Synthesis of Photocleavable Linear Macromonomers by ATRP and Star Macromonomers by a Tandem ATRP−Click Reaction: Precursors to Photodegradable Model Networks

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ABSTRACT: Atom transfer radical polymerization (ATRP) and the copper-catalyzed azide−alkyne cycloaddition (CuAAC) were utilized for the synthesis of photodegradable polymeric materials by two complementary schemes. Linear azido-telechelic macromonomers possessing a photocleavable functionality at the center were synthesized by ATRP and subsequent end-group modification. These macromonomers were cross-linked with a tetrafunctional alkyne by CuAAC to form insoluble materials which degraded upon exposure to UV light of 350 nm to yield soluble star polymer products of defined molecular weight. Complementary to this approach, four-armed star polymers possessing photocleavable arms and terminal azides were prepared by a novel one-pot CuAAC/ATRP reaction followed by end-group modification. These star polymers were cross-linked with a linear, bifunctional alkyne to yield insoluble materials which, upon exposure to UV light, degraded to yield linear polymers of defined molecular weight.

Introduction

Degradable polymeric materials hold much promise in the areas of waste reduction,[1−4] lithography,[5,6] and biomaterials.[7,8] In addition to being the primary degradation route for lithographic applications, polymer photodegradation[9] has been extensively studied with hopes of both preventing it, thereby increasing the mechanical lifetime of the parent material,[10,11] and controlling it for the development of designer degradable plastics.[12] Although much has been accomplished regarding the synthetic and theoretical aspects of photodegradable polymers, many opportunities for the development of novel photodegradable materials remain. For example, to our knowledge all known photodegradable polymers cleave at random sites along the polymeric backbone. Such reactions depend on the existence of chromophores (usually ketones, aromatic groups, or light-absorbing impurities usually resulting from oxidation[11]) in the polymer chain,[4,12,13] the addition of small molecule radical initiators which act as chromophores,[9,14] or the existence of cleavable metal−metal bonds on the polymer backbone.[14,15] In contrast, relatively little attention has been paid to polymers containing photocleavable sites at precisely defined locations within the polymer chain. Such polymers, as precursors to cross-linked materials, could potentially yield degradation products of defined structure and size. In our efforts to prepare degradable polymeric model networks[16] (MNs) derived from well-defined macromonomers (MACs), we began to investigate the incorporation of photocleavable functionalities at precise locations within a MAC, thereby allowing spatial control of the photodegradation of the parent MN.

The unique compatibility of atom transfer radical polymerization (ATRP)[17] and the recently emerged copper(I)-catalyzed azide−alkyne cycloaddition (CuAAC),[18,19] also termed a "click"[20] reaction, has been employed for the synthesis of a range of novel materials.[21−26] In addition, ATRP has been used for the preparation of a number of photoactive polymers and degradable materials.[8,27−30] We recently reported the synthesis of ozonizable MNs comprised of an ozonizable azido-poly(*tert*-butyl acrylate) (ptBA) MAC cross-linked with tri- and tetrafunctional small molecule alkynes.[25] This study showed that degradation of the MNs occurred primarily at the olefin moieties located at the center of the MACs and that the major degradation products were three- and four-arm star polymers depending on which cross-linker was used (tri- or tetrafunctional alkyne, respectively). If the olefin moieties could be exchanged with photocleavable functionalities, then this strategy could be extended to yield photodegradable MNs.

Scheme 1A outlines this strategy as it pertains to photodegradable MNs. It begins with polymerization from a bifunctional ATRP initiator (**i**) containing a photocleavable moiety at its center to yield a halo-telechelic polymer (**ii**) whose number-average molecular weight (M_n), x, can be defined by the ATRP conditions. Subsequent end-group modification of **ii** with sodium azide yields an azido-functional MAC (linear-MAC). CuAAC with a tetrafunctional alkyne yields a model network with pore sizes defined by x and tetrafunctional branching points (linear-MN). Irradiation with light of the appropriate wavelength should yield four-arm star polymers as the primary product whose M_n is equal to $2x$ or twice that of the linear-MAC.

Rather than starting with linear MACs, one can also prepare MNs from star polymer MACs.[16,31,32] Scheme 1B describes this orthogonal approach. It begins with polymerization from a tetrafunctional ATRP initiator (**iii**) containing one photocleavable functionality for each ATRP initiation site. The resulting four-arm star polymer (**iv**) possesses halogen atoms at the terminus of each arm, and an $M_n = y$. Conversion of the halogen end groups to azides to yield star-MAC, and cross-linking with a bifunctional alkyne yields MNs having pore sizes defined by

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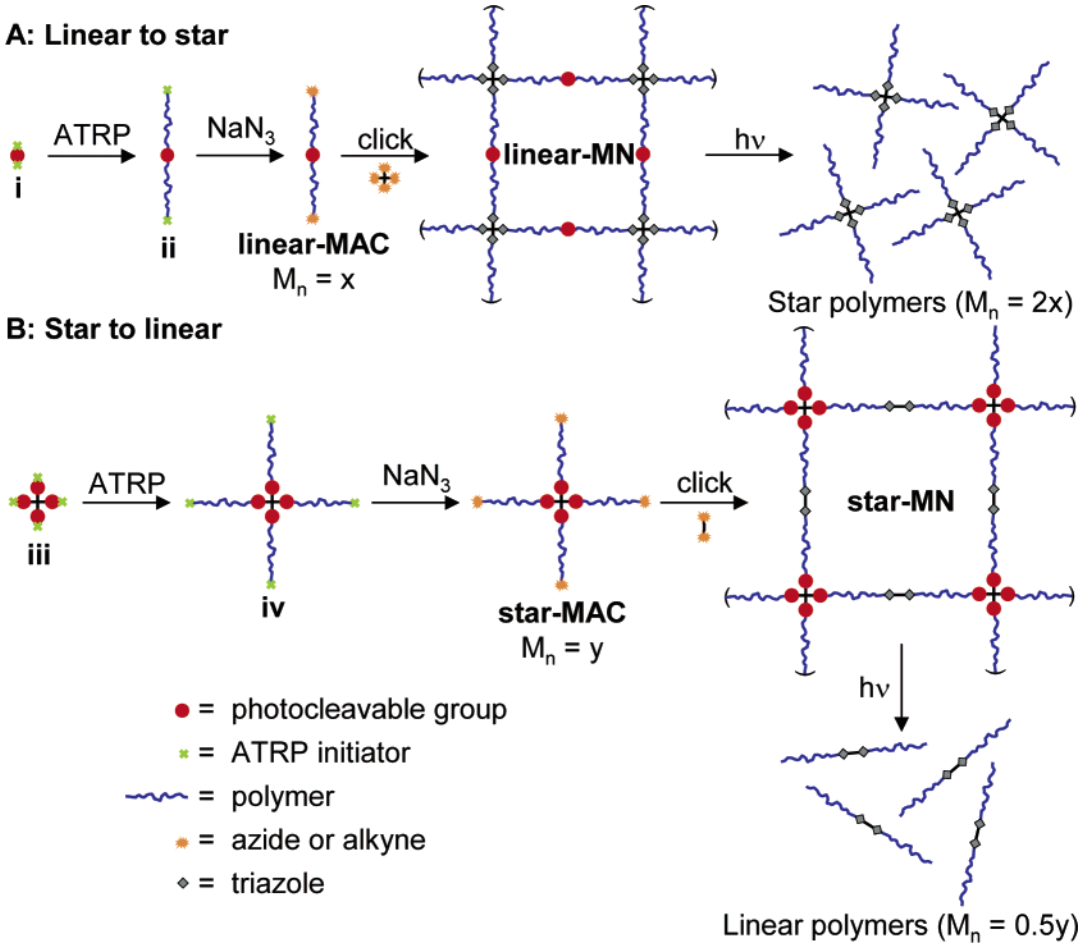
Scheme 1. Photodegradable MN Design Strategies



y and tetrafunctional branching points (star-MN). In this case, however, irradiation with light would be expected to yield linear polymers whose M_n is 0.5*y* or half that of star-MAC.

