

Photodegradable cross-linked polymer derived from a vinylic rotaxane cross-linker possessing aromatic disulfide axle*

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Abstract: A new concept for photodegradable cross-linked polymers utilizing characteristics of rotaxane cross-links and aromatic disulfides is proposed. The cross-linked polymer is obtained by the radical polymerization of a vinyl monomer in the presence of a [3]rotaxane-type cross-linker having two radically polymerizable groups. The [3]rotaxane-type cross-linker was prepared in 93 % yield by the typical rotaxane-forming reaction using a dumbbell-shaped aromatic disulfide possessing a bis(ammonium salt) moiety and a crown ether wheel tethered by a hydroxymethyl group (96 %) and the subsequent vinyl group-endowment (80 %). The radical polymerization of methyl methacrylate (MMA) in the presence of the cross-linker (0.1 mol %) at 60 °C afforded solvent-insoluble polymer in 90 % yield. When the polymer was swollen to a gel in dimethylformamide (DMF) and a small part of the gel was UV-irradiated, the gel was promptly solubilized, probably via the photochemical scission of the S–S linkage of the interlocked aromatic disulfide, causing the efficient decomposition of the rotaxane cross-links. The recovered poly(methyl methacrylate) bearing a small amount of crown ether moiety has a molecular weight of M_n 170 kg/mol (M_w/M_n 2.1) that indicated the occurrence of the site-selective photodegradation.

Keywords: polymer chemistry; rotaxanes; supramolecular chemistry.

INTRODUCTION

Stimuli-responsive smart materials have collected considerable attention to not only the progress of fundamental chemistry but also development of advanced and sophisticated materials such as actuators [1–10]. Photodegradable gels are one family of these smart materials, mainly directed toward intelligent devices based on sol–gel transitions [11–13], drug delivery systems exploiting photocontrolled substrate release [14], photorheological fluids [15,16], photodriven dynamic pattern formation [17,18], and so on [19–22]. Most of the photodegradable systems are based on the cleavage of weak noncovalent bonds such as hydrogen bonds, π – π interactions, and hydrophobic interactions, accompanying the photoresponsive structural change of the key structure. Therefore, the properties of the gels are attributed to the inclusion of the noncovalent bonds, leading to chemical and thermal instability of the gel. In addition, soaking the gel in excess good solvent over the gel point causes the decomposition of the gel.

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Recognizing such backgrounds, we envisaged that photoreactive aromatic disulfide linkages would serve as crucial cross-linking bonds yielding chemically stable covalently cross-linked polymers equipped with photodegradable properties, although the aromatic disulfide linkages would not be employed without limitations. The main problem is the very short life-time of aromatic thiyl radical generated by photoinduced homolysis of aromatic disulfide [23]. The thiyl radical as a side-chain group recombines with other thiyl radicals to disturb the effective photo-decross-linkings. To overcome this problem, we noticed the usefulness of interlocked structures such as rotaxanes used at the cross-linking structure. Namely, if the cross-linked polymer containing aromatic disulfide moieties as the axle components of its rotaxane cross-links are successfully prepared using [3]rotaxane cross-linker as shown in Fig. 1, the photochemical homolytic cleavage of the disulfide linkage results in the effective decross-linking to give a soluble polymer via the deslippage of the axle from the wheel, because the recombination between the deslipped thiyl radicals no longer results in the cross-linking but in the formation of non-interlocked disulfide. This photo-decross-linking system features no injury to the trunk polymer upon decross-linking because the photochemical event occurs only at the axle component.

