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Responsive Gels Based on a Dynamic Covalent Trithiocarbonate Cross-Linker

Renaud Nicolaÿ,[†] Jun Kamada,[†,‡] Abigail Van Wassen,[†] and Krzysztof Matyjaszewski*,[†]

[†] *Center for Macromolecular Engineering, Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, and* [‡] *Material Science Laboratory, Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan*

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ABSTRACT: Dimethacrylate trithiocarbonate was synthesized and used as a dynamic covalent cross-linker to prepare PMMA and PSt gels via radical polymerization. The swelling properties of the PMMA gels were studied and showed that in the presence of radicals the gels reorganize to accommodate forces generated by the swelling processes. This reshuffling of the cross-link network yields an increase in the swelling ratio (up to 300% increase) of the PMMA gels. Two different radical generators, a thermal initiator and a Cu^I/L complex, were successfully used to trigger the reorganization of the gels. To illustrate the broad utility of the procedure, three discrete pieces of gels were fused into one single piece to demonstrate that dynamic covalent cross-linkers can be used to prepare materials that can be reprocessed and/or undergo self-repair.

Introduction

Dynamic covalent chemistry relates to chemical reactions carried out reversibly under conditions of equilibrium control.[1] The reversible nature of the reactions introduces the prospects of "error checking" and "proof-reading" into synthetic processes where dynamic covalent chemistry can operate. Since the formation of products occurs under thermodynamic control, product distributions depend only on the relative stabilities of the final products. In kinetically controlled reactions, it is the differences in free energy between the transition states leading to the products that determine the relative proportions of the individual products.

Therefore, dynamic covalent chemistry provides an opportunity to readjust the product distribution of a reaction, even after the initial products have been formed, by changing one or more of the reaction parameters (e.g., concentration, temperature, and presence or absence of a template).[2] This characteristic of dynamic covalent chemistry has led to interesting discoveries in polymer chemistry.

For example, the formation of reversible covalent bonds is the foundation of all controlled radical polymerization processes. Indeed, the dynamic equilibrium between dormant and active species, which is central to every controlled radical polymerization (CRP) techniques, is obtained via dynamic covalent bonds; namely the alkyl-halogen or alkyl-pseudohalogen bond in atom transfer radical polymerization (ATRP),[3−8] the alkoxyamine bond in nitroxide-mediated polymerization (NMP),[9−12] and the alkyl-sulfur bond of dithioester, trithiocarbonate, dithiocarbamate, and xanthate chain transfer agents (CTAs), in reversible addition−fragmentation chain transfer (RAFT) polymerization.[13−17]

Dynamic covalent polymers exhibit features originating from the reversibility of the dynamic covalent bonds. Unlike conventional polymers that are irreversibly formed, dynamic covalent polymers can adjust their structure and reorganize at the molecular level under appropriate conditions, even after polymerization.[2] The two dynamic covalent bonds, which have been exploited to the greatest degree in the preparation of polymers or gels that exhibit specific responsive properties, are C=N bonds in imine derivatives[18−26] and C−O bonds in alkoxyamine moieties.[27−35] It was recently reported that the use of an alkoxyamine based cross-linker allowed preparation of polymer gels capable of undergoing reorganization.[35] Polymer networks prepared with this cross-linker can be degraded or "decrosslinked" by heating the polymer network with an excess of a low molar mass alkoxyamine. In addition, the mesh size of the polymer network could be extended by heating the gels at high temperature (100 °C) in the presence of styrene (St). Such dynamic chemical gel systems have the advantage of providing a stable network structure in the absence of external stimuli, whereas one can change the network structure under certain conditions in a similar manner to physical gel systems. On the other hand, the use of alkoxyamine-containing cross-linker, and in particular TEMPO based alkoxyamines, implies that high temperatures (typically ≥ 100 °C) must be used to allow the dynamic exchange to occur and, furthermore, limits the monomers capable of insertion in the network to styrenic monomers.

A covalently cross-linked network that is able to undergo photomediated reversible cleavage of its backbone was recently reported. The reversible cleavage of the backbone allows chain rearrangement and rapid stress relief at ambient conditions without mechanical property degradation.[36] The key to this reversible backbone cleavage is an addition−fragmentation chain transfer reaction. The diffusion of radicals through the cross-linked matrix initially occurs by reaction of a radical with a chain transfer moiety present within the polymer network. The intermediate formed in this initial reaction in turn fragments and reforms the initial functionality and a new radical (Scheme 1). This addition−fragmentation process alters the topology of the network, but the polymer chemistry and overall network connectivity remain unchanged. In the absence of radical termination events or other side reactions, the number of allyl sulfide groups, and hence network strands, remains unchanged, although relaxation of the stress in each bond is facilitated by the alternating cleavage and reformation reactions (Scheme 1).

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*Corresponding author: Tel +1-412-268-3209; e-mail km3b@andrew.cmu.edu.