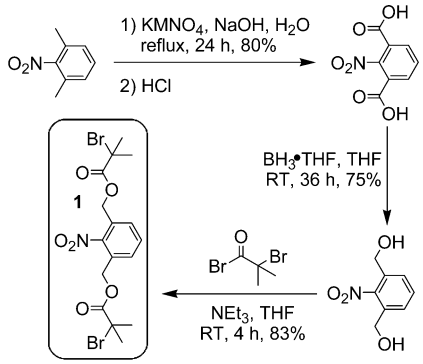
Results and Discussion

Photocleavable Linear Polymers to Star Polymers. Scheme 1A, linear to star, requires a photocleavable linear MAC possessing azides at both termini.

Photocleavable functionalities have been widely studied in the context of protecting groups for organic synthesis and linkers for solid-phase peptide synthesis[33,34] but have also found application in the synthesis of polymeric materials.[35,36] One of the most common photocleavable protecting groups is the nitrobenzyloxycarbonyl (NBOC) group which degrades via a photoinduced intramolecular hydrogen abstraction, followed by thermal reactions which eventually yield, most often, an aldehyde and a carboxylic acid.[34,37] Nitro functionalities have been incorporated into polymers by postpolymerization modification,[35] free radical polymerization,[38−40] or ATRP[41] from an initiator containing a nitro group, and ATRP from *p*-nitrophenyl methacrylate,[42] but no examples of polymers prepared by ATRP that possess the NBOC functionality have been reported.

For our purposes, we chose to begin with the NBOC group as our photocleavable unit both because synthetic transformations involving the required precursors are simple and the photocleavage is known to generally proceed in high yield.[34] Also, the ~350 nm absorbance of the NBOC functionality should allow selective absorption by the NBOC group, since other functionalities present in ptBA should not absorb significantly at this wavelength, thereby providing photocleavage at a specific site. Synthesis of a bifunctional ATRP initiator, **1**, containing an NBOC at its center is described in Scheme 2.

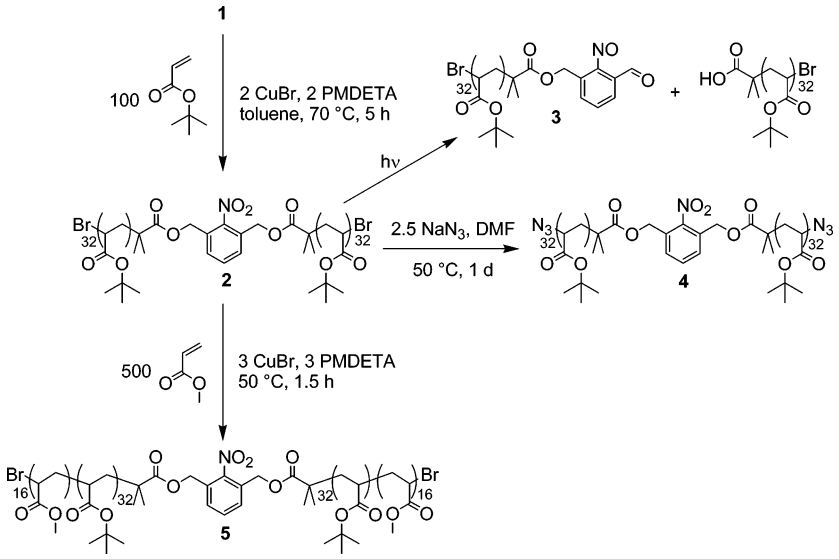
Scheme 2. Synthesis of Bifunctional Photodegradable ATRP Initiator 1



Literature methods were followed for the oxidation of 1,3-dimethylnitrobenzene[43] and subsequent reduction of the resulting diacid to yield the versatile intermediate 2-nitro-1,3-benzenedimethanol.[44] Treatment of this diol with excess α-bromoisobutyryl bromide in the presence of triethylamine yielded compound **1** in 83% yield after purification. ATRP of tBA from **1** using CuBr catalyst, PMDETA ligand, and toluene solvent yielded α,ω-bromo-ptBA, **2**, possessing the NBOC functionality at its center (Scheme 3).

Figure 1 shows that the polymerization reaction was well controlled, exhibiting the kinetic characteristics of a living polymerization.[17]

Scheme 3. Synthesis of Linear, α,ω-Bromo-ptBA 2 from Photodegradable Initiator 1; UV Degradation of 2 Yields Linear Polymer 3 Having M_n = 0.5 That of 2; Treatment of 2 with Sodium Azide Yields α,ω-Azido-ptBA Macromonomer 4; To Ensure a High Degree of Chain-End Functionality in 2, ATRP of Methyl Acrylate Was Performed Using 2 as a Macroinitiator To Yield Block Copolymer 5



The ^{1}H NMR spectrum of **2** (Figure 2) clearly shows the aromatic and methylene protons of the NBOC group along with the resonance corresponding to the terminal protons alpha to the bromine atoms.

The IR spectrum (Figure 3) agrees with that previously reported for ptBA, with an additional peak corresponding to the nitro functionality.

The UV−vis spectra of **1** and **2** (Figure 4) indicate the presence of the nitro functionality in both molecules by the absorbance near 350 nm.

Last, the SEC trace of **2** shown in Figure 5 confirms the low polydispersity (PDI) expected from ATRP and yields an M_n in close agreement with the value obtained by integration of the ^{1}H NMR resonances.

Irradiation of **2** dissolved in 90:10 THF:water (0.01 M) with 350 nm light yielded photocleavage products **3** (Scheme 3) accompanied by a dramatic change in the UV−vis spectrum (Figure 4). The cleavage was complete after 80 min as confirmed by SEC analysis (Figure 5). Importantly, the M_n determined by SEC was one-half that of **2**, confirming cleavage at the center of **2**.

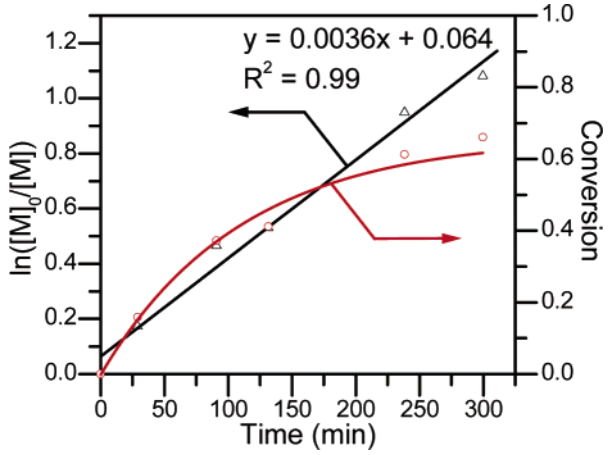


Figure 1. Kinetics of ATRP polymerization of tBA from **1** indicating the "living" nature of the polymerization process.[17] For such polymerizations, the natural log of initial monomer concentration divided by the monomer concentration at a given time is linear with time. Furthermore, the percent conversion of monomer fits an inverse exponential function with time.

In order to proceed with **2** as a precursor to a photocleavable MAC for MN synthesis, it was necessary to confirm a high degree of retention of terminal bromines. This was achieved by preparation of a block copolymer using isolated **2** as a macroinitiator for the ATRP of methyl acrylate (Scheme 3). The resulting polymer, **5**, prepared in a similar manner to the ATRP of **2**, possessed a monomodal SEC trace and a lower PDI than **2**, indicating a high degree of chain end functionality in **2** (Figure 5).