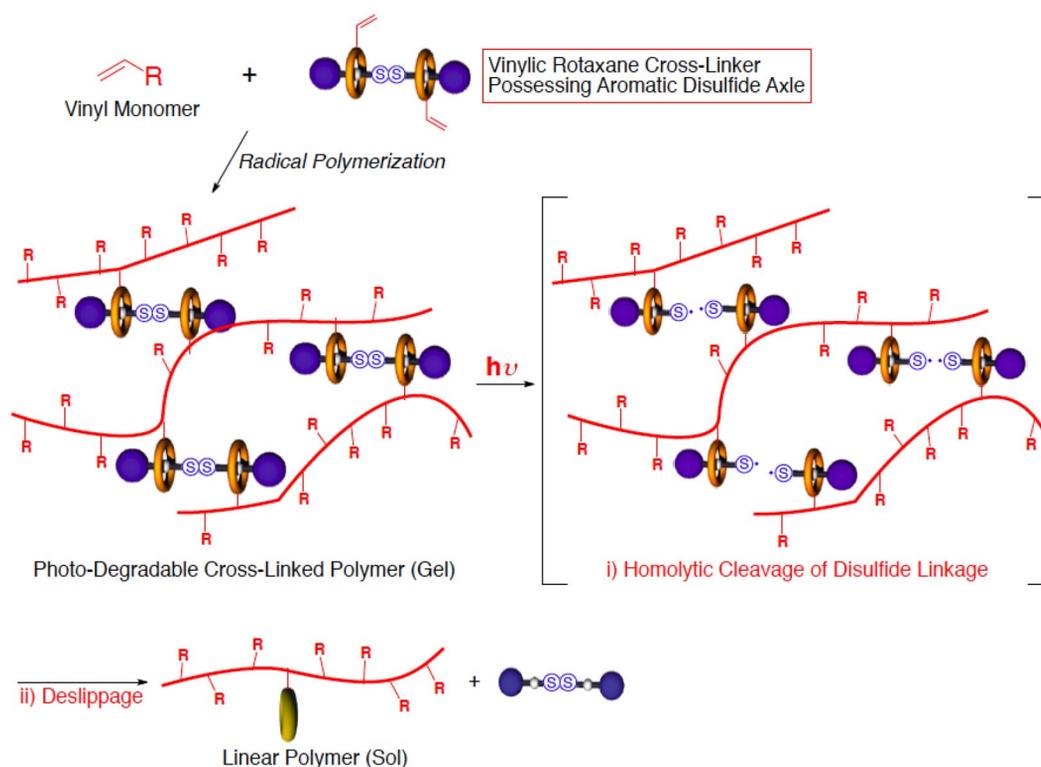


Fig. 1 Synthesis of cross-linked polymer having rotaxane cross-links using [3]rotaxane cross-linker and photodegradation of the cross-linked polymer by photoirradiation through the decomposition of rotaxane-cross-links via the photocleavage of disulfide linkage.

Herein, we describe the synthesis of a [3]rotaxane-type cross-linker consisting of a photoreactive aromatic disulfide axle and the construction of a photodegradable cross-linked polymer by radical polymerization of a vinyl monomer exploiting the [3]rotaxane cross-linker. It turned out that the rotaxane-cross-linked polymer swollen in dimethylformamide (DMF) was photoresponsive enough to change to DMF-soluble polymer by a direct photoirradiation through the efficient decomposition of the rotaxane cross-links.

EXPERIMENTAL

General methods

Dumbbell-shaped bis(ammonium salt) **1** possessing an aromatic disulfide was prepared according to the previously reported method [24]. Hydroxymethyldibenzo-24-crown-8-ether **2** was prepared according to the literature [25]. Karenz MOI[®] **4** was given by Showa Denko K.K. Other reagents and solvents were commercially available and used without further purification.

¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a JEOL AL-400 spectrometer using CDCl₃ as the solvent, calibrated using tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. FAB HRMS spectra were obtained at the Center for Advanced Materials Analysis, Tokyo Institute of Technology on request. The UV irradiation was carried out on a mercury-xenon lamp MAX-302 (Asahi spectra). SEC analyses were carried out on a JASCO PU-2080 plus pump with a JASCO UV-1570 (UV detector) and a JASCO RI-1530 (RI detector) equipped with consecutive linear polystyrene gel columns TOSO TSK gel GMHXL and G5000HXL at 30 °C. Thermogravimetric analysis (TGA) was carried out on a Shimadzu TGA-50 instrument at N₂ atmosphere (flow rate of 50 mL/min) to determine 10 % weight decomposition temperature (*T*_{d10}) at which 10 % weight loss was observed. Differential scanning calorimetry (DSC) analyses were carried out with a Shimadzu DSC-60 instrument at N₂ atmosphere (flow rate of 50 mL/min) to determine glass transition temperature (*T*_g). Preparative gel permeation chromatography (GPC) was carried out using an HPLC LC-918 instrument by Japan Analysis Industry, Co. Ltd. with a Megapak-Gel 201CP (Guard Column), a Megapak-Gel 201C, and a JAIGEL-H.