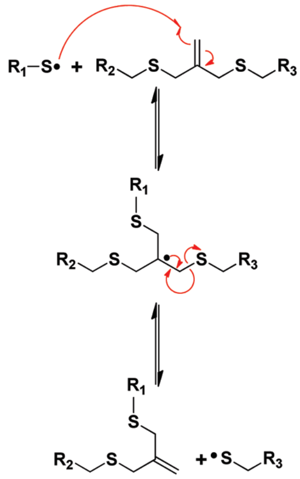
It was demonstrated that under photoirradiation (320 to 500 nm, 30 mW/cm^2) the photoinitiators present in the network produce radicals that diffuse throughout the network via addition−fragmentation chain transfer reaction with the allyl sulfide functionalities. As a result, the polymer backbone is repeatedly cleaved, stress is alleviated, and the backbone is reformed in a less stressed conformation.[36]

In the present work, we introduce a new approach to prepare dynamic covalent polymer networks. This approach relies on the use of a dimethacrylate cross-linker containing a trithiocarbonate (TTC) moiety, **3** (Scheme 2). The swelling properties of poly(methyl methacrylate) (PMMA) gels prepared with **3** were studied and exhibited an improved swelling ratio compared to "conventional" covalent gels, presumably due to the reshuffling of the gels. The influence of the type of cross-linker (permanent, dynamic covalent, or a mixture thereof), the cross-link density and the specific stimulus catalyzing the reorganization of the gels were evaluated. To exemplify that dynamic covalent cross-linkers might be used to prepare materials that can self-heal and/or be repaired, three discrete pieces of gel prepared with **3** as a dynamic cross-linker were fused into one-single piece.

Experimental Section

Materials. Methyl methacrylate (MMA, 99%), styrene (St, 99%) and 2-hydroxyethyl methacrylate (HEMA, 97%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove inhibitors or antioxidants. Tetrahydrofuran (THF) was distilled under N_2 from sodium benzophenone. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) purchased from Aldrich was recrystallized from methanol and stored in a refrigerator prior to use. S,S′-Bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate was synthesized according to a procedure previously reported in the literature.[37] All other reagents, including copper bromide, diethyl azodicarboxylate (DEAD) solution 40 wt % in toluene, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), triphenylphosphine, and solvents were purchased from Aldrich with the highest purity available and used as received without further purification.

Scheme 1. Reaction Mechanism for Chain Transfer to Allyl Sulfide



Analyses. NMR spectra were recorded on a Bruker instrument operating at 300 MHz.

Synthesis of Trithiocarbonate Cross-Linker, 3. A 100 mL three-necked round bottomed flask was equipped with a stirring bar, nitrogen inlet, dropping funnel, and thermometer. The flask was charged with S,S′-bis(α,α′-dimethyl-α″-acetic acid)-trithiocarbonate (12.3 g, 43.6 mmol) and triphenylphosphine (39.4 g, 150 mmol) and subsequently deoxygenated by purging with nitrogen for 30 min. 2-Hydroxyethyl methacrylate (18.8 mL, 155 mmol) and anhydrous tetrahydrofuran (240 mL) were added. The flask was immersed in an ice bath, and a solution of diethyl azodicarboxylate (26.1 g, 150 mmol) in 45 mL of toluene was added dropwise at a rate that allowed the temperature of the reaction mixture to be maintained below 10 °C. Upon completion of the addition, the flask was removed from the ice bath and the solution was allowed to stir at room temperature overnight (16 h) and subsequently at 40 °C for 3 h. The reaction mixture was cooled to room temperature, diluted with 1 L of dichloromethane, and washed twice with 200 mL portions of saturated aqueous sodium bicarbonate solution. The aqueous layers were combined and back-extracted with 100 mL of dichloromethane. The combined organic layers were dried over magnesium sulfate then concentrated under vacuum. The product was purified by flash column chromatography (eluent: hexanes/dichloromethane 8:2 gradually increasing to dichloromethane/ethyl acetate 7/3) to afford 15.4 g (yield = 69.6%) as an orange/yellow oil. ^{1}H NMR ($CDCl_3$) δ: 6.17−6.07 (m, 2H), 5.62−5.54 (m, 2H), 4.33 (s, 8H), 1.97−1.90 (m, 6H), 1.64 (s, 12H). ^{13}C NMR ($CDCl_3$) δ: 218.57, 172.49, 167.04, 136.00, 126.11, 63.57, 62.15, 56.15, 25.14, 18.32.

General Procedure for the Synthesis of PMMA Gels. In a typical experiment, the cross-linker **3** (568 mg, 1.12 mmol), AIBN (129 mg, 0.785 mmol), and anisole (3 mL) were charged to a flask and bubbled with N_2 for 30 min. MMA (6 mL, 56.1 mmol) was added and the flask was placed in an oil bath thermostatted at 65 °C for 24 h. All remaining volatile compounds were subsequently removed under vacuum.

General Procedure for Swelling Experiments with the PMMA Gels in the Presence of AIBN. In a typical experiment, 3 pieces of PMMA gel (76.9 mg, 14.0×10^{-3} mmol of trithiocarbonate functions) and anisole (15.3 g) were placed in a flask. The gels were allowed to swell for at least 6 h at RT. AIBN (1.15 mg, 6.97×10^{-3} mmol) was added to the flask and the solution was bubbled with nitrogen for 30 min. The flask was then placed in an oven thermostatted at 60 °C for the desired amount of time.

General Procedure for Swelling Experiments with the PMMA Gels in the Presence of CuBr/PMDETA. In a typical experiment, 3 pieces of PMMA gel (68.2 mg, 12.4×10^{-3} mmol of trithiocarbonate functions) and anisole (13.6 g) were added to a flask. The gels were allowed to swell for at least 6 h at RT. The solution was bubbled with nitrogen for 30 min and a solution of a CuBr/PMDETA complex (12.4×10^{-3} mmol) in 73 μL of deoxygenated anisole was added. The flask was then placed in an oven thermostatted at 60 °C for the desired amount of time.

