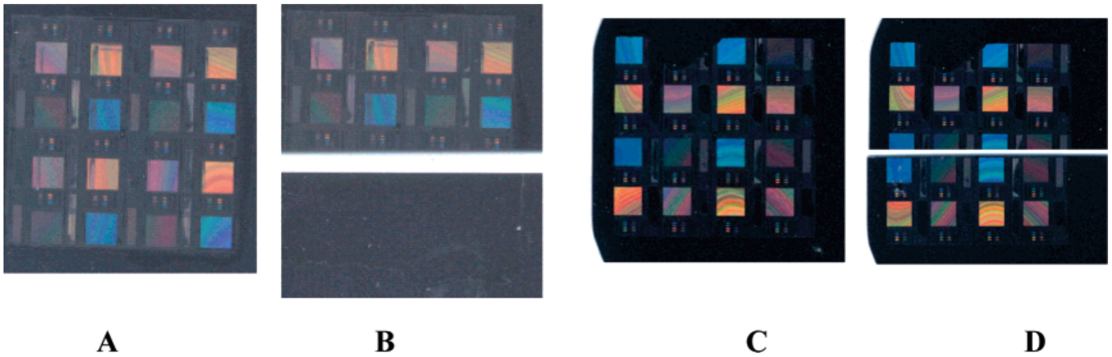
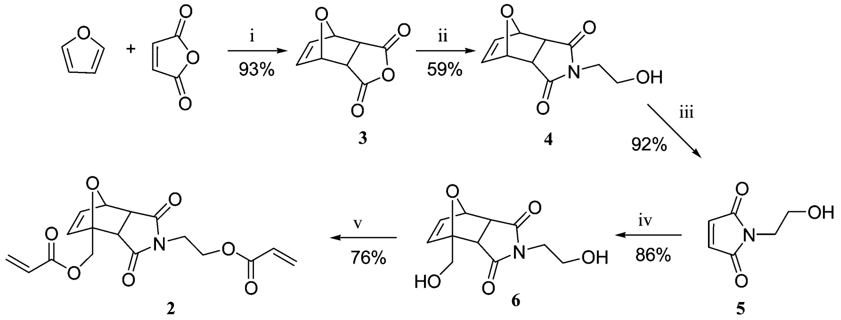


Figure 5. (A) Wafer patterned with ADA cross-linker. (B) Cleaved wafer, bottom half refluxed in acidic THF. (C) EGDA patterned wafer. (D) Cleaved wafer, bottom half refluxed in acidic THF.

Scheme 2. Synthesis of DA Diacrylate Cross-Linker (2)[a]



[a] (i) benzene, Δ; (ii) MeOH, ethanolamine, Δ; (iii) toluene, Δ; (iv) benzene, furfuryl alcohol, Δ; (v) DCM, TEA, acryloyl chloride, 0 → room temp.

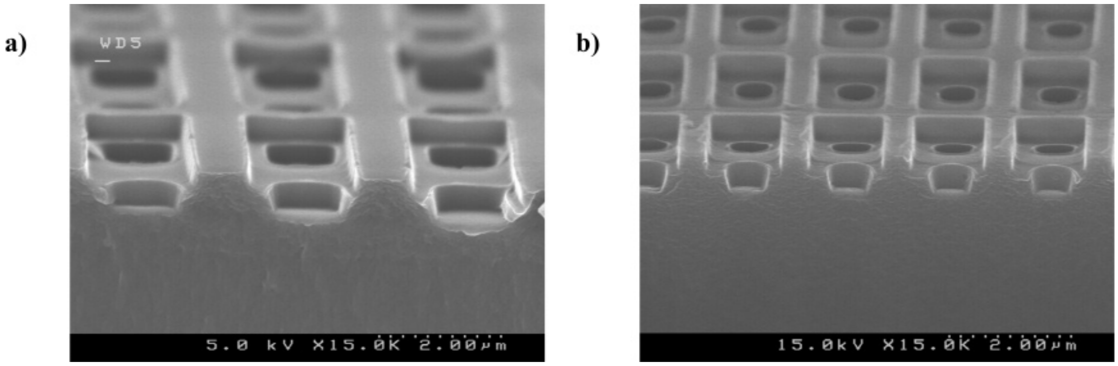


Figure 6. SEM images of 500 nm vias formed by imprint using (a) 10% (wt/wt) DA cross-linker and (b) 20% (wt/wt) DA cross-linker.

links in the initial branched polymer. At present this monomer has not been utilized in an S-FIL resist due to low solubility in conventional formulations.