Synthesis of [3]rotaxane **3**

To a solution of dumbbell-shaped bis(ammonium salt) possessing an aromatic disulfide **1** (402 mg, 0.413 mmol) and hydroxymethyldibenzo-24-crown-8-ether **2** (593 mg, 1.24 mmol) in a mixed solvent of CHCl₃–CH₃CN (7:3, 4.1 mL) was added benzenethiol (4.3 μL, 0.040 mmol) at room temperature. The mixture was warmed to 50 °C and stirred for 20 h and concentrated in vacuo. The resulting material was purified by preparative GPC to give the corresponding [3]rotaxane **4** (760 mg, 0.394 mmol) in 96 % yield as a pale yellow solid; m.p. 127.4–128.1 °C; ¹H NMR (400 MHz, 298 K, CDCl₃) δ 7.60 (br, 4H), 7.36 (s, 2H), 7.29 (s, 4H), 7.10 (t, *J* = 2.6 Hz, 8H), 6.84–6.52 (m, 14H), 4.71 (br, 4H), 4.53 (br, 8H), 4.14–4.04 (m, 8H), 3.71–3.62 (m, 8H), 3.50–3.35 (m, 8H), 1.19 (s, 36H) ppm; ¹³C NMR (100 MHz, 298 K, CDCl₃) δ 151.5, 147.4, 146.9, 146.2, 137.7, 134.7, 131.4, 130.1, 127.6, 123.5, 123.1, 121.5, 119.9, 112.5, 111.9, 111.8, 111.3, 70.6, 70.5, 70.2, 70.0, 67.7, 64.7, 52.9, 52.1, 34.8, 31.3 ppm; IR (NaCl) ν 3435, 2923, 1644, 1505, 1455, 1362, 1253, 1125, 1057, 913, 843, 744 cm⁻¹; FAB HRMS (matrix: NBA) [M–HPF₆–PF₆⁻] calc'd. for C₉₄H₁₂₉N₂O₁₈S₂, 1637.8682; found 1637.8781.

Synthesis of [3]rotaxane cross-linker **5**

To a solution of [3]rotaxane **3** (96.4 mg, 0.050 mmol) in CH₂Cl₂ (1.0 mL) was added Karenz MOI[®] **4** (56.0 μL, 0.40 mmol) and dibutyltindilaurate (DBTDL, 3.0 μL, 5.0 μmol) at 0 °C. The mixture was warmed to room temperature and stirred for 5 h. To the mixture was added Karenz MOI[®] **4** (56.0 μL, 0.40 mmol). The resulting mixture was stirred for 3 h, diluted with CH₂Cl₂, washed with sat. aq. NaHCO₃, dried over MgSO₄, filtered, and concentrated in vacuo. The resulting material was purified by preparative GPC to give the corresponding [3]rotaxane cross-linker **5** (90 mg, 0.040 mmol) in 80 % yield as a colorless solid; m.p. 101.0–102.5 °C; ¹H NMR (400 MHz, 298 K, CDCl₃) δ 7.59 (br, 4H), 7.34 (s, 2H), 7.26 (s, 4H), 7.12 (q, *J* = 8.7 Hz, 8H), 6.82–6.58 (m, 14H), 6.11 (s, 2H), 5.56 (s, 2H), 5.39 (t, *J* = 5.7 Hz, 1.5H), 4.97 (s, 4H), 4.72 (s, 4H), 4.52 (t, *J* = 5.7 Hz, 4H), 4.22 (t, *J* = 5.7 Hz, 4H), 4.14–3.90 (m, 16H), 3.89–3.40 (m, 32H), 3.52 (t, *J* = 5.7 Hz, 4H), 1.92 (s, 6H), 1.18 (s, 36H) ppm;