General Procedure for the Mending Experiments. In a typical experiment, 3 pieces of PMMA gel (607 mg, 110×10^{-3} mmol trithiocarbonate functions) and anisole (1 mL) were inserted

Scheme 2. Synthesis of the Trithiocarbonate Crosslinker, 3

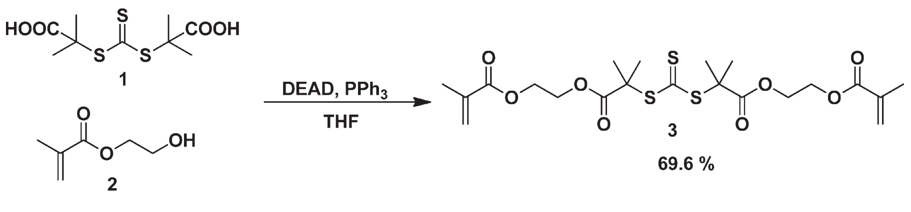
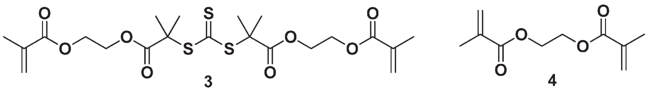


Table 1. Synthesis of PMMA Gels Using a TTC Cross-Linker[a]

entry	MMA/**3**/EGDMA/AIBN
1	10/1/0/0.7
2	10/0.8/0.2/0.7
3	10/0.5/0.5/0.7
4	50/1/0/0.7
5	200/1/0/0.7

[a] Experimental conditions: entries 1−3, MMA/anisole = 2/1 v/v, 60 °C, 24 h; entries 4−5, MMA/anisole = 2/1 v/v, 65 °C, 24 h.

Scheme 3. Dynamic Covalent Trithiocarbonate Crosslinker, 3, and Permanent Crosslinker, EGDMA, 4



into a sealed vial. The gels were allowed to swell for 1 h at RT while the flask was deoxygenated by bubbling nitrogen through the reaction medium. A quantity (1.26 mL) of deoxygenated St (11 mmol) was added to the flask followed by a solution of CuBr (15.8 mg, 110 × 10^{-3} mmol) and PMDETA (23 × 10^{-3} mL, 110 × 10^{-3} mmol) in 0.25 mL of deoxygenated anisole. The vial was placed in an oven thermostatted at 60 °C for 4 h. The resulting gel was then placed in a vacuum oven (50 °C) to remove all volatile compounds. The gel appeared to have fused into one single piece when examined in the dry state. The dry gel was then swollen for 6 h in THF to check if the three pieces were really fused together. The gel remained as one single piece, even in the swollen state.

Results and Discussion

Synthesis of the Trithiocarbonate Cross-linker, 3. The TTC cross-linker, **3**, was prepared in one step with a yield of 69.6%, via a Mitsunobu reaction between S,S′-bis(isobutyric acid)-trithiocarbonate,[37] **1**, and 2-hydroxyethyl methacrylate (HEMA), **2** (Scheme 2).

Synthesis of PMMA Gels with the Trithiocarbonate Cross-linker, 3. It has been shown that CTAs based on S,S′-bis(isobutyric acid)-trithiocarbonate, **1**, are inefficient chain transfer agents for the RAFT polymerization of MMA. The polymerization of methyl methacrylate under RAFT conditions with such CTAs present the characteristic features of a conventional free radical process.[37,38]

PMMA gels were prepared using a combination of the TTC cross-linker **3** and a permanent cross-linker, namely ethylene glycol dimethacrylate (EGDMA), **4** (entries 1, 2, and 3 in Table 1). A constant ratio MMA/**3**+EGDMA/AIBN of 10/1/0.7 was used in these experiments, and only the ratio **3**/EGDMA was modified (Scheme 3).

To study the influence of the concentration of dynamic covalent bonds on the swelling properties of gels, PMMA gels were also prepared using three different ratios of MMA/TTC cross-linker (10, 50 and 200; entries 1, 4, and 5 in Table 1, respectively). In our system, the trithiocarbonate moiety links polymer chains through a long spacer (17 atoms), which can facilitate high conversion of methacrylate cross-linker. If unreacted pendant vinyl groups still exist in the gels, they can react with carbon radicals during the following reshuffling process. This would increase the overall cross-linking density and should decrease the swelling properties of the gels.

The swelling properties of these gels were subsequently measured in anisole.

