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Synthesis of Polyester-Polystyrene Hybrid Gel by PET-RAFT Polymerization in “RAFT Gel” and the Role of Dynamic Covalent Bonding in Its Self-Healing Properties

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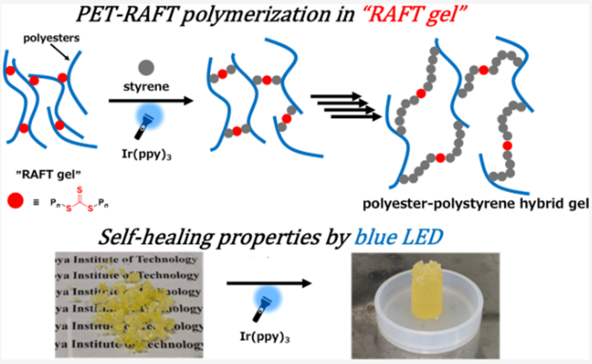
ABSTRACT: We describe photoinduced electron/energy transfer reversible addition-fragmentation chain transfer (PET-RAFT) radical polymerization of styrene mediated by a gelatinous agent (“RAFT gel”). The resulting polymer possesses self-healing properties via dynamic covalent bonding. First, we synthesized poly[(butylene thiomalate)-*co*-(butylene adipate)] by chemoselective ternary polycondensation of thiomalic acid, adipic acid, and 1,4-butanediol. Next, we prepared gels in which cross-linking points are trithiocarbonates via the reaction of 1,1′-thiocarbonyldiimidazole with the pendant mercapto group in the parent polyesters. We named this type of gel, "RAFT gel" because the cross-linking points of the gel also act as RAFT agents. After swelling of this gel by a styrene monomer, we polymerized the monomer inside the gel by a PET-RAFT polymerization procedure triggered by irradiation with blue LED light for several hours catalyzed by tris(2-phenylpyridinato)iridium (III) [$Ir(ppy)_3$] as a photoredox catalyst. A previously reported method initiated by 2,2′-azobis(isobutyronitrile) reported a poor grafting efficiency (ca. 50%), but it was dramatically improved (>99%) here by using the PET-RAFT technique. We also found that the polymerization rate using RAFT gel was faster than using a synthesized low-molecular-weight trithiocarbonate model RAFT agent, TTC-I. After a two-step degradation of the prepared gel via aminolysis and subsequent saponification, we characterized the number-averaged molecular weight of the branched poly(styrene)s. Additionally, we performed compression tests in order to evaluate the gel’s self-healing properties via dynamic covalent bonds, targeting a new type of photosensitive glue for poly(styrene) foams.



INTRODUCTION

The dramatic development of polymer materials has improved our lives for the better.[1] Polymer materials are still integral parts of our daily consumables, and at the same time, the diversity of their desired properties is expanding.[2] To respond to these urgent demands by consumers, it is no longer possible to solve these issues with a single type of polymer material. Therefore, techniques for chemically and physically mixing two more kinds of polymers are necessary.[3] However, miscibility of different types of polymers is generally extremely low compared with that of low-molecular-weight molecules because of the entropic penalty of polymer molecules and lack of favorable interactions to compensate.[4]

Aliphatic polyesters are known as biodegradable polymers and biocompatible materials and so are expected to be environmentally friendly.[5,6] On the other hand, vinyl polymers, such as poly(styrene) and poly(methyl methacrylate) [poly(MMA)], are used widely because of their excellent thermal and mechanical properties but are not generally seen as being biodegradable. We aimed to express the frontier results that polyester and vinyl polymer have different properties, and when the two are mixed together, a material with new properties that take advantage of the strong points of each polymer may be synthesized.

A successful blend of vinyl polymers and polyesters might combine their strengths, yet to date, there are only a few reports dealing with miscible blends of these materials.[7−9] Therefore, a new facile pathway to introduce vinyl polymer segments directly into a polyester backbone via covalent bonds is a topic of particular interest to polymer chemists, although there have been no reports until now of this to the best of our knowledge.

Since its discovery in 1998,[10] reversible addition-fragmentation chain transfer (RAFT) radical polymerization has been used in various studies dealing with controlled polymerization of vinyl monomers, due to its simplicity, versatility, and fidelity of end groups. The most familiar chemicals in RAFT radical

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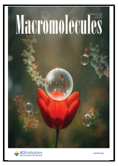

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polymerization are organic sulfur compounds called RAFT agents, including trithiocarbonate,[10] dithiocarbonate,[11] xanthate,[12] and dithiocarbamate,[13] in which the choice of suitable monomers for controlled polymerization depends on the structure of the RAFT agent. Most RAFT agents are solid or liquid at around room temperature, although we have already reported gelled RAFT agents and named them RAFT gels.[14,15] While there are many examples of gelation or cross-linking of monodisperse vinyl polymers with well-defined structure after polymerization using a conventional nongelled RAFT agent,[16−21] reported examples of the synthesis of gels using a gelatinous RAFT agent as the reversible addition-fragmentation type of chain transfer agent are very restricted.[15]

The gelatinous RAFT agent is synthesized by the reaction of polyesters with pendant mercapto groups, prepared by chemoselective dehydration polycondensation, with 1,1′-thiocarbonyldiimidazole (TCDI) as a cross-linker. The polymerization of styrene using this gelatinous RAFT agent has already been reported using 2,2′-azobis(isobutyronitrile) (AIBN) as the radical trigger.[15] The evolution of this approach reported here using photoinduced electron/energy transfer (PET) has enabled us to make the important step of fabricating miscible gel composites of polyesters and vinyl polymers directly. Also, while our previous method[15] required high temperatures and high initiator concentrations, resulting in low grafting efficiency (<50%), which represents the presence of linear vinyl polymer or branching initiated by AIBN itself, our new approach results in remarkably improved efficiency (>99%).