^{13}C NMR (100 MHz, 298 K, CDCl_3) δ 156.5, 151.4, 147.3, 147.2, 146.9, 137.9, 136.0, 135.1, 134.9, 131.4, 130.1, 129.9, 127.6, 126.0, 123.5, 123.1, 121.6, 121.1, 112.5, 112.3, 112.0, 70.6, 70.5, 70.1, 70.0, 67.9, 67.7, 66.2, 63.7, 52.9, 52.1, 40.1, 34.8, 31.3, 18.3 ppm; IR (NaCl) ν 3431, 2958, 2360, 2341, 2273, 1719, 1637, 1518, 1507, 1455, 1358, 1320, 1297, 1253, 1167, 1126, 1106, 1058, 949, 844, 749 cm^{-1} ; FAB HRMS (matrix: NBA) $[\text{M}-\text{PF}_6^-]$ calc'd. for $\text{C}_{108}\text{H}_{148}\text{F}_6\text{N}_4\text{O}_{24}\text{PS}_2$, 2093.9567: found 2093.9577.

Typical procedure for the synthesis of photodegradable network polymer 6

To [3]rotaxane cross-linker **5** (22.4 mg, 10 μmol) prepared as above was added azobisisobutyronitrile (AIBN) (16.4 mg, 0.10 mmol), methyl methacrylate (MMA) (1.07 mL, 10 mmol), and DMF (0.5 mL). The mixture was degassed via the freeze thaw technique repeatedly, replaced to a polypropylene sealed tube, and then warmed at 60 $^\circ\text{C}$ for 19 h to yield a solvent-insoluble gelled material. The gel was purified by swelling in DMF, MeOH, and CH_2Cl_2 to remove unreacted materials, and gently dried at room temperature for 1 d and in vacuo for 1 d to afford the corresponding network polymer **6** having interlocked disulfide bonds at the cross-linking points in 90 % yield; no T_g was observed; T_{d10} 329 $^\circ\text{C}$; IR (NaCl) ν 3617, 3446, 2925, 2848, 1737, 1482, 1396, 1255, 1146, 986, 751 cm^{-1} .

Typical procedure for the photodegradation of 6

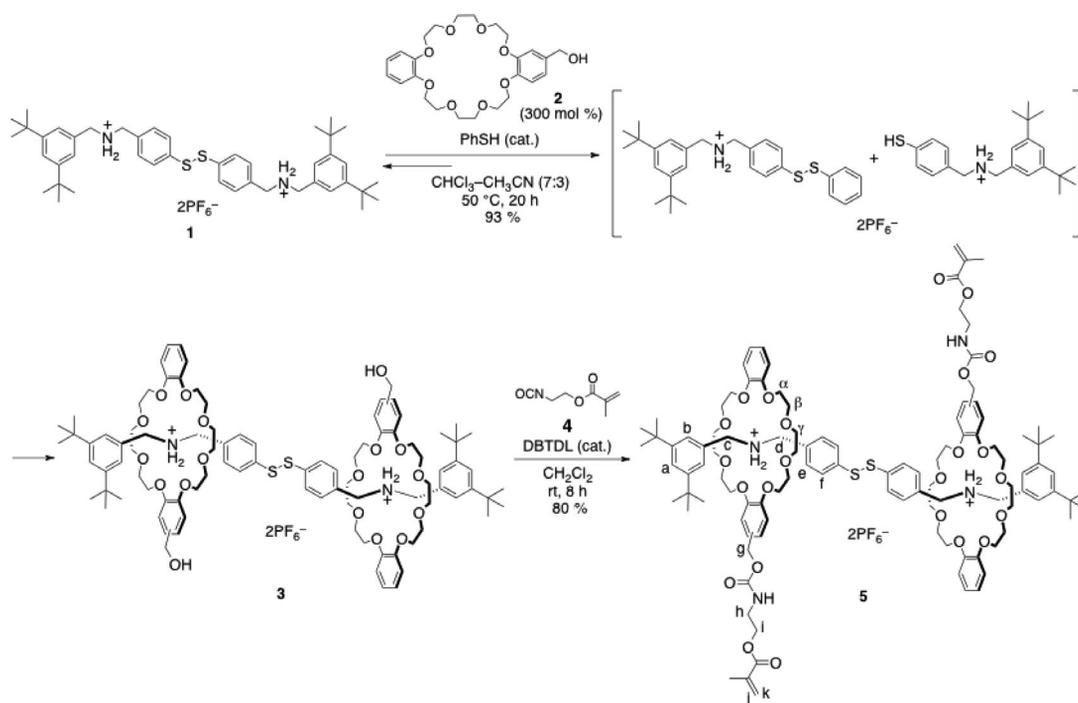
The obtained network polymer **6** was soaked in DMF at room temperature for 2 d to give the swollen organo-gel. The gel was UV-irradiated at room temperature for 30 min to result in a degradation of the gel. The sol part was precipitated in MeOH to give a white solid, which was collected by filtration and dried in vacuo for 1 d to give the PMMA trunk polymer; M_n 170 kDa; M_w/M_n 2.1; T_g 124.9 $^\circ\text{C}$; T_{d10} 323 $^\circ\text{C}$; IR (NaCl) ν 3002, 2953, 1732, 1480, 1445, 1390, 1244, 1185, 1148, 989, 842, 752 cm^{-1} .