Swelling Properties of PMMA Gels: Determining the Effect of the Nature of the Cross-Linker. Neutral polymer gels are able to swell in low-polarity solvents, such as anisole, because the increase in entropy associated with polymer solvation can stretch the polymer chains between cross-linking points despite their restorative forces. In other words, the swelling is caused by the imbalance between the repulsive forces among the polymer chains and the contractile forces due to stretching of elastically active networked structures.[39]

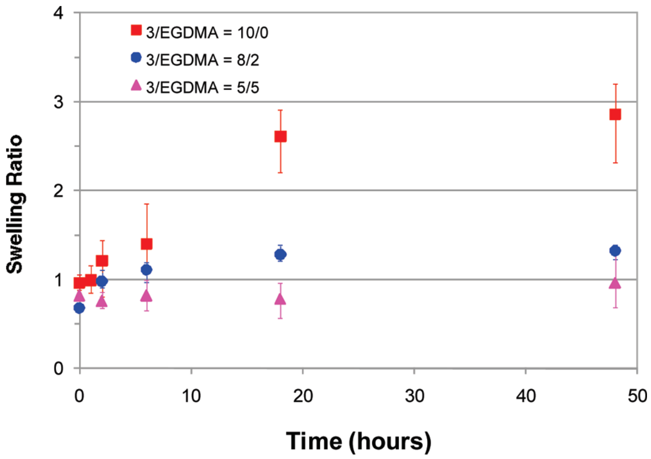


Figure 1. Effect of the ratio TTC cross-linker/permanent cross-linker on the swelling ratio of PMMA gels prepared using a ratio MMA/**3**+EGDMA/AIBN = 10/1/0.7. Swelling test conditions: $[\mathbf{3}]_0/[\text{AIBN}]_0$ = 1/0.5 in anisole (99.5 wt %) at 60 °C for 48 h. Three pieces of gel were tested for each series. The gels were swollen in anisole for a minimum of 6 h before the test.

The compatibility of the polymer chains with the organic solvents and the cross-linking density of the networked structures both play a key role in the swelling and collapsing of neutral polymer gels. Reducing the amount of cross-linker increases the ability of the gel to swell, but stable networks cannot form if the cross-linking density is too low.

Therefore, it should be possible to illustrate the dynamic covalent nature of gels prepared with the TTC cross-linker, **3**, by measuring the swelling ratios of the gels. The swelling ratio (SR) is defined as the weight ratio of the amount of absorbed solvent over that of the dry gel (eq 1). The dynamic covalent nature of the TTC cross-linker should allow the gels to reorganize under the appropriate stimuli, which in turn should decrease the contractile restorative forces generated by the swelling.

$$\text{Swelling Ratio} = \frac{Wt_{\text{swollen}} - Wt_{\text{dry}}}{Wt_{\text{dry}}} \qquad (1)$$

The SR of gels prepared with different ratios **3/**EGDMA (10/0, 8/2 and 5/5) but a constant ratio MMA/**3**+EGDMA/AIBN of 10/1/0.7 were measured first (Figure 1). The swelling experiments were conducted in anisole at 60 °C for 48 h with 0.5 equivalent (equiv) of AIBN compared to the TTC units present in the gels. Three pieces of gel were tested for each series. AIBN was used in these experiments to provide radicals that triggered the dynamic covalent response from TTC moieties.

The initial SRs were very similar for the three ratios **3**/EGDMA, as the overall cross-linking density was the same for these three gels (note: the gels were always allowed to swell for a minimum of 6 h before measurement of the initial SR). However, the behavior of the gels was different when they were subsequently swollen at 60 °C in the presence of AIBN. The SR remained nearly constant, going from 0.82 to 0.96, when 50% of permanent cross-linker was used in the formation of the gel. When only 20% of permanent cross-linker was employed, the SR ratio increased significantly from 0.68 to 1.32. If the only cross-linker present in the gels was the TTC cross-linker, the SR increased by 198% from 0.96 to 2.86. To confirm that these results were not due to partial degradation of the gels in the presence of AIBN, the gels were completely dried after the swelling test and reweighed. The mass of the dry gels, before and after the swelling experiment, showed only a small change, 1.3%, for the three specimens prepared with **3** as sole cross-linker. This result demonstrates that the increase in the SRs is not the result of gel degradation.

These initial results also indicate that when 50% of permanent cross-linker was used, the gel structure was essentially "fixed" by the permanent cross-links. While reshuffling between TTC cross-linking points likely occurred, the overall structure of the gels was maintained. On the other hand, when the concentration of permanent cross-linking point was lower or nil, the gels were able to reorganize, which partially lowered the contractile forces and yielded an increase of the swelling ratios.

Swelling Properties of PMMA Gels: Effect of the Stimulating Agent. To better understand the effect of the nature of the stimulus on the reorganization of the PMMA gels prepared with a TTC cross-linker, swelling experiments were conducted using either AIBN or CuBr/PMDETA as the catalyst for the dynamic covalent reorganization. These experiments should provide the information required to assess whether the increase in SR was predominantly due to the reorganization of the cross-linking points within the gels, or mainly resulted from a decrease in the cross-link density. The SR of gels that were prepared without permanent cross-linker and with a ratio MMA/**3**/AIBN of 50/1/0.7 and swollen in anisole at 60 °C for 48 h in the presence of 0.5 equiv of AIBN or 1 equiv of CuBr/PMDETA are compared based on the number of TTC units present in the gels (Figure 2). Three pieces of gel were tested for each series.