Conclusions

Three cleavable diacrylate cross-linkers were successfully synthesized and incorporated into individual polymer networks. Compounds **1** and **2** have been incorporated into S-FIL resist formulations and have been shown to give adequate mechanical properties upon template removal, while polymer networks containing compounds **1** and **10** were shown to degrade via acid-catalyzed hydrolysis or thermolysis, respectively. Compound **10** was unable to be incorporated into a resist formulation due to insolubility, despite various attempts to improve its solubility through structural modification. Solid-state NMR analysis of cross-linker **2** in a PMMA polymer matrix indicated that the oxo-tricyclic linker does undergo cycloreversion upon heating, but despite this evidence, all attempts to strip polymer films have failed. Research continues within our group to understand this unusual observation. Compounds **2** and **10**, while more synthetically involved, provide attractive points of study as they do not require the addition of an external reagent such as acid but only require heating. Acetal compound **1** does require the use of an acidic stripping solvent but is clearly preferred as it is synthetically more easily accessible, was effectively incorporated into a photopolymerizable resin, patterned using S-FIL, and subsequently stripped via acid-catalyzed hydrolysis from its silicon substrate. Additionally, the ability to both photopolymerize and easily hydrolyze diacrylate **1** may make it useful for various other photocurable, strippable applications.

Experimental Section

General Methods and Materials. All solvents and reagents were obtained from Aldrich and were used without further purification except where noted. Dry DCM and dry TEA were obtained by distillation over CaH while furfuryl alcohol and acryloyl chloride were fractionally distilled prior to use. Solution state ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Plus 300 MHz instrument. All chemical shifts are reported in ppm downfield from TMS using the residual protonated solvent as an internal standard (DMSO-d_6, ^{1}H 2.49 ppm and ^{13}C 39.5 ppm) ($CDCl_3$, ^{1}H 7.29 ppm and ^{13}C 77.0 ppm). Coupling constants are expressed in Hz. HRMS (CI) was obtained on a VG analytical ZAB2-E instrument, and IR

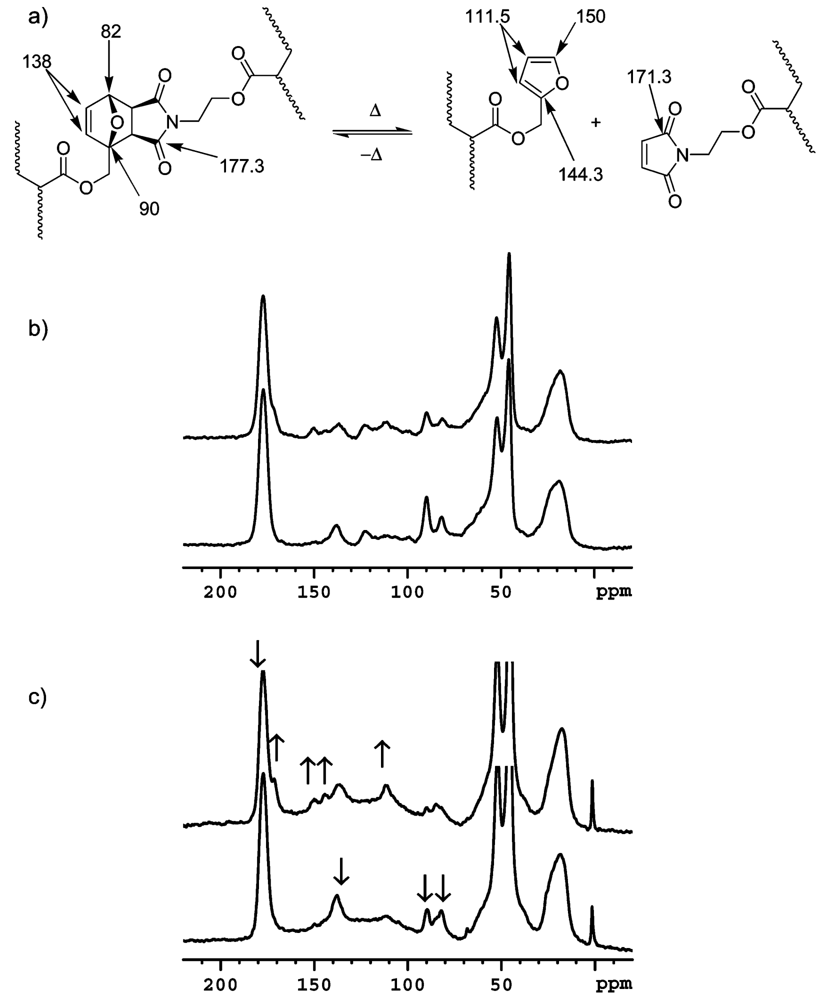
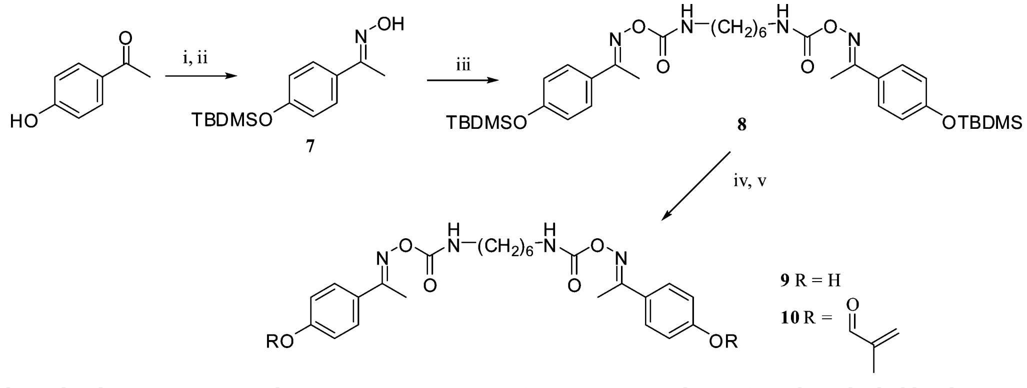