RESULTS AND DISCUSSION

Synthesis of [3]rotaxane cross-linker 5. Scheme 1 shows the synthetic route for [3]rotaxane cross-linker **5** having two polymerizable groups that is applicable to vinyl polymerization to a network polymer having interlocked cross-links consisting of an aromatic disulfide axle.

Dumbbell-shaped bis(ammonium salt) possessing an aromatic disulfide linkage (**1**) [24] and hydroxymethyl group-substituted dibenzo-24-crown-8-ether **2** [25] were prepared according to the literature. Building upon our previous work [26–31], a catalyst (benzenethiol, 10 mol %) for a reversible exchange reaction of thiol–disulfide was added to the mixture of **1** and **2** in CHCl_3 – CH_3CN (7:3). The mixture was stirred at 50 $^\circ\text{C}$ for 19 h. The purification of the product was carried out by preparative GPC to yield [3]rotaxane **3** in 93 % yield. Urethane-forming functionalization of **3** with Karenz MOI **4** proceeded smoothly to afford the corresponding [3]rotaxane cross-linker **5** with methacrylate groups on each crown ether wheel, ready for radical polymerization. The structure of the rotaxane was determined by ^1H NMR (Fig 2), ^{13}C NMR, IR, and HRMS spectra.

Figure 2 shows the ^1H NMR spectra of the axle **1**, the wheel **2**, and [3]rotaxane **5**. In spectrum (C), the characteristic signals (c and d) of benzylic protons of the axle component of **5** appeared as broad peaks due to the geminal coupling, strongly supporting the interlocked structure formation in good accordance with the literature [32–34]. The signals originating from the olefinic protons and the good agreement of the observed HRMS with the theoretical value afforded direct evidence for the introduction of the methacrylate moieties.



Scheme 1 Synthesis of [3]rotaxane cross-linker **5**.