Conversion of the chain ends of **2** to azides[45,46] by treatment with sodium azide in DMF proceeded efficiently to yield MAC **4** (Scheme 3). The ^{1}H NMR spectrum of **4** (Figure 2) is similar to that of **2** with the exception of the expected shift in signal corresponding to the terminal protons from 4.1 to 3.7 ppm. The

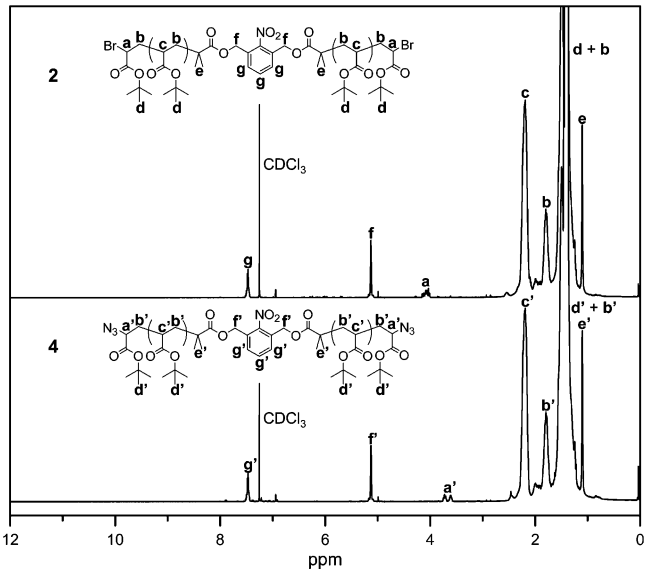


Figure 2. 400 MHz ^{1}H NMR spectra for α,ω-bromo-ptBA **2** and α,ω-azido-ptBA **4** in $CDCl_3$ clearly showing the conversion of the bromine end groups (resonance a) of **2** to azides (resonance a′). As expected, the chemical shifts of the proton resonances in **2** deriving from the initiator **1** (e, f, g) and the polymer backbone (b, c, d) remain relatively unchained upon conversion to **4** (e′, f′, g′ and b′, c′, d′, respectively).

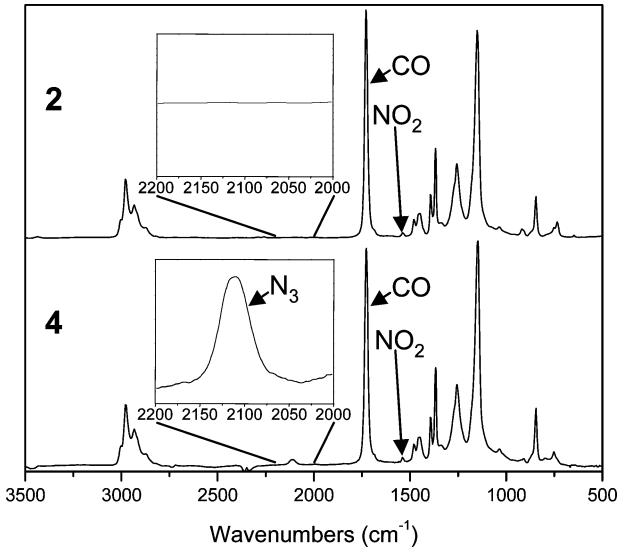


Figure 3. FTIR spectra for α,ω-bromo-ptBA **2** and α,ω-azido-ptBA **4** showing the incorporation azide groups into **4** and the presence of the nitro functionality in both polymers.

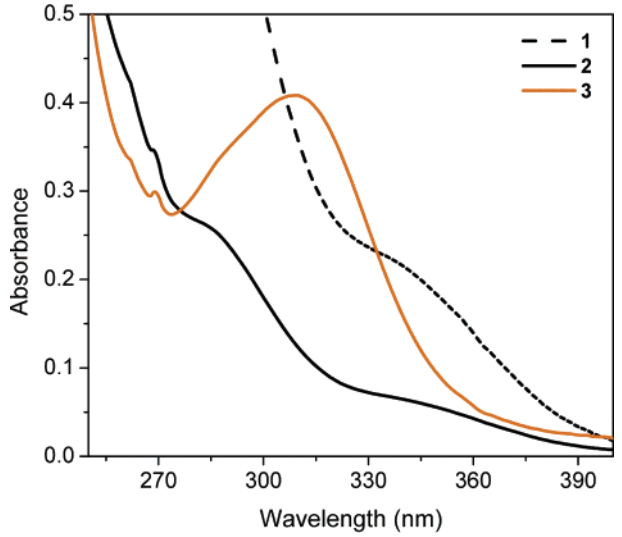


Figure 4. UV−vis spectra of bifunctional ATRP initiator **1**, α,ω-bromo-ptBA **2**, and the linear polymer obtained upon irradiation of **2** with UV light (**3**). The spectra for both **1** and **2** show absorptions near 350 nm corresponding to the nitro functionality. This absorbance is absent in the spectrum of **3**, indicating that the nitro functionality is lost during the photoreaction leading to cleavage of **2**.

IR spectrum of **4** (Figure 3) possesses an absorbance at ∼2100 cm^{-1}, confirming the presence of azide groups. The photocleavage of **4** seemed to not reach completion, as we observed a high molecular weight shoulder in the SEC trace that did not disappear upon extended irradiation. We suggest that photoinduced cross-linking of the azide groups with polymer backbone sites of **4** via a nitrene intermediate[47] may compete to a small degree with the desired photocleavage, giving rise to a high molecular weight side product.

Cross-linking of **4** with the tetrafunctional alkyne **8** (Scheme 4) using CuAAC conditions similar to the ATRP conditions described above (CuBr catalyst, PMDETA ligand, and/or base) with the exception of DMF solvent yielded MN **6**, which was insoluble in all solvents. Repeated exposure of **6** to fresh dichloromethane produced a colorless gel material that swelled extensively (the equilibrium swelling ratio of **6** in dichloromethane was 23 ± 1.5) in organic solvent and collapsed in water. SEC analysis of the extracted dichloromethane showed

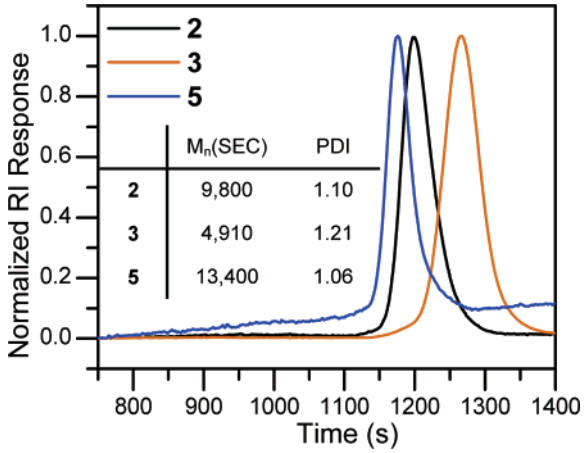
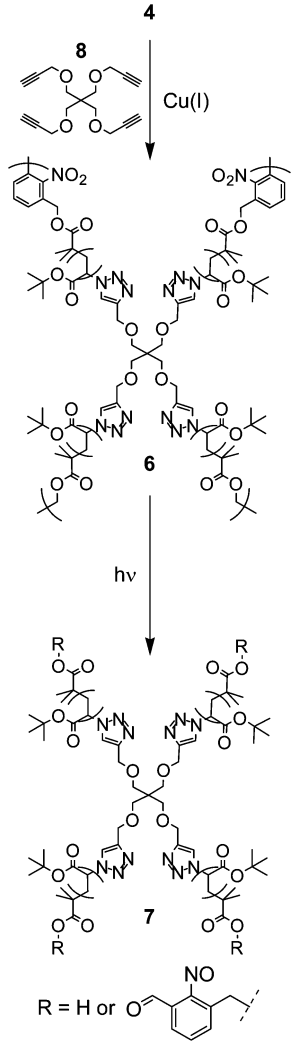


Figure 5. SEC traces for α,ω-bromo-ptBA **2**, the product of photodegration of **2** (**3**), and block copolymer **5**. As expected, the M_n of **3** is ∼0.5 that of **2**, confirming photocleavage at the center of **2**. The polydispersity of **5** is lower than **2**, indicating that **2** possessed a high-degree of chain-end bromine functionality as expected from the ATRP process.