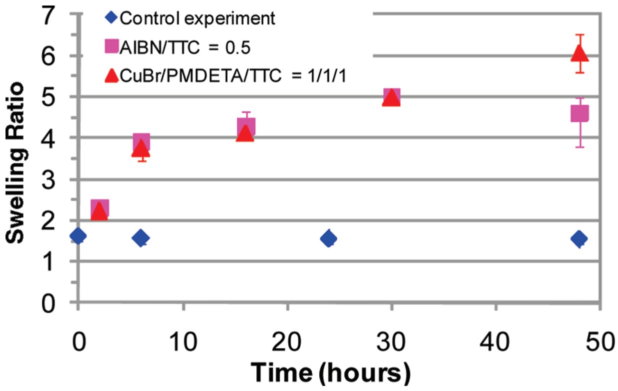


Figure 2. Swelling ratio of PMMA gels prepared using a ratio MMA/**3**/AIBN = 50/1/0.7. Swelling test conditions: control experiment, in anisole (99.5 wt %) at 60 °C for 48 h; $[\mathrm{AIBN}]_0/[\mathbf{3}]_0 = 0.5$, in anisole (99.5 wt %) at 60 °C for 48 h; $[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0/[\mathbf{3}]_0 = 1/1/1$, in anisole (99.5 wt %) at 60 °C for 48 h. Three pieces of gel were tested for each series. The gels were swollen in anisole for a minimum of 6 h before the test.

As expected, the SRs of the control experiment specimens did not change during the swelling test. This indicates that the swollen gels had reached their equilibrium state before the start of the tests and that they were stable under these conditions. The latter claim can be further confirmed by comparing the weight of the dry gels before and after swelling experiments, which were the same in the case of the control experiment (Table 2).

When AIBN and CuBr/PMDETA were used as stimuli for dynamic covalent reorganization of the gels, the SRs increased with time. When free radicals, generated by the decomposition of AIBN (0.5 equiv compared to TTC cross-linker **3**), were used to induce gel reorganization, the SR ratio increased by 202% from 1.52 to 4.59. The mass of the dry gels after the swelling experiments was 9.6% lower than that of the dry gels before the swelling experiments, indicating that a part of the gel became soluble. When CuBr/PMDETA (1/1 equiv compared to TTC cross-linker **3**) was used as stimulus for gel reorganization, the SR ratio increased by 298%, going from 1.52 to 6.05. The mass of the dry gels after the swelling experiments was 5.9% lower than that of the dry gels before the swelling experiments, indicating that a small fraction of the gel also became soluble.

When free radicals, generated by the decomposition of AIBN, were used as stimuli for the reorganization of the gels, a decrease of the cross-linking density was expected. This should depend on the ability of the isobutyronitrile radical, **5**, (generated by the thermal decomposition of AIBN) to add to the trithiocarbonate function present in the gel, and on the competitive fragmentation of the intermediate radical, that can release back either the original isobutyronitrile radical, **5**, or an isobutyrate moiety, **6** (Scheme 4). The constrained network may reduce the efficiency of degenerative transfer and therefore of the reshuffling process. Released polymeric radicals can recombine intermolecularly and form permanent cross-link, otherwise they can react intramolecularly or disproportionate. The intramolecular coupling and disproportionation can reduce the overall cross-linking density.

The steric hindrance of the trithiocarbonate group is very important, as these moieties are located within the gel and have two isobutyrate substituents. Therefore, the efficiency of addition of the isobutyronitrile radicals to the TTC moiety is low. In addition, the isobutyronitrile is a better leaving group than the isobutyrate.[14,40] Consequently, after its addition to the trithiocarbonate function, the isobutyronitrile radical should be predominantly released back.

These two properties of the isobutyronitrile radicals, that is, poor addition efficiency to the trithiocarbonate moiety and retro-fragmentation, can explain why less than 10% of the gel was solubilized during the swelling test with a ratio AIBN/TTC = 0.5.

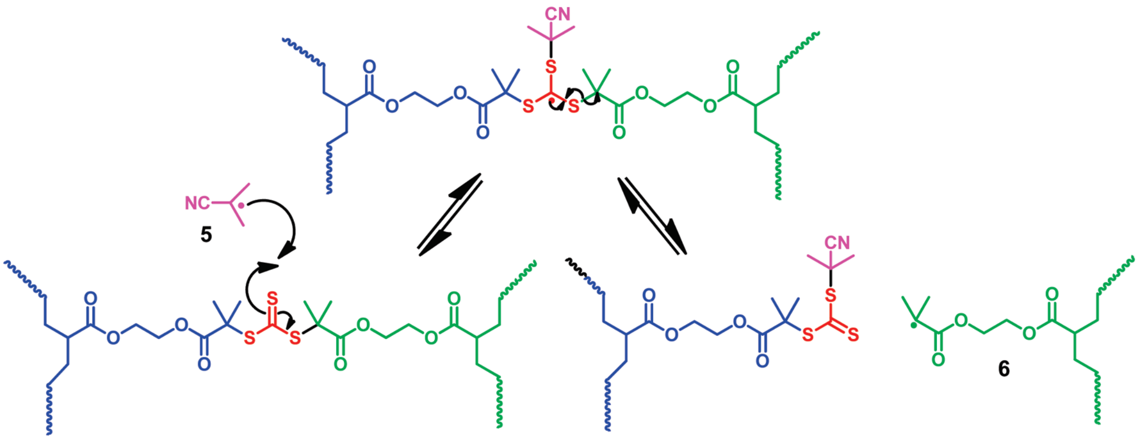
When CuBr/L complexes were used as a stimulus for the reorganization of the gels, no significant decrease of the cross-linking density was expected. Indeed, in the absence of radical termination events, the cross-linking density should not be affected during the reshuffling of the cross-linking points (Scheme 5).