Figure 7. (a) Forward and reverse Diels−Alder reactions with ^{13}C NMR signal assignments in ppm. (b) $^{1}H \rightarrow {}^{13}C$ cross-polarization/magic-angle spinning spectra, with sideband suppression via TOSS, for species **2** before (bottom trace) and after (top trace) heating at 130 °C. (c) Quantitative ^{13}C Bloch decay/magic-angle spinning spectra for species **2** before (bottom trace) and after (top trace) heating at 130 °C. Key peaks in the Bloch decay spectra, which are indicative of the reverse Diels−Alder chemistry, are labeled with arrows that point up (171.3, 150, 144.3, and 111.5 ppm) or down (177.3, 138, 90, and 82 ppm) if the thermal treatment increases or decreases their signal intensities, respectively. Although parts a and b represent ^{13}C spectra generated by two distinct methods, thereby explaining absolute peak intensity differences in parts a vs b, the same behavior in thermally induced signal intensity changes are observed in each.

Scheme 3. Synthesis of Oxime Urethane Dimethacrylate[a]



[a] (i) TBDMSCl, imidazole; (ii) $NH_2OH\cdot HCl$, NaOH; (iii) $(OCN)_2(CH_2)_6$; (iv) HF−pyridine; (v) methacryloyl chloride.

Table 1. Decross-Linking Polymer Networks

	M_n	M_w	PDI
25 °C	20 000	87 000	4.23
150 °C with DBA	8 800	14 400	1.62

data were recorded on a Nicolet Avatar 360 FT-IR. Molecular weights (M_w) and polydispersity indices (PDI) were measured from DMF solutions using an Agilent 1100 Series GPC equipped with a set of two Agilent PLgel 5 mm cross-linked polystyrene columns (10^4 and 100 Å) and are reported relative to polystyrene standards. Melting points are not corrected. Thin layer chromatography (TLC) was visualized using either 254 nm UV light, ethanolic phosphomolybdic acid, or permanganate. Di(meth)acrylate photopolymerization kinetics studies were performed using real time FT-IR by a procedure previously reported.[16]

Acrylic Acid 2-[1-(2-acryloyloxy-ethoxy)-1-methyl-ethoxy]-ethyl ester (1). In a 250 mL round-bottom flask, 2-hydroxyethylacrylate (8.82 g, 75.96 mmol), 2,2-dimethoxypropane (3.62 g, 34.76