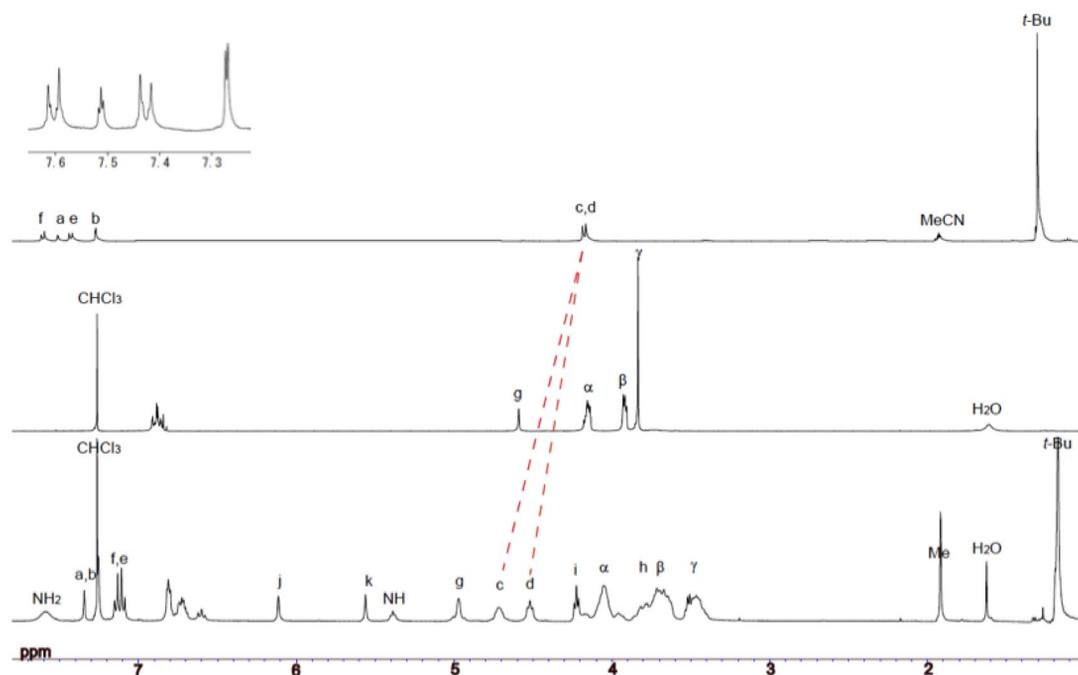
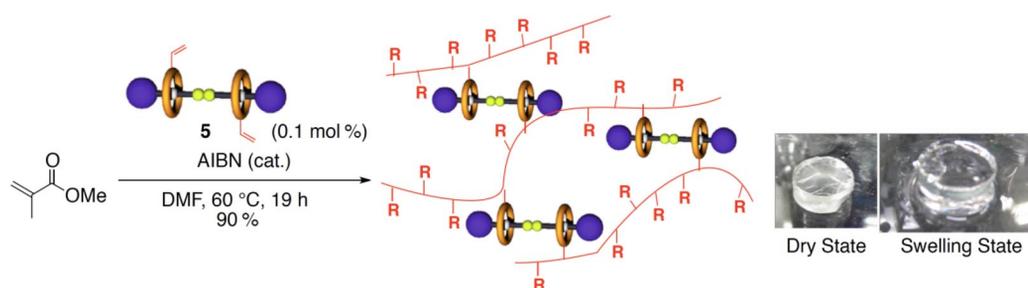


Fig. 2 ^1H NMR spectra (400 MHz, 298 K) of (A) **1** (in CD_3CN), (B) **2** (in CDCl_3), and (C) **5** (in CDCl_3).

Synthesis of cross-linked poly(methyl methacrylate) 6 using 5. [3]Rotaxane cross-linker **5** was employed as a cross-linker in the radical polymerization of MMA (Scheme 2). A mixture of MMA (1.07 mL), **5** (0.1 mol %), and AIBN (1.0 mol %) was heated at 60 °C for 19 h to afford a gelled product. The gel was purified by swelling in DMF, MeOH, and CH₂Cl₂ to remove unreacted materials, and gently dried at room temperature for 1 d and in vacuo for 1 d to yield the cross-linked polymer **6** in 90 % yield. The polymer had its decomposition temperature at 329 °C (T_{d10}), but no glass transition temperature, T_g . The IR spectrum showed a strong absorption around 1730 cm⁻¹ characteristic of the C=O bond of PMMA. Although no apparent signal based on the cross-linker was found, the solvent-insolubility and swellability clearly indicated the cross-linked structure of **6**. To evaluate the chemical stability, **6** was soaked in excess DMF for 1 d to give the swollen organo gel. It is noted that the swollen gel kept its shape in DMF after an additional 1 d without any degradation, being a good contrast to the instability of noncovalently cross-linked polymers in good solvent [13].