Scheme 4. CuAAC Cross-Linking of α,ω-Azido-ptBA 4 with Tetrafunctional Alkyne 8 Yields Cross-Linked Network 6 Possessing Tetrafunctional Branching Points and Pore Sizes Related to the M_n of 4; UV Irradiation of 6 Induces Photocleavage at the NBOC Functionalities To Yield Four-Armed Star Polymers 7 Having M_n Twice That of 4



no trace of polymer material, indicating that, within limits of detection, all of **4** reacted to form **6**. Furthermore, FTIR analysis

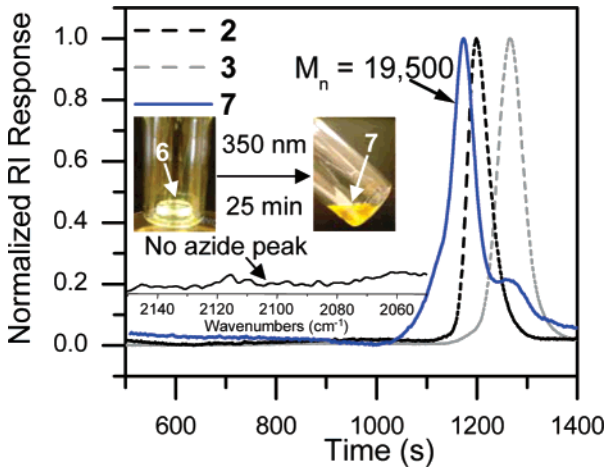


Figure 6. FTIR analysis of network **6** shows no remaining azide peak, indicating a high yield of the CuAAC reaction. Photodegradation of **6** yields a yellow solution which is expected to be largely composed of four-armed star polymer **7** possessing M_n equal to twice that of **4**. SEC analysis of this solution indicates it is composed primarily of a polymer whose M_n (19 500 Da) is approximately twice that of macromonomer **4** (9800 Da). A species having M_n equal to that of **3**, or half that of **4**, is also observed which corresponds to unreacted chain ends in the cross-linked network.

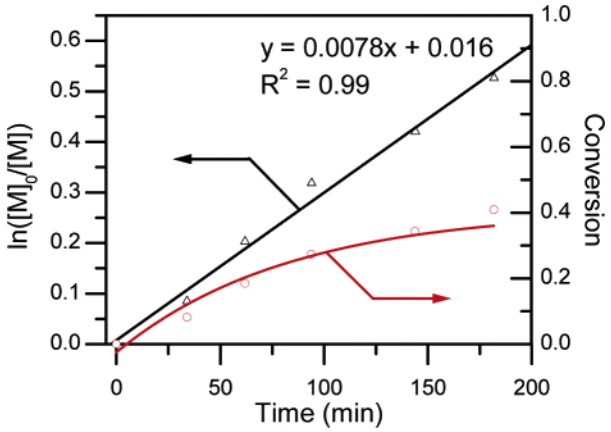


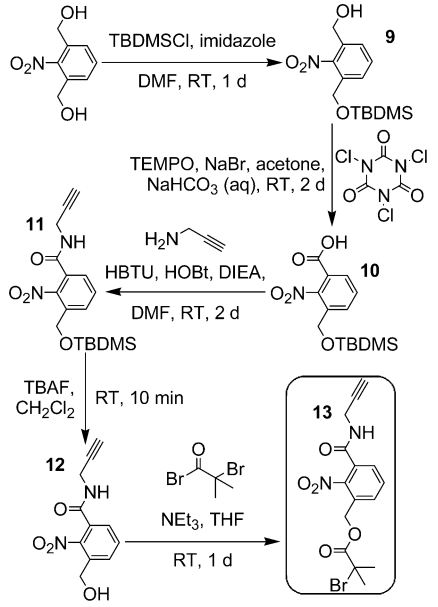
Figure 7. Kinetics of the ATRP synthesis of **15** confirming the "living" nature of the polymerization process.[17]

of **6** showed no remaining azide peak (Figure 6), indicating that most of the azides present on **4** reacted.

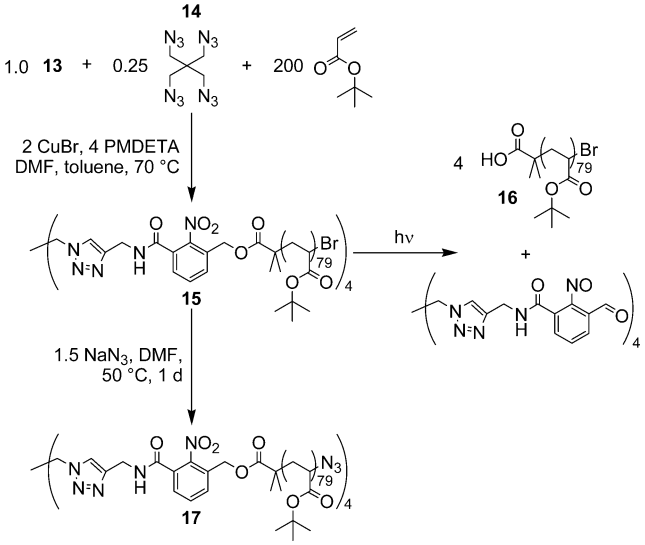
As Schemes 1 and 4 suggest, photodegradation of **6** should yield as the primary degradation product a four-arm star polymer, **7**, whose M_n (~19 600 Da) is twice that of **4** (~9800 Da). Irradiation of **6** swelled in 90:10 THF:water with 350 nm light for 25 min produced a light yellow liquid and no visible trace of insoluble material (Figure 6).

SEC analysis of this liquid indicated that the photoreaction was incomplete by the presence of a high molecular weight shoulder in the chromatogram. After irradiation for 3 days, the high molecular weight shoulder reached a minimum height, and a primary peak corresponding to a M_n of 19 500 Da was observed (Figure 6), confirming the presence of **7** and, consequently, the tetrafunctional branching points in the parent network. A peak at ~5000 Da was also observed (Figure 6), corresponding to unreacted chain ends in the parent MN. These may arise from slight variations from 1:1 stoichiometry of azides and alkynes in the cross-linking reaction or from incomplete reaction due to the immobility of the copper catalyst or the reactive azide and alkyne components in the sterically hindered MN environment. The remaining high molecular weight shoulder may be the result of nitrene side reactions as described above

Scheme 5. Synthesis of Photodegradable Acetylene-Functionalized ATRP Initiator 13



Scheme 6. Combining 13 with 0.25 equiv of Tetraazide 14 and 200 equiv of tBA in the Presence of Copper(I) Yields Bromo-Terminated Four-Armed Star Polymer 15, the Product of Simultaneous CuAAC and ATRP Reactions; UV Irradiation of 15 Yields Linear Polymers 16 Having M_n Equal to 0.25 That of 15; Treatment of 15 with Sodium Azide in DMF Yields Azido-Terminated Star Polymer 17



or incomplete photodegradation (although we consider the latter to be unlikely). One may note the time required for complete photodegradation is relatively long (3 days), which may be desirable for certain materials applications. If, however, accelerated photodegradation is required, one could introduce substituents onto the NBOC aromatic ring to vary the photodegradation kinetics. For example, the nitroveratroyloxycarbonyl (NVOC), which contains two methoxy substituents on the NBOC aromatic ring, is known to photocleave ~15% faster than the NBOC group.[48]

Photocleavable Star Polymers to Linear Polymers. As described above in Scheme 1B, photodegradable MNs can also be prepared by cross-linking of functional star MACs with small molecules. Such a method would require a photoactive star polymer whose arms are cleaved upon irradiation. Such a star polymer, to our knowledge, has not been reported, but encour-