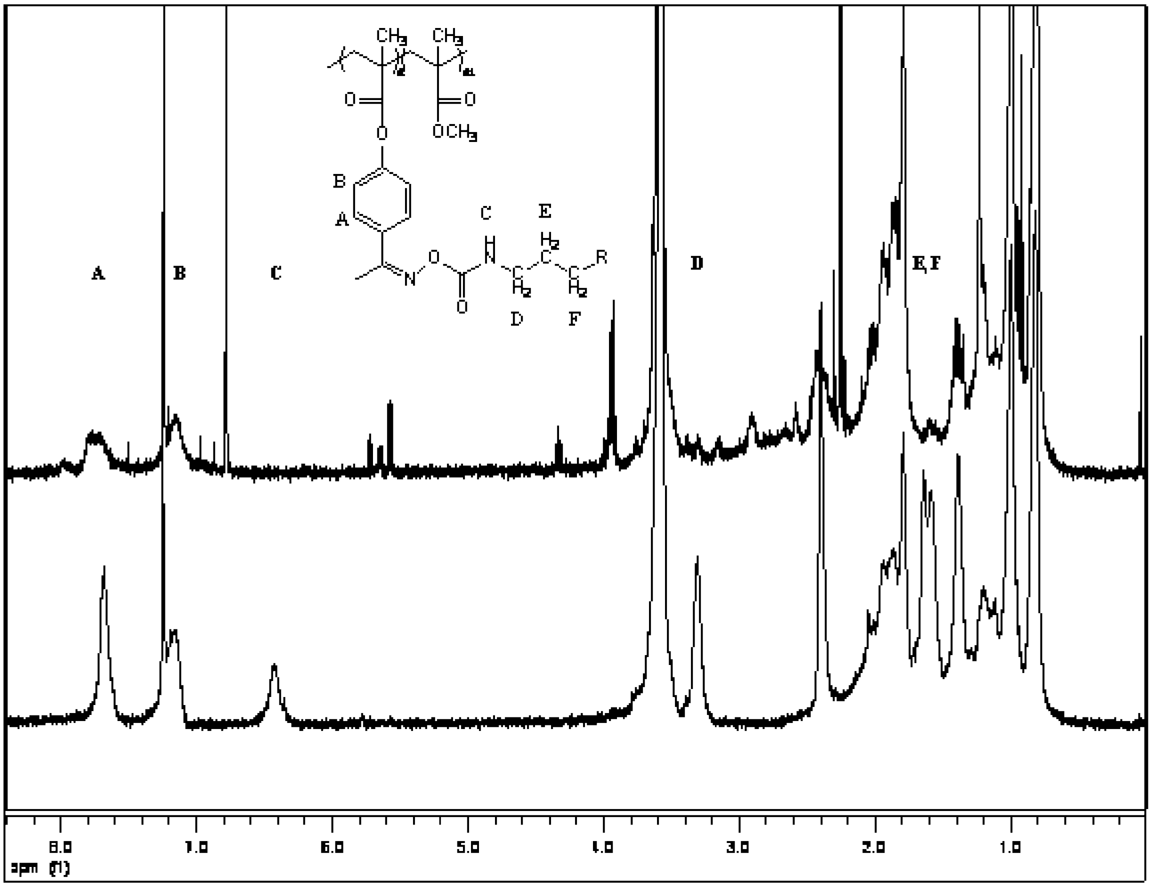


Figure 8. ^{1}H NMR spectra of polymer network before and after thermolysis. Protons at δ 2.25 and 6.78 correspond to residual mesitylene.

mmol), and 1 g of hydroquinone were stirred in benzene and distilled to remove the methanol−benzene azeotrope (58 °C). After 1 h, the remaining benzene was removed in vacuo. The resulting colorless liquid was purified via flash column chromatography using DCM as the eluent to provide the title compound as a colorless oil (3.78 g, 13.88 mmol, 39.9%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25 (dt, $J_1 = 17.44$, $J_2 = 1.37$, 2H), 5.98 (m, 2H), 5.67 (dt, $J_1 = 10.26$, $J_2 = 1.37$, 2H), 4.12 (m, 4H), 3.53 (m, 4H), 1.21 (d, $J = 1.03$, 6H); ^{13}C NMR ($CDCl_3$) δ 165.67, 130.59, 127.98, 99.80, 63.49, 58.53, 24.41; HRMS CI+ ($[M + H]^+$ calcd = 273.1338, found = 273.1339); FT-IR (oil) ν = 2992.41, 2950.00, 2882.01, 1735.45, 1410.94, 1297.84, 1193.90, 1063.10, 985.33 cm^{-1}.