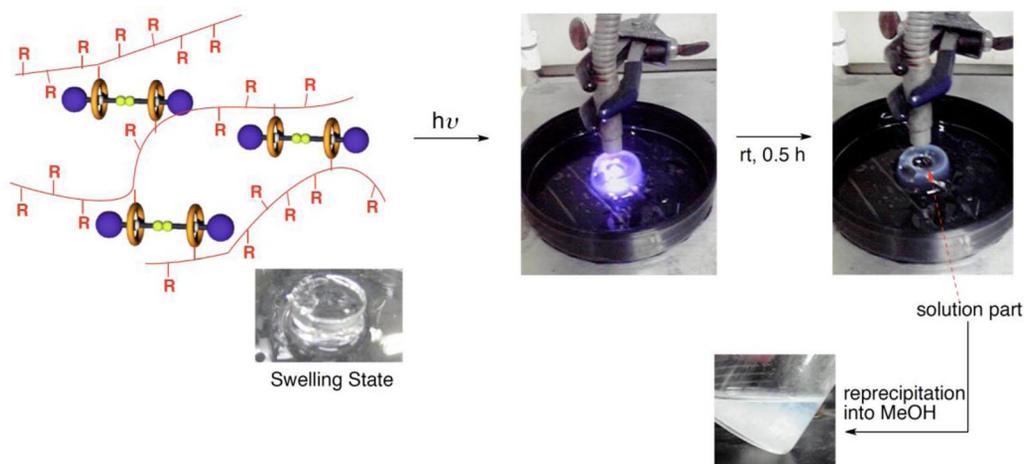


Scheme 2 Synthesis and photographs of cross-linked polymer **6** prepared by the radical polymerization in the presence of the rotaxane cross-linker **5**.

Photodegradation of cross-linked PMMA 6. Having the swollen gel **6** in DMF in hand, we next investigated the photodegradation behavior (Scheme 3). The UV-irradiation of the gel at room temperature caused the rapid and selective degradation of **6**. Namely, the solubilization of the gel took place only at the irradiated part within 30 min, implying the occurrence of the photoresponsive decross-linking. This is probably due to the homolysis of S–S linkage of the aromatic disulfide of the rotaxane moiety and subsequent deslippage of the axle component from the wheel leading to the decomposition of the network structure of **6**. The dethreading of the axle component that was stabilized by the intramolecular hydrogen bonding in DMF as a highly polar solvent is well consistent with the previously reported results concerning the solvent polarity-dependent complex formation of *sec*-ammonium/crown ether-type rotaxane [35]. Thermal degradation of **6** is ruled out because of its stability mentioned above.

The photoirradiated part became completely soluble in DMF, clearly indicating that the removal of the cross-linking points was efficient. The DMF-soluble product was precipitated in MeOH, and the white precipitate was collected by filtration. The resulting product soluble in various organic solvents such as CHCl₃ was subjected to structural analyses. SEC analysis clearly revealed the formation of polymer whose molecular weight was M_n 170 kDa (M_w/M_n 2.1, based on polystyrene standards). The ¹H NMR spectrum of the polymer indicates that the polymer is mainly composed of PMMA structure.

Thus, the site-selective photochemical decomposition of cross-linked polymer using photodissociation capability of an aromatic disulfide linkage that is incorporated into the cross-linker was achieved.



Scheme 3 Photodegradation of **6** swollen in DMF at room temperature. The irradiated part became homogeneous and was precipitated into MeOH.

CONCLUSION

In this work, we have disclosed a general protocol for a photodegradable cross-linked polymer system. The key material is the [3]rotaxane-type cross-linker that has two vinyl groups for radical polymerization on the two wheels and one photoactive aromatic disulfide linkage in the center of the axle. Since the polymer is covalently cross-linked by the rotaxane cross-linking points, the cross-linked polymer is stable unlike supramolecularly cross-linked ones, unless the photoirradiation is carried out. From the cross-linked PMMA **6** obtained from MMA and [3]rotaxane cross-linker **5**, soluble PMMA containing a small part of the crown ether moiety was collected via the site-selective degradation by the photoirradiation to DMF-swollen gel of **6**. The present protocol provides a concept for photodegradable polymers that is applicable to many vinyl monomers. The high efficiency of the decross-linking suggests the potential usefulness of this protocol capable of opening broad applications to versatile photoresponsive smart materials. The development of photoresist materials and drug delivery systems exploiting this system will be important future work.

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