Photo-Responsive Materials

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# Photo-controlled Growth of Telechelic Polymers and End-linked Polymer Gels**

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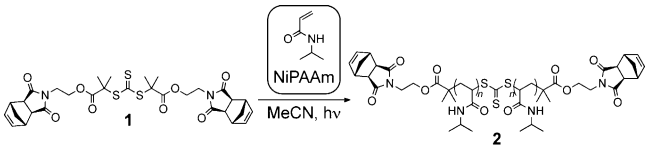
*In memoriam Nicholas J. Turro*

Photo-responsive polymeric networks (PRPNs) have broad applications as externally tunable smart materials.[1] Typical photo-response behaviors include photo-motility,[2] photo-degradation,[1a,c,3] photo-functionalization,[1b,4] photo-induced plasticity,[1d,5] and photo-induced self-healing.[6] We reasoned that if appropriately designed photo-initiators were inserted within the chains of a polymer network, then subsequent photo-controlled radical polymerization (photo-CRP) in the presence of new monomer could offer a novel "photo-growth" mechanism for triggered alteration of network pore size and composition.[7]

Since the seminal work of Otsu et al.,[8] photo-CRP reactions have garnered extensive interest thanks to their unique ability to be switched between "on" and "off" states.[9] Trithiocarbonates (TTCs) are particularly useful initiators for photo-CRP;[10] no exogenous radical initiator is required, and unlike related reversible addition fragmentation chain transfer (RAFT) polymerizations where the initiator fragment is attached to a fraction (typically 10%) of the polymer chain ends, synthesis of 100% chain-end functional polymers is possible.[11]

We designed a new bis-norbornene TTC (**1**) to serve as both a photo-CRP initiator, and as a source of reactive norbornene groups for preparation of PRPNs (Scheme 1, see Supporting Information for synthetic details).[10a,12] Compound **1** possesses a characteristic broad absorbance above 300 nm due to the TTC moiety (Figure S1). Photo-CRP of *N*-isopropylacrylamide (NiPAAm) from **1** (Scheme 1) was carried out in a degassed 8 mL reaction vial using an 8 W UV lamp with peak emission at 352 nm. Reactions were kept at room temperature using a circulating water bath.

Polymerization of NiPAAm to yield α,ω-norbornene telechelic poly(NiPAAm)(**2**) proceeded with excellent control under these conditions (Figure 1; see also Figures S2 and S3 and Tables S1 and S2 in the Supporting Information). The results from a representative reaction with a starting NiPPAm/**1** ratio of 250:1 are summarized in Figure 1 A. The




***Scheme 1.*** Bis-norbornene TTC (**1**) used for the photo-controlled radical polymerization (photo-CRP) of NiPAAm.

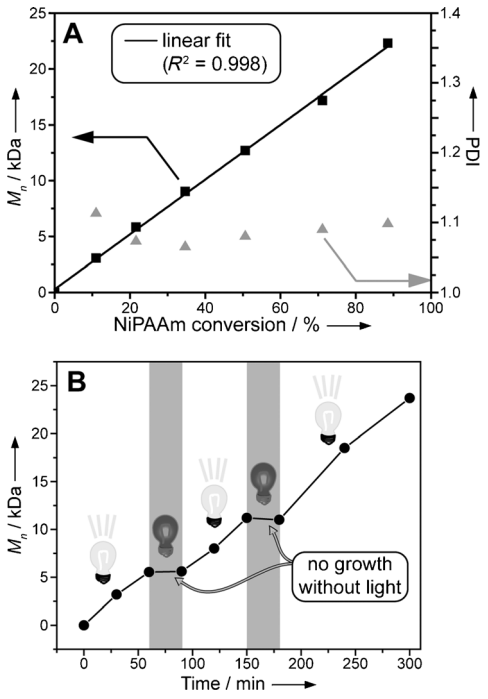



***Figure 1.*** A) Evolution of the number-average molecular weight ($M_n$) and PDI as a function of monomer conversion during the photo-CRP process. B) "On/off" plot demonstrates that polymer growth only occurs in the presence of light.

number-average molecular weight ($M_n$) increased linearly with monomer conversion while the polydispersity index (PDI) remained low (ca. 1.10) throughout the entire process. In contrast, heating **1** and NiPAAm to 80 °C in the absence of light gave no conversion after 5 h. Finally, purified samples of poly(NiPAAm) (**2**) could be used as efficient macroinitiators for chain extension in the presence of new NiPAAm and UV light (Figure S5).