Synthesis of 4,10-Dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (3). To a flame dried 500 mL round-bottom flask with a magnetic stir bar was added maleic anhydride (40.009 g, 408 mmol), benzene (200 mL), and furan (30 mL). The reaction was stirred at room temperature under nitrogen atmosphere for 24 h. The product precipitated out of solution and was collected via vacuum filtration and washed with diethyl ether. The colorless product was 100% exo by NMR analysis and used without further purification (yield 93.3%). mp 114−116 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.566 (s, 2H), 5.334 (s, 2H), 3.296 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 171.5, 136.8, 81.6, 49.1; HRMS ($[M + H]^+$ calcd = 167.0344, found = 167.0344); FT-IR (KBr) ν = 3091, 3032, 2998, 1858, 1785, 1215 cm^{-1}

Synthesis of 4-(2-Hydroxy-ethyl)-10-oxa-4-aza-tricyclo[5.2.1.0^{2,6}]-dec-8-ene-3,5-dione (4). To a flame dried 100 mL three-neck round-bottom flask with a magnetic stir bar and reflux condenser was added 4,10-dioxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (10.0 g, 60.2 mmol) followed by dry methanol (20 mL) and ethanolamine-(3.68 g, 60.2 mmol). The solution turned dark orange and was brought to reflux for 24 h. The flask was cooled to room temperature, and after 2 h product began to crystallize. The mixture was stored in the freezer overnight, and the precipitate was collected by vacuum filtration. The filtrate volume was reduced by rotary evaporation and allowed to crystallize, and a second crop of crystals was collected (yield 59%). mp 135−137 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.535 (s, 2H), 5.108 (s, 2H), 3.402 (s, 4H), 2.912 (s, 2H); ^{13}C NMR (DMSO-d_6) δ 176.5, 136.5, 80.3, 57.3, 47.1, 40.6; HRMS ($[M + H]^+$ calcd = 210.0766, found = 210.0770); IR (KBr) ν = 3480, 3097, 2971, 2932, 2894, 1769, 1686 cm^{-1}.

Synthesis of 1-(2-Hydroxyethyl)-1*H*-pyrrole-2,5-dione (5). To a 100 mL round-bottom flask equipped with a stir bar and vigreaux condenser was added 4-(2-hydroxyethyl)-10-oxa-4-aza-tricyclo-[5.2.1.0^{2,6}]dec-8-ene-3,5-dione (4.419 g, 21.1 mmol) and toluene (50 mL). The reaction was refluxed for 7 h. The resulting mixture was hot filtered, and the product crystallized from solution upon cooling. The colorless solid was collected via vacuum filtration and used without further purification (yield 92%). mp 70−72 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.999(s, 2H), 4.774 (br, 1H), 3.442 (br, 4H); ^{13}C NMR (DMSO-d_6) δ 171.1, 164.5, 57.9, 39.9; HRMS ($[M + H]^+$ calcd = 142.0504, found = 142.0503); IR (KBr) ν = 3363.54, 2919.34, 2853.04, 2355.80, 1706.08, 1407.73, 1162.43 cm^{-1}.

Synthesis of 1-(Hydroxymethyl)-10-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione-2-aminoethanol (6). To a 100 mL round-bottom flask equipped with a magnetic stir bar and reflux condenser was added 1-(2-hydroxyethyl)-1*H*-pyrrole-2,5-dione (**5**) (1.301 g, 9.2 mmol), benzene (20 mL), and freshly distilled furfuryl alcohol (0.8 mL, 9.3 mmol). The reaction was refluxed for 24 h. Product precipitated from the reaction mixture overnight. The mixture was cooled to room temperature. The product was collected via vacuum filtration and washed with diethyl ether to produce a colorless crystalline solid (yield 86%). Scale up of this procedure resulted in a mixture of endo and exo isomers. Increased reaction times provided the pure exo isomer. mp 110−116 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.508 (br, 2H), 5.061 (s, 1H), 4.931 (t, $J = 5.7$ Hz, 1H), 4.757 (t, $J = 5.7$ Hz, 1H), 4.020 (dd, $J = 12.6$, 6 Hz, 2H), 3.671 (dd, $J = 12.6$, 5.4 Hz, 1H), 3.395 (br, 4H), 3.027 (d, $J = 6.3$ Hz, 1H), 2.864 (d, $J = 6.3$ Hz, 1H); ^{13}C NMR (DMSO-d_6)