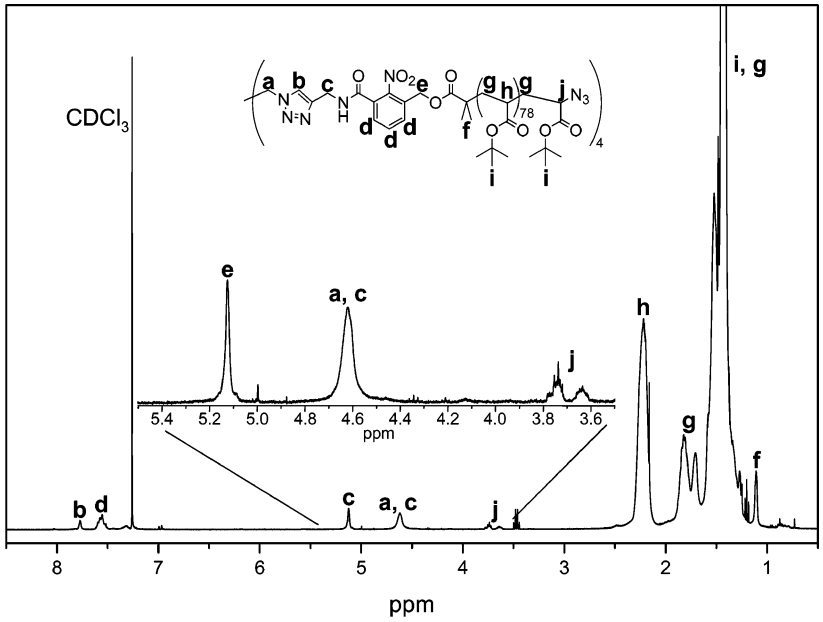


Figure 8. 400 MHz ^{1}H NMR spectrum of azido-terminated star polymer **17** in $CDCl_3$. Resonances a, c, d, e, and f correspond to protons present in initiator **13** and tetraazide **14**. The triazole proton's resonance, b, confirms that the CuAAC reaction occurred. Resonances g, h, and i correspond to the backbone protons of the ptBA chain, and resonance j corresponds to the protons alpha to the azide groups. The absence of a resonance at ~4.2 confirms that the bromine end groups of **15** were converted to azides in high yield.

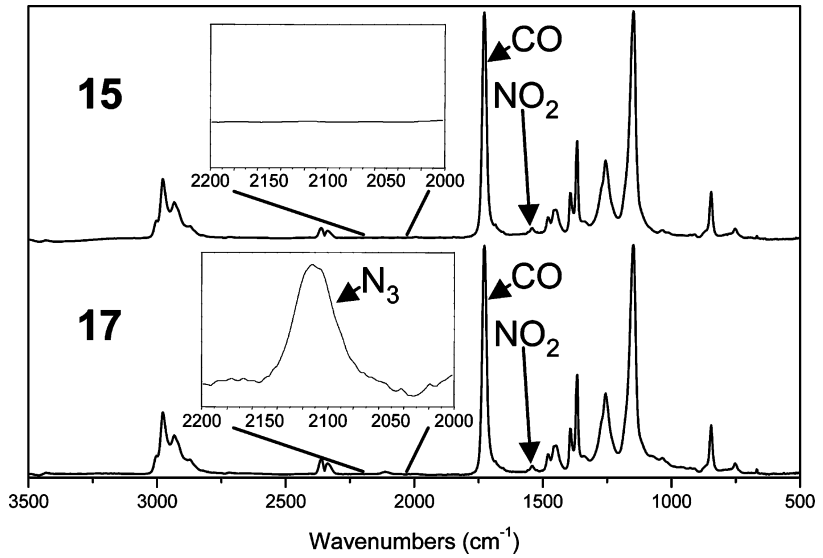


Figure 9. FTIR spectra for bromo-terminated star polymer **15** and azido-terminated star polymer **17** showing the incorporation azide groups into **17** and the presence of the nitro functionality in both polymers.

aged by the recent reports of one-pot star polymer syntheses,[49−59] the utilization of CuAAC for the synthesis of star polymers,[24] and recent studies in tandem catalysis pertaining to macromolecule synthesis,[60,61] we set out to prepare such a molecule via a one-pot strategy. First, as noted above, the conditions for ATRP and CuAAC are essentially identical, with the important catalytic entity being Cu(I) in both cases. We therefore designed a one-pot star polymer synthesis using a small, tetrafunctional azide. The initiator **13** has an alkyne separated from the initiation site by an NBOC functionality, thus enabling cleavage of the resulting polymer from the alkyne. Synthesis of **13** (Scheme 5) commenced with mono-TBDMS protection of 2-nitro-1,3-benzenedimethanol to give alcohol **9**, followed by oxidation[62] to the acid **10**. Coupling of propargyl amine to the acid functionality provided amide **11**, which was deprotected to give alcohol **12**. Treatment with α-bromoisobutyryl bromide in the presence of triethylamine gave the desired compound **13**.

Treatment of **13** with 0.25 equiv of tetraazide **14** (see safety note[63]) and 200 equiv of tBA with CuBr catalyst, PMDETA ligand, and 50−50 toluene−DMF solvent yielded star polymer **15** (M_n(SEC) = 37 200, PDI = 1.11), the result of tandem CuAAC coupling and ATRP (Scheme 6).

The kinetics of the polymerization indicates the living nature of ATRP (Figure 7), and the star polymer nature of the polymer product was confirmed by ^{1}H NMR spectroscopy and SEC analysis.

Photodegradation of **15** by irradiation with 350 nm light yielded linear degradation products (Scheme 6, **16**) having M_n-(SEC) = 10 300, in close agreement with the M_n value for each arm obtained by ^{1}H NMR (Figure 10). Conversion of the bromine end groups of **15** to azides by treatment with NaN_3 in DMF yielded star MAC **17** (Scheme 6). Figure 8 shows the ^{1}H NMR resonances in **17** corresponding to the triazole proton resulting from the CuAAC reaction, the methylene protons from

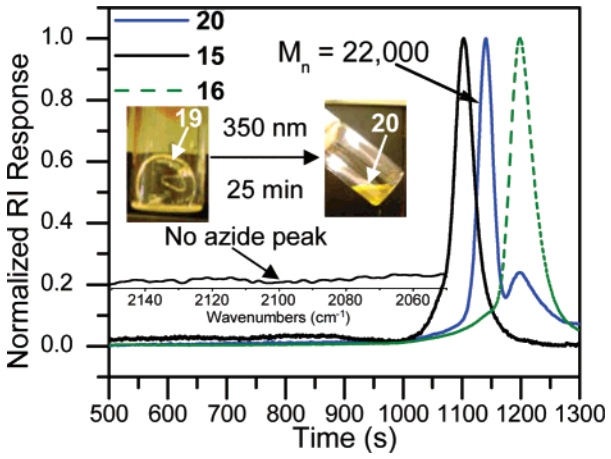
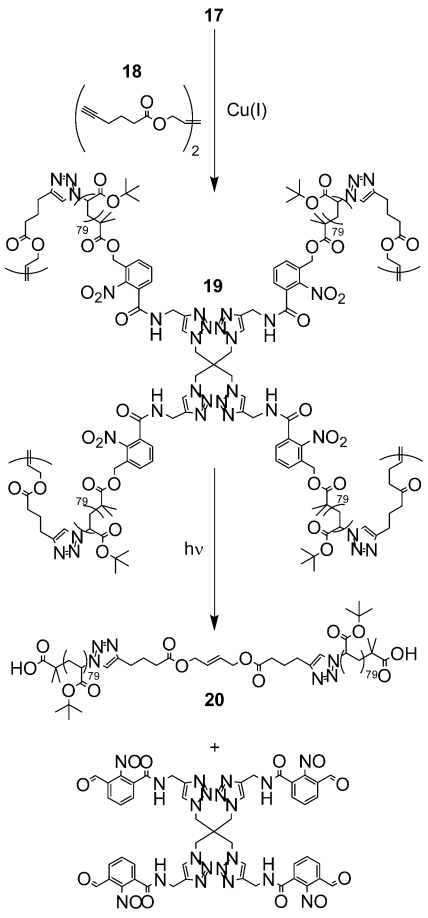


Figure 10. SEC analysis of polymers **15** (M_n = 37 200 Da, PDI = 1.11), **16** (M_n = 10 300 Da, PDI = 1.21), and **20**. FTIR analysis of network **19** shows no remaining azide peak, indicating a high yield of the CuAAC reaction. Photodegradation of **19** yields a yellow solution which is expected to be largely composed of linear polymers **20**, possessing M_n equal to half that of **17**. SEC analysis of this solution indicates it is composed primarily of a polymer whose M_n (22 000 Da) is approximately half that of star macromonomer **17** (37 200 Da). A species having M_n equal to that of **16**, or 0.25 that of **17**, is also observed which corresponds to unreacted chain ends in the cross-linked network.