Table 2. Swelling Tests for PMMA Gels Prepared with a Ratio MMA/3/AIBN = 50/1/0.7[a]

entry	stimulus	weight of the dry gels before swelling experiments (mg)	weight of the dry gels after swelling experiments (mg)	weight change (%)	SR
1		71.2	71.0	−0.3	1.52
2	AIBN	93.5	84.5	−9.6	4.59
3	CuBr/PMDETA	68.2	64.2	−5.9	6.05

[a] Swelling test conditions: entry 1, in anisole (99.5 wt %) at 60 °C for 48 h; entry 2, $[\mathrm{AIBN}]_0/[\mathbf{TTC}]_0 = 0.5$, in anisole (99.5 wt %) at 60 °C for 48 h; entry 3, $[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0/[\mathbf{TTC}]_0 = 1/1/1$, in anisole (99.5 wt %) at 60 °C for 48 h. Three pieces of gel were tested for each series. The gels were swollen in anisole for a minimum of 6 h before the test.

Scheme 4. Reorganization in the Presence of Radicals Formed by the Decomposition of AIBN of Gels Prepared with TTC Crosslinker 3



Scheme 5. Reorganization in the Presence of CuBr/L Complex of Gels Prepared with TTC Crosslinker 3

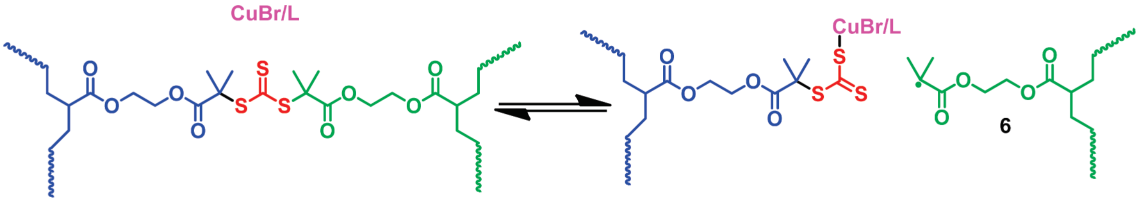


Table 3. Effect of the Ratio AIBN/TTC on the SR of PMMA Gels Prepared with a Ratio MMA/3/AIBN of 50/1/0.7[a]

AIBN/TTC	weight of the dry gels before swelling experiments (mg)	weight of the dry gels after swelling experiments (mg)	weight change (%)	SR
0	71.2	71.0	−0.3	1.52
0.1	94.8	86.8	−8.4	3.96
0.5	93.5	84.5	−9.6	4.59
1	78.3	70.5	−10.0	5.06
20	87.0	63.7	−26.8	8.00

[a] Swelling test conditions: in anisole (99.5 wt %) at 60 °C for 48 h. Three pieces of gel were tested for each series. The gels were swollen in anisole for a minimum of 6 h before the test.

Table 4. Effect of the Initial Crosslink Density on the Ability of PMMA Gels to Reorganize[a]

entry	MMA/**3**[b]	stimulus[c]	weight loss of the dry gels after swelling experiments(%)	SR
1	10		0	1.21
2	10	AIBN	1.4	2.86
3	10	CuBr/PMDETA	2.3	2.89
4	50		0.3	1.52
5	50	AIBN	9.6	4.59
6	50	CuBr/PMDETA	5.9	6.05
7	200		not measured	4.07
8	200	AIBN	7.0	5.91
9	200	CuBr/PMDETA	9.9	7.03

[a] Swelling test conditions: in anisole (99.5 wt %) at 60 °C for 48 h. Three pieces of gel were tested for each series. The gels were swollen in anisole for a minimum of 6 h before the test. [b] All the gels were prepared using a ratio **3**/AIBN of 1/0.7 at 60 °C (entries 1−3) or 65 °C (entries 4−9) for 24 h, in anisole (MMA/anisole = 2/1 (v/v)). [c] When AIBN was used as stimulus, a ratio AIBN/TTC of 0.5 was used; when CuBr/PMDETA was used as stimulus, a ratio TTC/CuBr/PMDETA of 1/1/1 was used.

In this case, the small decrease of the mass of the dry gels after swelling experiments (5.9%) could reflect the formation of soluble hyper-branched polymers during the reorganization of the gels.

The effect of changing the ratio AIBN/TTC was also studied. The SRs of gels prepared with a ratio MMA/**3**/AIBN of 50/1/0.7 were followed in anisole at 60 °C for 48 h, using ratios AIBN/TTC of 0, 0.1, 0.5, 1, and 20 (Table 3). Three pieces of gel were tested for each set of conditions.

The SR increased from 3.96 to 8.0 as the ratio AIBN/TTC was increased from 0.1 to 20 (Table 3). Increasing the ratio AIBN/TTC generated a higher radical concentration during the swelling experiments, which led to a decrease in the cross-link density and a partial solubilization of the gels (Table 3). However, the fact that only 27% of the gel dissolved after 48 h at 60 °C, when 20 equiv of AIBN was used, confirms the poor addition efficiency of the formed radicals to the trithiocarbonate moiety and retro-fragmentation of isobutyronitrile radicals.

Swelling Properties of PMMA Gels: Effect of the Cross-link Density. The effect of the initial cross-link density on the ability of PMMA gels to reorganize was also studied. The SRs of PMMA gels prepared with a ratio MMA/**3** of 10, 50, and 200 were measured at 60 °C in pure anisole and in the presence of 0.5 equiv of AIBN, or 1 equiv of CuBr/PMDETA, compared to the TTC moieties present in the gels (Table 4).