δ 176.4, 174.9, 138.1, 136.5, 91.6, 80.2, 58.9, 57.3, 49.9, 47.8, 40.5; HRMS ($[M + H]^+$ calcd = 240.0872, found = 240.0872); IR (KBr) ν = 3423.20, 3078.45, 2919.34, 1692.82, 1407.73, 1182.32, 1029.83 cm^{-1}.

Synthesis of {4-[2-(Acryloyloxy)ethyl]-3,5-dioxo-10-oxa-4-azatricyclo[5.2.1.0^{2,6}]dec-8-en-1-yl}methyl Acrylate (2). To a flame dried 100 mL round-bottom flask equipped with a magnetic stir bar was added 1-(hydroxymethyl)-10-oxatricyclo[5.2.1.0^{2,6}]dec-8-ene-3,5-dione-2-aminoethanol (0.943 g, 3.9 mmol). After purging the apparatus with nitrogen, dry DCM (20 mL) and freshly distilled TEA (1.5 mL) were added. To this solution, freshly distilled acryloyl chloride (0.800 mL, 9.8 mmol) was added dropwise via a syringe. The reaction was stirred overnight in an ice bath shielded from light then extracted with aqueous NH_4Cl, H_2O, and brine. The organic layer was dried over $MgSO_4$, filtered, and 50 μL of a 1 mg/mL solution of *p*-methoxyphenol in toluene was added as a radical inhibitor and then reduced in vacuo. The colorless oil was used without further purification (yield 76%). ^{1}H NMR (300 MHz, DMSO-d_6) δ 6.583 (m, 1H), 6.465 (d, J = 5.7 Hz, 1H), 6.358−5.871 (m, 6H), 5.120 (d, J = 1.5 Hz, 1H), 4.833 (d, J = 12.9 Hz, 1H), 4.385 (d, J = 12.9 Hz, 1H), 4.181 (m, 2H), 3.660 (m, 2H), 3.106 (d, J = 6.3 Hz, 2H), 3.033 (d, J = 6.3 Hz, 2H); ^{13}C NMR (DMSO-d_6) δ 176.0, 174.7, 165.1, 165.0, 137.3, 136.8, 132.2, 131.8, 128.2, 127.8, 88.8, 80.5, 61.5, 60.5, 49.7, 48.3, 37.1; HRMS ($[M + H]^+$ calcd = 348.1083, found = 348.1082); IR (KBr) ν = 3091, 2952, 2252, 1770, 1716, 1631, 1405, 1332, 1266, 1180, 1067, 982 cm^{-1}.

4-*tert*-Butyldimethylsilyloxyacetophenone. To a three-neck round-bottom flask containing 25 mL of dry DMF was added 4-hydroxyacetophenone (7.4 mmol) and cooled to 0 °C with stirring. Imidazole (24.42 mmol) and *tert*-butyldimethylsilyl chloride (8.14 mmol) were added portionwise, and the reaction was allowed to warm to room temperature and stirred for 16 h. The reaction mixture was diluted with EtOAc, and the organic fraction was washed with $NaHSO_4$, $NaHCO_3$, and brine, then dried over $MgSO_4$, and concentrated in vacuo to produce a colorless oil. The crude product was purified by flash chromatography on silica (2:1 hexane−ethyl acetate (Hex−EtOAc)) to produce a colorless oil which solidified upon standing. Yield 96%; mp 40−43 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.21 (s, 9H), 0.96 (s, 6H), 2.52 (s, 3H), 6.85 (d, J = 4.2, 2H), 7.86 (d, J = 4.2, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.4, 18.21, 25.55, 26.32, 119.85, 130.47, 130.84, 160.24, 196.83; FT-IR υ_{max} = 3489, 3045, 2959, 2925, 2853, 1680, 1593, 1501, 1467, 1414, 1361, 1169 cm^{-1}; LRMS (CI): m/z = 251. HRMS (CI): m/z calcd for $C_{14}H_{22}SiO_2$ ($M + H^+$) 251.1467, found 251.1471.