Scheme 7. CuAAC Cross-Linking of Azido-Terminated Star Polymer 17 with Bifunctional Alkyne 18 Yields Cross-Linked Network 19 Possessing Tetrafunctional Branching Points and Pore Sizes Related to the M_n of 17; UV Irradiation of 19 Induces Photocleavage at the NBOC Functionalities To Yield Linear Polymers 20 Having M_n One-Half That of 17



14 and **13**, the aromatic protons of **13**, the terminal protons adjacent to the azide groups, and the backbone and *tert*-butyl protons of ptBA.

Comparison of the FTIR spectra of **15** and **17** confirms the existence of azide groups in **17** (Figure 9).

CuAAC cross-linking of **17** with a bifunctional alkyne (**18**) under the same conditions used for the linear polymers described above yielded insoluble gel materials **19** (Scheme 7). The equilibrium swelling ratio of **19** swollen in dichloromethane was 42 ± 2.5. As expected, network **19** had a greater swelling ratio than network **6** due to its greater molecular weight between cross-links. As for network **6**, the FTIR spectrum of **19** showed no remaining azide peak (Figure 10) and SEC analysis of the extracted dichloromethane showed no trace of polymer material.

As described in Schemes 1 and 7, photodegradation of **19** should yield a linear polymer **20**, with M_n approximately one-half that of the star polymer **17** as the primary degradation product. Irradiation of the 90:10 THF:water swollen material for 25 min yielded a light yellow liquid and no visible trace of the insoluble material (Figure 10).

Continued irradiation for 2 days and SEC analysis yielded product **20** which possessed the expected M_n, confirming the presence of tetrafunctional branching points in the parent MN (Figure 10). As for the case with the linear MACs, there existed a low molecular weight SEC peak (~10 000 Da) corresponding to unreacted arms of the star MACs (Figure 10).

Conclusions

We show here the synthesis and light-induced disassembly of photodegradable MNs from two complementary strategies: cross-linking of cleavable linear MACs with tetravalent connectors and cross-linking of cleavable tetravalent MACs with linear connectors. These results include the first examples of a photocleavable MAC and a star polymer with photocleavable arms and the first simultaneous assembly of a star polymer using ATRP and CuAAC events. The outstanding compatibility and functional group tolerance of the ATRP and CuAAC reactions makes the preparation of these responsive materials especially easy and amenable to the incorporation of a variety of structural and functional features.

Experimental Section

Materials. All reagents were purchased from Aldrich Chemical Co. and were used as received unless otherwise mentioned. The *tert*-butyl acrylate (tBA) and methyl acrylate (MA) monomers were distilled over calcium hydride before use. Toluene and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) were bubbled with argon for 15 min prior to use in polymerization reactions. 2-Nitro-1,3-benzenedimethanol,[44] hexynoyl chloride,[64] pentaerythrityl tetraazide (**14**),[63,65] and tetrakis(2-propynyloxymethyl)methane[66−68] (**8**) were synthesized according to literature procedures.

Measurements. Size exclusion chromatography (SEC) measurements were performed on a Knauer GPC system with a Knauer K-2301 refractive index detector and a Spark Holland Basic Marathon autosampler. Three Polymer Laboratories 5 μm particle size PLgel columns (one 100 Å and two MIXED-D pore types) placed in series were employed for the chromatography. The system was calibrated against linear polystyrene standards ranging in molecular weight from 580 to 377 400 Da. Experiments were performed at room temperature in THF eluant with a flow rate of 1.0 mL/min.

Synthesis of 2-Nitro-1,3-bis(bromoisobutyryloxy)benzene (1). A solution of 2-nitro-1,3-benzenedimethanol (1.50 g, 8.19 mmol) and triethylamine (1.82 g, 18.02 mmol) in anhydrous THF (20 mL) was added dropwise to a stirring solution of α-bromoisobutyryl bromide (4.14 g, 18.02 mmol) in anhydrous THF (60 mL) at 0 °C under argon atmosphere. A white precipitate formed immediately. The reaction was allowed to warm to room temperature and was stirred overnight under argon. After this time, the reaction mixture was filtered to remove insoluble salts, concentrated on a rotary

evaporator, redissolved in ethyl acetate, and washed three times with water. The organic layer was dried over magnesium sulfate and concentrated on a rotary evaporator to yield a yellow oil which was purified by column chromatography (30% EtOAc:hexanes) to yield **1** (3.27 g, 83%) as a colorless oil which crystallized upon cooling in a 2 °C refrigerator. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59 (b, 3 H), 5.33 (s, 4 H), 1.94 (s, 12 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 176.0, 171.0, 131.4, 129.8, 129.2, 63.4, 55.1, 30.5. IR (cm^{-1}): 3003, 2980, 2933, 1739, 1534, 1464, 1363, 1271, 1154, 1109. FAB HRMS calcd for $C_{16}H_{19}Br_2NO_6$ $[M + H]^+$: 479.9657; found: 479.9665.

ATRP Synthesis of Bromo-Telechelic, Photocleavable ptBA (2). CuBr (112 mg, 0.781 mmol) and **1** (188 mg, 0.391 mmol) were added to a clean, dry, round-bottom flask, which was subsequently evacuated for 15 m and backfilled with argon. Freshly distilled tBA (5.0 g, 39.0 mmol) was added via a degassed syringe followed by degassed toluene (2.5 mL) and PMDETA (130 mg, 0.781 mmol). The reaction flask was immediately submerged in liquid N_2 until frozen, evacuated for 15 min, removed from liquid N_2, and backfilled with argon. When the mixture thawed completely, the flask was submerged in a 70 °C oil bath and stirred for 5 h under an argon atmosphere. Aliquots were taken at varied intervals for kinetic analysis by ^{1}H NMR. After 5 h, the reaction flask was opened to air, and the viscous, black mixture was diluted with tetrahydrofuran (20 mL) and frozen in liquid N_2. After thawing, the mixture was passed through a column of neutral alumina, concentrated on a rotary evaporator, precipitated in a 10:1 volume of 50−50 methanol−water three times, dissolved in diethyl ether, dried over $MgSO_4$, filtered, concentrated on a rotary evaporator, and dried in vacuo for 2 days to yield **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (br, 3 H), 5.15 (s, 4 H), 4.08 (br, 2 H), 2.23 (br, 64 H), 1.82 (br, 24 H), 1.53 (br, 82 H), 1.44 (br, 576 H), 1.13 (s, 12 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 176.8, 174.4, 149.0, 131.3, 130.0, 125.8, 82.6, 80.6, 62.7, 42.0, 37.5, 35.9, 28.2. IR (cm^{-1}): 2977, 2933, 2879, 1730, 1540, 1448, 1394, 1369, 1258, 1154, 846, 736. THF-SEC: $M_n = 9800$, $M_w = 10\,780$, PDI = 1.10.