In principle, polymer growth during photo-CRP can be temporally and spatially controlled.[9h,j,l,m] To demonstrate

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temporally controlled synthesis of **2**, NiPAAm and **1** were exposed to UV light for 60 min. After this time, the reaction was kept in the dark for 30 min. GPC analysis immediately after irradiation and after the 30 min dark period showed no mass change (Figure 1B). Continued irradiation of the same mixture led to renewed polymer growth. The $M_n$ versus monomer conversion displayed a linear relationship across irradiation cycles; the PDI remained close to 1.1 (Figure S4).

Based on the mechanism for photo-CRP (Scheme S1), lower light intensity should lead to a lower concentration of propagating radicals, which should in turn lead to increased polymerization control via preclusion of bimolecular radical termination processes. Representative reactions were conducted under conditions identical to the examples above, but with varied UV intensity (0.7 cm from lamp, 2 cm, and 3 cm from UV lamp rather than 1 cm). As expected, with lower intensity light the PDI could be decreased to ca. 1.04 at the expense of increased reaction time (Tables S3–S5).

The AM1.5 solar spectrum possesses a maximum at 550 nm with very little irradiation at wavelengths lower than 300 nm. We reasoned that photo-CRP from **1** could be performed via exposure to sunlight (i.e., sunlight-CRP).[13] A degassed solution of NiPPAm (2 M in MeCN) and **1** (300 equivalents of NiPAAm to **1**) was placed in a vial. The vial cap was sealed with electrical tape and placed on the roof of building #6 on the MIT campus in the mid-afternoon during July of 2012. The reaction temperatures were kept near 0 °C using an ice bath. In a representative case (data collected on July 11th, 2012, from 10 a.m. to 3 p.m., Figure 2) we found that within 5 h the polymerization reached over 70% monomer conversion to give **2** with $M_n = 16.7$ kDa and PDI of 1.09.

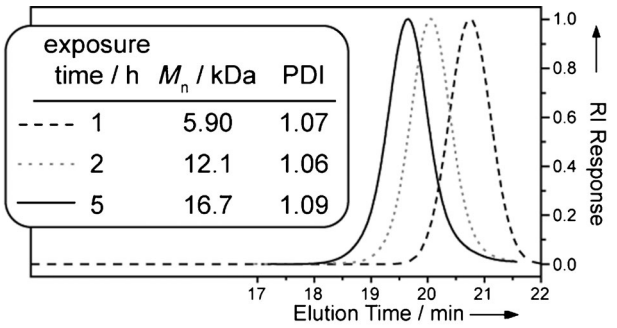



***Figure 2.*** GPC results for sunlight-CRP of NiPAAm from **1**.

$^1$H NMR spectroscopy and MALDI-TOF mass spectrometry were used to confirm the presence of norbornene groups on the chain ends of **2** prepared via sunlight-CRP. In a representative $^1$H NMR spectrum (Figure 3A), resonances that correspond to the protons from the norbornene chain ends were observed at 6.25, 4.00, 3.57, 3.04, and 2.64 ppm. The MALDI-TOF spectrum of **2** (Figure S6A) exhibits a single set of peaks whose masses agree with the calculated mass of **2** for various degrees of polymerization (DPs). These data strongly suggest that only a single telechelic polymer product is formed during the sunlight-CRP process.