1-(4-*tert*-Butyldimethylsilyloxyphenyl)-ethanone Oxime (7). To a solution of $NH_2OH{\cdot}HCl$ (42.6 mmol) in 30 mL of absolute ethanol and 50 mL of water was added a solution of NaOH (29.75 mmol) in 30 mL of water with stirring. To this solution was added 4-*tert*-butyldimethylsilyloxyacetophenone (8.5 mmol). The reaction vessel was equipped with a condenser and refluxed for 18 h. Upon completion, as determined by TLC (2:1 Hex−EtOAc), the reaction was cooled to room temperature and the aqueous layer was extracted with DCM (3×). The organic fractions were combined, washed with $NaHCO_3$, dried over $MgSO_4$, and concentrated under vacuo to produce an off-white oil. The product was purified by flash chromatography on silica (2:1 Hex−EtOAc) to produce a white powder. Yield 86.5%; mp 70−71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.212 (s, 6H), 0.987 (s, 6H), 2.291 (s, 3H), 6.847 (d, J = 8.7, 2H), 7.529 (d, J = 8.7, 2H), 9.081(s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.23, 128.59, 127.56, 120.14, 25.63, 18.23, 12.48, −4.407; FT-IR (film) υ_{max} = 3271, 3019, 1600, 1507, 1467, 1262, 1209 cm^{-1}; LRMS (CI): m/z = 266. HRMS (CI): m/z calcd for $C_{14}H_{23}SiNO_2$ ($M + H^+$) 266.15763, found 266.157536.

***N,N*′-Bis(1-(4-*tert*-butyldimethylsilyloxyphenyl)-ethanone Oximocarbamoyl)-1,6-hexanediamine (8).** To a solution of **7** (4.85 mmol) in 20 mL of dry THF was added hexamethylene diisocyanate (2.2 mmol). The reaction solution was heated to reflux with stirring overnight then concentrated under vacuo, and the crude product was purified by flash column chromatography on silica (2:1 Hex−EtOAc) to produce a colorless viscous oil upon drying under high vacuum. Yield 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.171 (s, 18H), 0.938 (s, 12H), 1.356 (m, 4H), 1.536 (m, 4H), 2.334 (s, 6H), 3.277 (q, J = 6.8, 4H), 6.48 (t, J = 6, 4H), 6.829 (d, J = 6.8, 4H), 7.527 (d, J = 6.8, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ −4.516, 14.112, 18.099, 25.492, 26.233, 29.609, 40.874, 120.084, 127.599, 128.05, 155.583, 157.867, 159.341; FT-IR (film) υ_{max} = 3409, 3012, 2919, 2853, 1712, 1600, 1507, 1208 cm^{-1}.

***N,N*′-Bis(1-(4-hydroxy-phenyl)-ethanone Oximocarbamoyl)-1,6-hexanediamine (9).** To a solution of **8** (7.16 mmol) in 50 mL of dry THF in a three-neck round-bottom flask under a N_2 atmosphere at 0 °C was added HF−pyridine (1 mL 70% HF) dropwise over ∼5 min. The reaction was allowed to warm to room temperature and stirred for ∼2 h. Upon addition, the solution turned cloudy immediately and after 2 h had become a thick white suspension. The reaction was monitored by TLC (2:1 Hex−EtOAc), and upon completion the reaction mixture was neutralized with $NaHCO_3$ and a chalky white precipitate rose to the top. The mixture was filtered, and the precipitate washed with H_2O-*d*, collected, and dried under high vacuum to produce a white chalky solid which decomposed before melting (126−128 °C). Yield 84.6%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.285 (s, 4H), 1.48 (s, 4H), 2.258 (s, 6H), 3.075−3.123 (m, 4H), 6.806 (d, J = 8.8, 4H), 7.49 (t, J = 5.6, 2H), 7.697 (d, J = 4, 4H), 9.924 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.27, 26.012, 29.39, 33.19, 115.24, 125.15, 128.56, 154.98, 158.79, 159.58; FT-IR (Nujol) υ_{max} = 3364, 3171, 1706, 1593, 1461, 1375 cm^{-1}.