As expected, the SRs increased as the cross-link density was decreased (Table 4). For gels with the highest cross-linking density, an increase in the SR of 136 and 139%, compared to the control experiment, was observed when the gels were swollen in the presence of AIBN and CuBr, respectively (Table 4; entries 1, 2, and 3). For the gels with an intermediate cross-link density, an increase in the SR of 202 and 298%, compared to the blank experiment, was observed when the gels were swollen in the presence of AIBN and CuBr, respectively (Table 4; entries 4, 5, and 6). The gels with the lowest cross-linking density displayed an increase of the SR of 45.2 and 72.7%, compared to the blank experiment, when the gels were swollen in the presence of AIBN and CuBr, respectively (Table 4; entries 7, 8, and 9).

The effect of the gel reorganization on the SRs was lowest for the PMMA gels with the lowest cross-link density (MMA/**3** = 200). This could be explained by the fact that a lower concentration of TTC moieties decreases the probability of dynamic covalent exchange between TTC units. Also, this lower concentration of active TTC functions might increase the probability of loop formation, which would have a negative impact on the swelling ratio. The lower increase in SR observed for the gels prepared with a ratio MMA/**3** of 10 compared to the gel prepared with a ratio MMA/**3** of 50 can plausibly be explained by the fact that gel reorganization is controlled by a fine balance between the probability of dynamic covalent exchange (which increases with the cross-link density) and the freedom of movement of the chains (which decreases with the cross-link density).

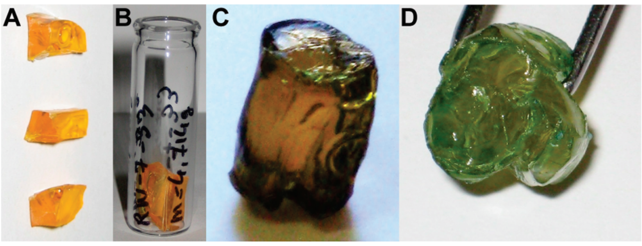


Figure 3. Pictures of PMMA gels before and after mending. (A,B) Three pieces of dry PMMA gel, prepared using a ratio MMA/**3**/AIBN = 50/1/0.7, before mending; (C) dry gel after mending; (D) swollen gel (for 6 h in THF) after mending.

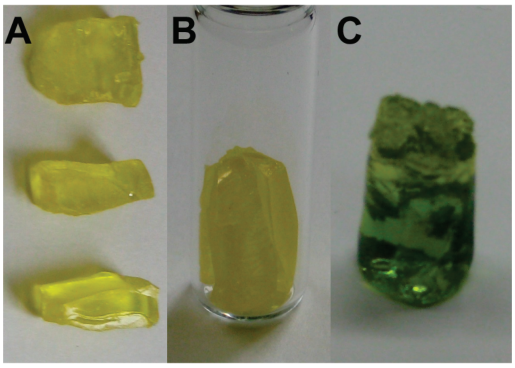
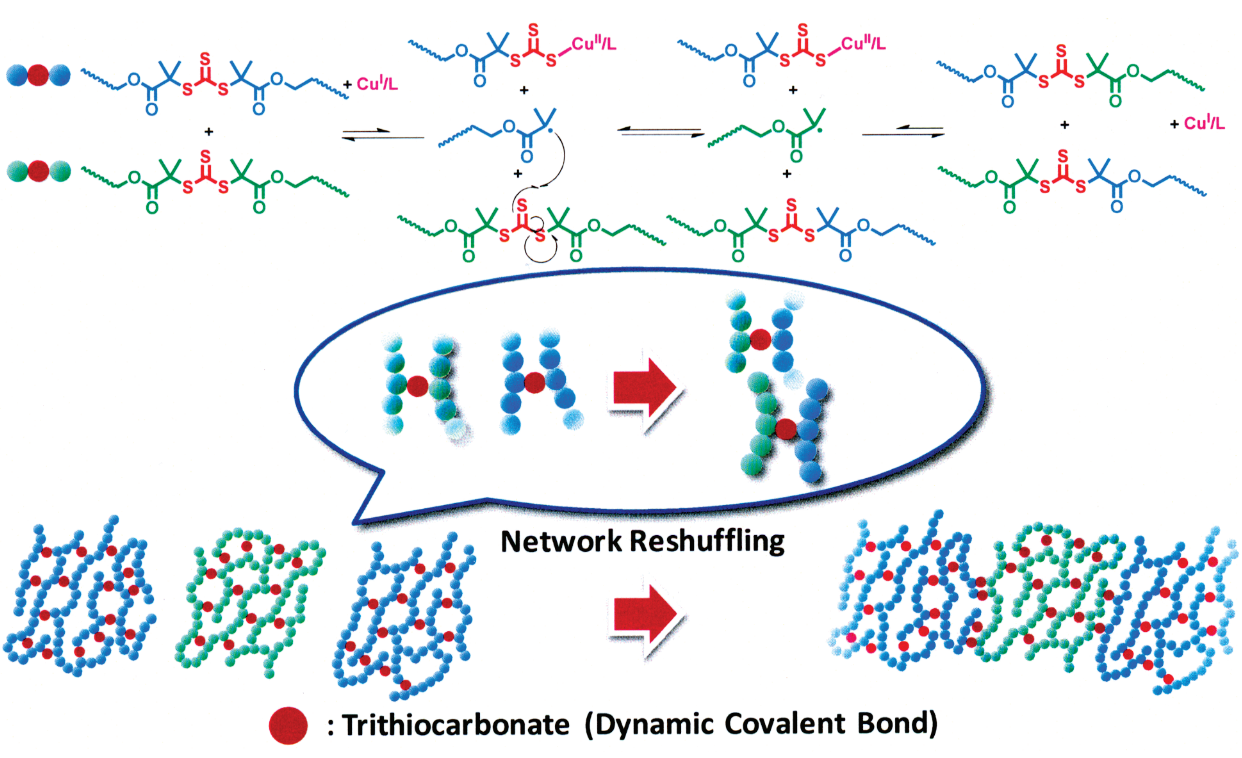