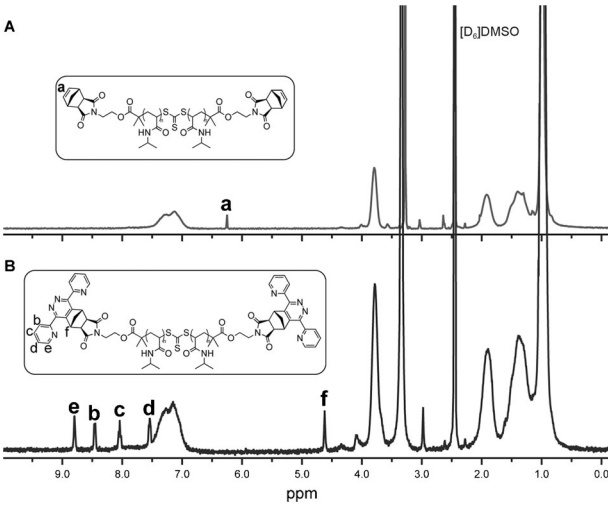


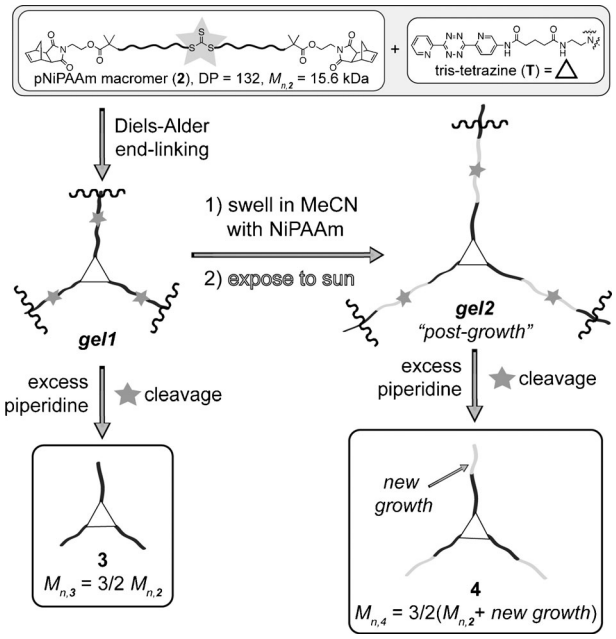

***Figure 3.*** A) $^1$H NMR of **2** in [D$_6$]DMSO (top) with key peaks labeled. B) $^1$H NMR of **2** after reaction with dipyridyl tetrazine for 5 h, oxidation with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), and purification by repeated precipitation in diethyl ether.

To demonstrate selective functionalization of the norbornene chain ends, a sample of **2** was allowed to react with excess 3,6-di-2-pyridyl-1,2,4,5-tetrazine for 8 h at room temperature in dimethyl sulfoxide (DMSO).[14] The $^1$H NMR spectrum of the resulting 3,6-di-2-pyridyl-1,2-pyridizine (DPP)-telechelic polymer obtained after oxidation and purification (Figure 3B) shows complete loss of the norbornene olefinic resonances (6.25 ppm) and the appearance of four new aromatic resonances from the DPP moieties. The MALDI-TOF MS spectrum of the DPP-telechelic polymer shows a single distribution of masses (Figure S6B); no unreacted **2** is observed.

We next sought to utilize **2** as a precursor for PRPNs that could grow in the presence of NiPAAm monomer and sunlight. End-linked polymer gels were prepared via a R-$A_2$ + R-$B_3$ Diels–Alder reaction between **2** and tris-tetrazine **T** in DMSO (**gel1**, Scheme 2). **Gel1** samples swelled extensively in fresh DMSO or MeCN without dissolution (Figure S7). The swelling ratio in DMSO—i.e., the swollen gel weight divided by the dry weight—was $28 \pm 2$.

Photo-CRP mediated insertion of new NiPAAm monomers directly into the network chains of **gel1** should lead to new materials (**gel2**, Scheme 2) with a larger molecular weight between junctions, and a corresponding increased swelling ratio. **Gel1** samples were swollen under nitrogen atmosphere for 2 d in pure MeCN (control) or a 2 M solution of NiPAAm in MeCN. After removal of excess solvent, the vials were sealed with electrical tape and exposed to natural sunlight for various times. Afterwards, the samples were brought indoors and characterized.

**Gel2** samples that were irradiated for 5 h in the presence of NiPAAm monomer possessed an average DMSO swelling ratio of $48 \pm 3$. This increased ratio compared to **gel1** could arise from two sources: 1) the desired photo-growth of new polymer (Scheme 2), or 2) introduction of defects—e.g., dangling chains and elastically inactive loops—into the networks via radical reshuffling.[6a,c] If the latter mechanism were




***Scheme 2.*** End-linking **2** with a tris-tetrazine (**T**) to give a gel network. Piperidine-mediated gel degradation yields soluble three-arm star polymers (**3** and **4**) whose masses depend on the molecular weight between crosslinks of the parent network.