Synthesis of Azido-Telechelic, Photocleavable ptBA (4). Sodium azide (106 mg, 1.63 mmol) was added to a round-bottom flask containing **2** (7.0 g, 0.783 mmol) dissolved in DMF (74 mL). The reaction mixture was stirred at 50 °C for 1 day, after which time it was allowed to cool to room temperature, diluted with ether (50 mL), and washed four times with water (100 mL). The organics were concentrated on a rotary evaporator and precipitated into a 10:1 volume of 50−50 methanol−water. After decanting the methanol−water solution, the remaining solid was dissolved in diethyl ether, dried over $MgSO_4$, filtered, concentrated on a rotary evaporator, and dried for 2 days in vacuo to yield **4** (6.30 g, 90%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (br, 3 H), 5.15 (s, 4 H), 3.69 (br, 2 H), 2.23 (br, 64 H), 1.82 (br, 24 H), 1.53 (br, 82 H), 1.44 (br, 576 H), 1.13 (s, 12 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 176.7, 174.5, 149.1, 131.3, 130.0, 125.7, 82.6, 80.5, 62.7, 61.4, 42.1, 37.4, 35.8, 28.2. IR (cm^{-1}): 2977, 2933, 2879, 2112, 1730, 1540, 1448, 1394, 1369, 1258, 1154, 846, 736.

ATRP Synthesis of Bromo-Telechelic, Photocleavable pMA-*b*-ptBA-*b*-pMA (5). Compound **2** (726 mg, 76.8 μmol) and CuBr (66.1 mg, 0.461 mmol) were added to a clean, dry, round-bottom flask which was subsequently evacuated for 15 min and backfilled with argon. Freshly distilled MA (3.31 g, 38.4 mmol) was added via a degassed syringe followed by degassed PMDETA (77.0 mg, 0.461 mmol). The reaction mixture was immediately frozen by submerging the flask in liquid N_2. The flask was then evacuated for 15 min, removed from liquid N_2, and backfilled with argon. After completely thawing, the reaction flask was submerged in a 50 °C oil bath and stirred for 1 h under an argon atmosphere, after which time the reaction flask was opened to air, and the viscous, black mixture was diluted with tetrahydrofuran (20 mL) and frozen in liquid N_2. After thawing, the mixture was passed through a column of neutral alumina, concentrated on a rotary evaporator, precipitated in a 10:1 volume of 50−50 methanol−water three times, dissolved in diethyl ether, dried over $MgSO_4$, filtered, concentrated on a rotary evaporator, and dried in vacuo for 2 days to yield **5** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (br, 3 H), 5.12 (s, 4 H), 4.20 (br, 2 H), 3.61 (br, 96 H), 2.20 (br, 115 H), 1.77 (br, 12 H), 1.63 (br, 40 H), 1.49 (br, 105 H), 1.39 (br, 744 H), 1.09 (s, 12 H). IR (cm^{-1}): 3008, 2979, 2934, 2870, 1732, 1539, 1479, 1448, 1394, 1368, 1257, 1152, 846. THF-SEC: $M_n = 13\,400$, $M_w = 14\,200$, PDI = 1.06.

Synthesis of 2-Nitro-3-(*tert*-butyldimethylsilyloxymethyl)-hydroxymethylbenzene (9). To a clean, dry round-bottom flask was added 2-nitro-1,3-benzenedimethanol (818 mg, 4.47mmol), anhydrous DMF (40 mL), and imidazole (304.2 mg, 4.47 mmol). The solution was maintained at 0 °C while *tert*-butyldimethylsilyl chloride (337 mg, 2.24 mmol) was slowly added. The resulting pale yellow solution was allowed to warm to room temperature and stirred overnight under argon before being diluted with ethyl acetate (100 mL), washed with water (5 × 50 mL), dried over $MgSO_4$, filtered, concentrated on a rotary evaporator, and purified by silica gel chromatography (30% EtOAc:hexanes) to yield 3-(*tert*-butyldimethylsilyloxymethyl)-2-nitrohydroxymethylbenzene as a yellow oil. The excess 2-nitro-1,3-benzenedimethanol was recovered and resubjected to the reaction conditions to yield **9** in 80% yield after three iterations. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, 1 H, $J = 7.1$ Hz), 7.51 (m, 2 H), 4.80 (s, 1 H), 4.71 (s, 1 H), 0.93 (s, 9 H), 0.099 (s, 6 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 148.0, 135.3, 134.0, 131.8, 129.0, 128.2, 62.09, 61.75, 26.2, 18.71, −5.16. FAB LRMS calcd for $C_{14}H_{23}NO_4Si$ $[M + H]^+$: 298.14; found: 298.72.

Synthesis of 3-(*tert*-Butyldimethylsilyloxymethyl)-2-nitrobenzoic Acid (10). An aqueous solution of 15% $NaHCO_3$ (18 mL) was added to a stirring solution of **9** (1.80 g, 2.69 mmol) in acetone (60 mL) at 0 °C. NaBr (133 mg, 1.29 mmol) and TEMPO (18.9 mg, 0.121 mmol) were then added followed by the slow addition of trichloroisocyanuric acid (2.81 g, 12.1 mmol). The resulting solution was allowed to warm to room temperature and stirring for 1 day, after which time 2-propanol (3.63 mL) was added. The mixture was filtered over Celite, concentrated on a rotary evaporator, dissolved in 18 mL of saturated Na_2CO_3, washed with EtOAc (3 × 10 mL), acidified with 1 M HCl, and extracted with ethyl acetate (3 × 50 mL). The resulting organics were dried over Na_2SO_4, filtered, concentrated on a rotary evaporator, and purified by silica gel chromatography (10% MeOH:CH_2Cl_2) to yield **10** (1.05 g, 56%) as a white solid. ^{1}H NMR (300 MHz, DMSO-d_6): δ 11.19 (s, 1 H), 7.86 (d, 1 H, $J = 6.9$ Hz), 7.75 (d, 1 H, $J = 8.2$ Hz), 7.66 (t, 1 H, $J = 6.9$), 4.72 (s, 2 H), 0.84 (s, 9 H), 0.032 (s, 6 H). ^{13}C NMR (300 MHz, DMSO-d_6): δ 166.1, 149.0, 133.8, 132.6, 131.7, 130.6, 127.5, 61.5, 26.5, 18.8, −4.8. FAB LRMS calcd for $C_{14}H_{21}NO_5Si$ $[M + H]^+$: 312.12; found: 312.52.

Synthesis of 3-(*tert*-Butyldimethylsilyloxymethyl)-2-nitro-*N*-propargylbenzamide (11). HBTU (183 mg, 0.482 mmol) and HOBt (65.1 mg, 0.482 mmol) were added to a stirring solution of **10** (150 mg, 0.482 mmol) in anhydrous DMF (4.82 mL) followed by *N*,*N*-diisopropylethylamine (187 mg, 1.45 mmol) and propargylamine (79.6 mg, 1.45 mmol). The resulting solution was stirred for 30 h at room temperature, after which time 25 mL of EtOAc was added, and the solution was washed with water (3 × 10 mL), aqueous saturated NH_4Cl (1 × 10 mL), and brine (1 × 10 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated on a rotary evaporator. The resulting oil was purified by silica gel chromatography (50% EtOAc:hexanes) to yield **11** as a white solid (92.3 mg, 55%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, 1 H, $J = 7.6$), 7.54 (t, 1 H, $J = 7.7$ Hz), 7.46 (d, 1 H, $J = 7.7$ Hz), 6.43 (b, 1 H), 4.79 (s, 2 H), 4.16 (m, 2 H), 2.67 (t, 1 H, 2.8 Hz), 0.92 (s, 9 H), 0.091 (s, 6 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 165.6, 146.9, 136.0, 131.6, 130.6, 130.3, 127.1, 79.1, 72.7, 61.2, 30.4, 26.3, 18.7, −5.1. FAB LRMS calcd for $C_{17}H_{24}N_2O_4Si$ $[M + H]^+$: 349.15; found: 349.45.