Figure 4. Pictures of PSt gels before and after mending. (A,B) Three pieces of dry PSt gel, prepared using a ratio St/**3**/EGDMA/AIBN = 100/1/1/0.2, before mending; (C) swollen gel (for 6 h in THF/MeOH) after mending.

Self-Healing of Gels Prepared with a TTC Cross-Linker. Gels/networks prepared with a dynamic covalent cross-linker, such as **3**, can potentially be reprocessed or undergo self-healing. Indeed, polymer networks containing reversible covalent bonds, based on acylhydrazone chemistry[26] or thermally reversible Diels−Alder reactions,[41] photosensitive bonds, based on ultraviolet light sensitive chitosan,[42] or noncovalent bonds, based on hydrogen bonding[43−45] or ionic interactions,[46] have been used to prepare self-healing materials.[47−49] A simple experiment, using the responsive gels prepared with the dynamic covalent trithiocarbonate cross-linker, was designed to illustrate this concept.

Three discrete pieces of PMMA gels (prepared using a ratio MMA/**3**/AIBN = 50/1/0.7) were placed in contact in a vial and swollen for one hour in anisole under a nitrogen atmosphere (Figure 3A,B). One hundred equivalents of deoxygenated St (compared to the TTC functions present in the gels) and 1 equiv of CuBr/PMDETA complex were introduced and the sealed vial was placed in an oven thermostatted at 60 °C for 4 h. Styrene was used to facilitate the mending process, as styryl radicals are expected to add rapidly to the trithiocarbonate function present within cross-linker **3**. All remaining volatile compounds were subsequently removed under vacuum at 50 °C to yield a single piece of dry gel (Figure 3C). The gel was subsequently swollen for 6 h in THF to check if the three pieces had really fused together and had not just agglomerated at the dry state. The gel remained as one single piece in the swollen state,

Scheme 6. Proposed Self-Healing Mechanism, via Reshuffling of Reversible Covalent Bonds, of Gels Prepared with a Trithiocarbonate Crosslinker



(Figure 3D). The fused PMMA gel displayed a green coloration due to the presence of residual copper(II) complexes.

PSt gels prepared using a ratio St/**3**/EGDMA/AIBN = 100/1/1/0.2 were used as model for a self-healing or gel fusion process that can take place in the absence of added monomer. The permanent cross-linker, EGDMA, was used in the preparation of the gels to ensure the integrity of the gels and prevent the process from yielding multiple small pieces of gel. The overall cross-linking density was similar to that in the experiment with PMMA gels. Three discrete pieces of PSt gel were placed in contact in a vial and swollen for one hour in anisole under nitrogen atmosphere (Figure 4A,B). One equiv of CuBr/PMDETA complex (compared to the TTC functions present in the gels) was introduced, and the sealed vial was placed in an oven thermostatted at 60 °C for 16 h. All remaining volatile compounds were subsequently removed under vacuum at 50 °C to yield a single piece of dry gel. The gel was subsequently swollen for 6 h in a 3/1 THF/MeOH mixture to check if the three pieces had really fused together and had not just agglomerated in the dry state. The gel remained as one single piece in the swollen state (Figure 4C). The fused PSt gel displayed a green coloration due to the presence of residual copper(II) complexes.

These two simple experiments demonstrate that dynamic covalent cross-linkers can be used to prepare materials that can be reprocessed and/or repaired. The proposed self-healing mechanism, via reshuffling of reversible covalent bonds, is shown in Scheme 6.

Conclusion

A dimethacrylate trithiocarbonate cross-linker (TTC) was synthesized in a single step Mitsunobu reaction between S,S′-bis(isobutyric acid)-trithiocarbonate and 2-hydroxyethyl methacrylate in 69% yield. PMMA gels were prepared by radical copolymerization of MMA in the presence of the TTC cross-linker. The swelling properties of the PMMA gels were studied. Under appropriate conditions, the PMMA gels reorganized, to accommodate forces generated by the swelling processes, yielding gels that exhibited an increase in the swelling ratio (up to 300% increase). Two different radical generators, a thermal initiator and a Cu^I/L complex, were successfully used to trigger the reorganization of the gels. Finally, to demonstrate that dynamic covalent cross-linkers can be used to prepare materials that can be reprocessed and/or undergo self-healing three discrete pieces of gels were fused into one single piece. Further experiments are currently ongoing to evaluate the influence of the dynamic covalent cross-linker structure and nature of the monomer, and of the polymerization procedure on the properties of the resulting gels. In addition, various stimuli are being investigated to trigger the reshuffling of the gels.

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