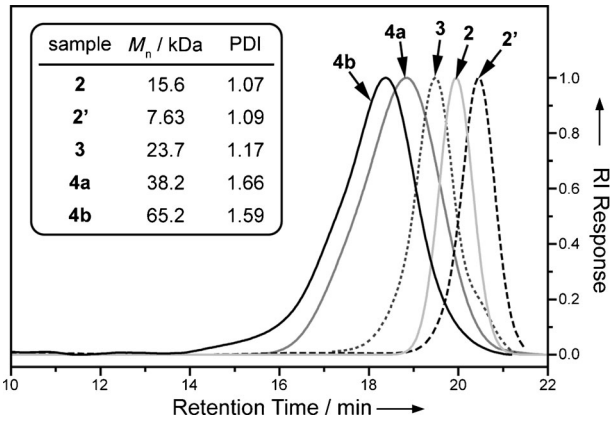



***Figure 4.*** GPC analysis of a sample of **2** (15.6 kDa), the same sample after exposure to excess piperidine (**2'**), **gel1** after exposure to excess piperidine (**3**), and two **gel2** samples after exposure to piperidine (**4a** and **4b**). As expected, the mass of sample **3** is approximately 3/2 that of **2**. Photo-growth leads to an increase in the length of network chains, which corresponds to the observed increase in mass from **3** to **4a** and **4b**.

operative under the experimental conditions, then the swelling ratio would increase *in the absence of monomer*. Control samples that were subjected to sunlight without NiPAAm possessed very similar swelling ratios before and after irradiation ($32 \pm 2$ versus $28 \pm 2$, respectively). These data suggest that under these conditions the network connectivity is not significantly altered by sunlight exposure alone;[6a] the increased swelling ratio for **gel2** most likely arises from new polymer growth.

A network disassembly experiment was designed to quantify the extent of photo-growth in **gel2** samples. Selective cleavage of the TTC groups within **gel1** should generate three-arm star polymers (**3**, Scheme 2) with $M_n$ values equal to three-halves that of the parent macromer **2**. Similar disassembly of **gel2** samples should yield star polymer products with masses equal to three-halves the sum of the mass of **2** plus the mass of new growth (**4**, Scheme 2). The extent of photo-growth can thus be quantified by TTC cleavage and GPC analysis of the soluble disassembly products. There are many established protocols for selective cleavage of TTC groups in soluble polymers.[15] After extensive screening using **1** and **2** as model compounds we found that treatment with excess piperidine for 5 h led to quantitative, selective TTC cleavage (Figure 4 and S8).

Exposure of **gel1** to piperidine yielded **3** with an average mass of 23.7 kDa (Figure 4), which agrees well with the expected mass of 23.4 kDa. Disassembly and GPC analysis of a **gel2** sample prepared after 5 h of sunlight irradiation in 2.0 M NiPAAm yielded polymer products (**4a**) with $M_n = 38.3$ kDa (Figure 4). This mass increase corresponds to insertion of approximately 86 NiPAAm units into each network chain. **Gel2** samples prepared after longer sunlight exposure time (8 h in 2.0 M NiPAAm in MeCN) yielded products (**4b**) whose masses correspond to insertion of approximately 292 NiPAAm units per TTC. In this case, a nearly three-fold chain extension was achieved without gel dissolution. The PDI values for **4a** and **4b** are increased compared to **3**, which is likely due to non-uniform TTC initiation throughout the gel. These results hint at the possibility of spatially tuning the location of gel growth, which would in turn introduce mechanical gradients throughout these materials.

Herein we report conditions for photo-CRP synthesis of norbornene-telechelic NiPAAm polymers. Gels formed by end-linking these polymers possess TTC moieties at the center of each network chain. Addition of new monomer to the gels, followed by exposure to sunlight, led to an increase in the average MW between crosslinks via direct extension of network chains. This "photo-growth" process represents a novel strategy for conversion of sunlight energy to mass in bulk materials, and opens the door to photo-controlled preparation of PRPNs with both mechanical and chemical three-dimensional composition gradients. Ongoing studies in our laboratories are aimed towards patterning regions of gel growth, studying the effect of photo-growth on network topology, use of alternative cross-linking strategies, and introduction of new monomers to pattern both pore size and pore composition.

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