Synthesis of 3-(2-Bromoisobutyryl)methyl-2-nitro-*N*-propargylbenzamide (13). TBAF (4.19 mL of a 1.0 M solution in THF) was added dropwise to a stirring solution of **11** (487 mg, 1.40 mmol) in THF (14 mL). TLC analysis showed complete reaction after 5 min, after which time the THF was removed on a rotary evaporator, and the resulting oil was dissolved in EtOAc (50 mL), washed with saturated NH_4Cl (2 × 20 mL), washed with water (2 × 50 mL),

dried over $MgSO_4$, and concentrated in vacuo. The resulting white solid (**12**) was dissolved in anhydrous THF (14 mL), triethylamine (184 mg, 1.81 mmol) was added, and the resulting solution was added dropwise to a stirring solution of α-bromoisobutyryl bromide (225 mg, 1.82 mmol) in THF (5 mL) at 0 °C. A white precipitate formed immediately. The mixure was allowed to warm to room temperature and stirred overnight under an argon atmosphere, after which time the solid salts were filtered, and the solvent was removed on a rotary evaporator. The resulting yellow oil was dissolved in ethyl acetate (50 mL) and washed with water (3 × 20 mL), dried over $MgSO_4$, concentrated in vacuo, and purified by silica gel chromatography (50% EtOAc:hexanes) to yield **13** (321 mg, 60%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.70 (d, 1 H, J = 7.1), 7.59 (m, 2H), 6.15 (b, 1 H), 5.33 (s, 2 H), 4.22 (m, 2 H), 2.31 (t, 1 H, J = 2.7 Hz), 1.93 (s, 6 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.4, 165.1, 148.1, 132.0, 131.9, 131.2, 130.2, 128.6, 78.8, 73.0, 63.5, 60.8, 55.6, 31.0. IR (cm^{-1}): 3293, 1739, 1657, 1540, 1461, 1363, 1274, 1157, 1106. FAB LRMS calcd for $C_{15}H_{15}BrN_2O_5$ $[M + H]^+$: 383.02; found: 383.20.

Synthesis of Bifunctional Alkyne Cross-Linker (18). Hexynoyl chloride (1.74 g, 13.3 mmol) was added dropwise to a stirring solution of butane-1,4-diol (0.901 g, 10.2 mmol) and triethylamine (1.35 g, 13.3 mmol) in methylene chloride (25 mL). A white precipitate formed immediately. The mixture was stirred overnight at room temperature, after which time it was filtered and concentrated on a rotary evaporator. The residue was dissolved in EtOAc (50 mL) and washed with water (2 × 25 mL), saturated aqueous Na_2CO_3 (2 × 25 mL), and brine (1 × 25 mL). The organic layer was dried over $MgSO_4$, filtered, concentrated on a rotary evaporator, and purified by silica gel chromatography (80% hexanes:EtOAc) using anisaldehyde stain to yield **18** as a colorless oil (2.00 g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.75 (m, 2 H), 4.69 (m, 2 H), 2.47 (t, 4 H, J = 7.3 Hz), 2.26 (m, 4 H), 1.97 (t, 2 H, J = 2.6 Hz), 1.85 (m, 4 H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 172.7, 128.1, 83.2, 69.2, 59.9, 32.7, 23.5, 17.8. FAB LRMS calcd for $C_{16}H_{20}O_4$ $[M + H]^+$: 277.14; found: 277.25.

Synthesis of 4-Arm ptBA Star Polymer (15). CuBr (115 mg, 0.80 mmol) was added to a clean, dry round-bottom flask which was evacuated for 5 min before backfilling with argon. Freshly distilled tBA (10.3 g, 80.0 mmol) and a degassed solution of **14** (23.6 mg, 0.100 mmol) in toluene (2.50 mL) were added via a degassed syringe. A solution of **13** (151 mg, 0.400 mmol) in DMF (2.50 mL) was bubbled with argon for 5 min and added to the reaction flask via a degassed syringe. The flask was immediately submerged in liquid N_2 until frozen, subjected to vacuum for 10 min, removed from liquid N_2, and backfilled with argon. After completely thawing, the light green reaction mixture was submerged in a preheated oil bath at 70 °C and stirred under argon atmosphere for 3 h. Samples were taken via a degassed syringe at various time intervals for kinetic analysis by ^{1}H NMR. When the reaction had reaction ~40% conversion, the flask was opened to air and submerged in liquid nitrogen to quench the reaction. Dilution with THF, passing through a neutral alumina column, concentration on a rotary evaporator, and precipitation (3× in a 10:1 volume of 50−50 methanol−water) yielded star polymer **15** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 4 H), 7.58 (br, 12 H), 5.15 (s, 8 H), 4.64 (br, 16 H), 4.12 (br, 4 H), 2.24 (br, 316 H), 1.84 (br, 163 H), 1.54 (br, 334 H), 1.45 (br, 1467 H), 1.13 (s, 24 H). IR (cm^{-1}): 3006, 2980, 2932, 2870, 1726, 1540, 1479, 1452, 1392, 1368, 1257, 1148, 846. M_n = 37 200, M_w = 41 290, PDI = 1.11.

Synthesis of Tetraazido-Functionalized ptBA Star Polymer (17). Star polymer **17** was prepared in a manner similar to linear polymer **4** using **15** as the substrate as opposed to **2**. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (s, 4 H), 7.58 (br, 12 H), 5.15 (s, 8 H), 4.64 (br, 16 H), 3.69 (br, 4 H), 2.24 (br, 316 H), 1.84 (br, 163 H), 1.54 (br, 334 H), 1.45 (br, 1467 H), 1.13 (s, 24 H). IR (cm^{-1}): 3005, 2982, 2933, 2870, 2110, 1728, 1540, 1479, 1452, 1391, 1369, 1259, 1148, 845.

General Method for Photodegradation of Polymers 2 and 15. A sample of polymer (**2** or **15**) was dissolved in 90% THF:water (0.01 M) in a clean glass vial. The vial was capped and placed in a Rayonet reactor and irradiated with UV light at 350 nm peak wavelength for 5 h.

General Method for Preparation of MNs 6 and 19. The MAC precursor (**4** or **17** for **6** or **19**, respectively) and CuBr (10 equiv per azide) were added to a clean glass vial which was capped with a septum and purged with argon for 5 min. Anhydrous DMF (30 wt % MAC) was added via a degassed syringe, followed by cross-linker (**8** or **18** for **6** or **19**, respectively, 1 equiv of alkyne to azide), and PMDETA (20 equiv per azide). The vial was immediately submerged in liquid N_2, evacuated for 5 min, and backfilled with argon while thawing. When the solution was completely thawed, the vial was placed in an ultrasonication bath for 10 s to homogenize the solution before placing it in a preheated oil bath at 40 °C under argon for overnight reaction to yield insoluble MNs which were deep blue in color due to the presence of trapped copper catalyst.

General Method for Measuring Swelling Ratios of 6 and 19. The insoluble MN material was swollen for a period of 1 week in methylene chloride with fresh solvent being added daily. The weight of the swollen sample was recorded, and then the sample was placed in an oven at 50 °C for 2 h to remove the solvent. The dry weight of the sample was measured, and the swelling ratio was calculated as the swollen weight divided by the dry weight.

General Method for Photodegradation of MNs 6 and 19. The insoluble MN materials were removed from the vials in which they were prepared and added to a larger vial containing fresh methylene chloride. For 2 days, the solvent was exchanged approximately every 10 h until the gel materials became colorless. After this time, the methylene chloride was removed and the MN was swollen in 90% THF:water. Excess THF:water was removed with a Pasteur pipet, and the vial containing the swollen material was capped tightly and placed in a Rayonet reactor under UV irradiation at 350 nm peak wavelength. Samples were taken at various times for SEC analysis. Complete degradation of insoluble material was observed after 25 min, but SEC analysis indicated that several days were needed for complete degradation.

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