***N,N*′-Bis(1-(4-methacryloyl-phenyl)-ethanone Oximocarbamoyl)-1,6-hexanediamine (10).** To a three-neck round-bottom flask containing ∼50 mL of dry DMF was added **9** (4.36 mmol) and cooled to 0 °C. Methacryloyl chloride (13 mmol) followed by Et_3N (13 mmol) were added dropwise, and the solution turned a pale yellow. The reaction mixture was protected from light and allowed to warm to room temperature and stirred for 18 h. Upon completion as determined by TLC (1% vol/vol MeOH−$CHCl_3$), the reaction mixture was diluted with H_2O-*d* and the aqueous fraction extracted with DCM (3×). The organic fractions were combined, washed with brine, dried over $MgSO_4$, and the solvent was removed in vacuo to yield a yellow viscous oil. The crude product was purified by flash column chromatography on silica (1% v/v MeOH−$CHCl_3$) to produce a light colored viscous oil which was dissolved in a minimum amount of diethyl ether and precipitated into pentane to provide the target compound as a white solid (723 mg, 24.98% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.296 (m, 4H), 1.488 (m, 4H), 2.00 (s, 6H), 3.107 (q, J = 6.4, 4H), 5.914 (s, 2H), 6.292 (s, 2H), 7.267 (d, J = 8.4, 4H), 7.915 (d, J = 8.8, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ 154.610, 152.120, 135.062, 132.146, 128.202, 127.996, 121.909, 29.252, 25.901, 17.963, 13.479; FT-IR (film) υ_{max} = 3380, 3051, 2919, 2859, 1736, 1501 cm^{-1}.

Imprint Patterning. Imprinted films were prepared using either a manual process or an automated process on an Imprio 55 imprint tool from Molecular Imprints Inc. For the manual imprint process, approximately 1 mL of the imprint precursor formulation was dropped onto a silicon wafer coated with AP410 (Silicon Resources, Inc.). The drop was covered with a quartz template having a 1 in.″ square contact area, and the fluid was allowed to spread to fill the gap between the wafer and template. After spreading, the fluid was exposed to i-line radiation for 200 s at approximately 12 mW/cm^2. The template was separated from the cured film, and the patterned wafer was then ready for decross-linking and strip testing.

The Imprio 55 uses a piezo-driven, microjet dispense system for controlled deposition of imprint precursors onto 8 in″ silicon wafers treated with AP410 adhesion promoter. The 1 in. square template was aligned and pressed into the fluid with 3−10 N of force for a preset time. Exposure was controlled by a shutter, which opens after the spreading is complete. The template was then lifted from the imprinted field. The wafer was removed from the tool for inspection and stripping experimentation.

ADA Pattern Stripping. Polymers films 1 μm thick containing the ADA cross-linker (**1**) were stripped by immersion in acidic THF for 1 min followed by rinsing with methyl isobutyl ketone. The stripping process was effective at 60 °C and at room temperature; although, heating reduced processing time.

Synthesis of Lightly Cross-Linked Poly(methyl methacrylate) Incorporating Thermally Labile Urethane Oxime Cross-Linker (10). To a solution of AIBN (1.2 mg, 0.008 mmol) in THF (2 mL) was added **10** (50 mg, 0.08 mmol) and methyl methacrylate (105 mg, 1.05 mmol). The solution was held at 50 °C overnight with stirring. Upon completion, the cross-linked polymer was precipitated into hexanes and collected by filtration. Yield 107 mg (69%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.770−7.592, 7.294−7.089, 6.509−6.356, 3.699−3.497, 3.371−3.242, 2.438−2.327, 2.120−0.752; $M_n = 20$ kg/mol, $M_w = 87$ kg/mol, PDI = 4.23 (PMMA standards).

Thermolysis of Lightly Cross-Linked Poly(methyl methacrylate). To a solution of dibutylamine (∼20 mg) in mesitylene (2 mL) was added poly(MMA-*co*-MMA-cross-linker) (37 mg). The solution was heated to reflux with stirring for 1 h before being cooled to room temperature. The polymer was precipitated into hexanes. The hexanes and mesitylene were removed via pipet and the polymer was taken up into THF. The polymer was reprecipitated into hexanes to remove liberated urea. The THF/hexanes were removed and the polymer was dried in vacuo. Yield 20 mg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.724−7.569, 7.202−7.044, 3.979−3.893, 3.684−3.405, 2.345−0.623; $M_n = 8.8$ kg/mol, $M_w = 14.4$ kg/mol, PDI = 1.62 (PMMA standards).

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