In this study, we focused on PET-RAFT polymerization, in which the polymerization proceeds in visible light by using a photoredox catalyst. The superior features of PET-RAFT polymerization are 2-fold. The first is that an external chemical, such as AIBN or BPO, is not required, as the RAFT agent necessarily acts as an initiator. This unique PET-RAFT polymerization procedure suppresses side reactions in the radical polymerization of vinyl monomers in “RAFT gel” (Figure 1), resulting in a large increase in grafting efficiency.

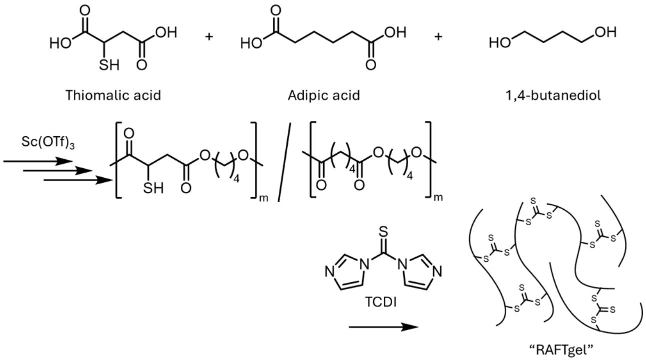

Figure 1. Preparation of RAFT gel.

Moreover, to develop a photosensitive glue for poly(styrene)-based foams, we investigated the self-healing behavior of the polymer hybrid via exchange of the dynamic covalent bonds acting as the cross-linkers of the polyester-poly(styrene) composite gel.

EXPERIMENTAL SECTION

Materials. Thiomalic acid (TMA) (>98%), adipic acid (ADA) (>98%), 1,4-butanediol (BD) (>98%), TCDI (>95%), tributylphosphine (>95%), styrene (>98%), tris(2-phenylpyridinato)iridium(III) (purified by sublimation), propylamine (>98%), and triethylamine (TEA) (>99%) were purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Toluene (super dehydrated), methanol (super dehydrated), tetrahydrofuran (super dehydrated), 2,2′-azobis-(isobutyronitrile) (AIBN), and magnesium sulfate ($MgSO_4$) were purchased from Wako Pure Chemical Industries, Ltd. (Osaka Japan). Sodium hydroxide (NaOH) and sodium chloride (NaCl) were purchased from Nacalai Chemical Industry Co., Ltd. (Kyoto, Japan). TOYOPEARL HW-40F was purchased from TOSOH Industry Co., Ltd. (Tokyo, Japan). Styrene was used after the removal of the inhibitor with activated alumina.

$Sc(OTf)_3$ Catalyzed Polycondensation of TMA, ADA, BD to Synthesize Poly[(butylene thiomalate)-*co*-(butylene adipate)]. In a two-necked round-bottom flask, TMA (0.018 mol), ADA (0.018mol), BD (0.036 mol), and $Sc(OTf)_3$ (7.2×10^{-4} mol) were mixed and stirred at 80 °C. After homogenization, the pressure was gradually decreased for 15 h to perform dehydration. Purification was carried out by reprecipitation with THF and an excess amount of *n*-hexane, as good and poor solvents, respectively. The synthesized polyester was dried under reduced pressure in a yield of 90%. ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 4.22−4.10 [br, $-\mathrm{CH_AH_BCOOC}H_2$, $-\mathrm{C}H_2\mathrm{OOCCH(SH)}$], 3.83−3.67 [m, $-\mathrm{C}H\mathrm{(SH)CH_AH_B}$], 3.02 [dd, $-\mathrm{CH(SH)CH_A}H_\mathrm{B}$, $J_1 = 17.0$ Hz, $J_2 = 8.9$ Hz], 2.77 [dd, $-\mathrm{CH(SH)C}H_\mathrm{A}\mathrm{H_B}$, $J_1 = 16.9$ Hz, $J_2 = 6.0$ Hz], 2.44−2.24 (br, $-\mathrm{S}H$, $-\mathrm{COC}H_2\mathrm{CH_2}$), 1.84−1.65 (m, $-\mathrm{OCH_2C}H_2$, $-\mathrm{COCH_2C}H_2$) (Figure S1). FT-IR (KBr disk, cm^{-1}): 3456 ($\nu_{\mathrm{O-H}}$), 2926 ($\nu_{\mathrm{C-H}}$), 1739 [$\nu_{\mathrm{C=O}}$(ester)], 1469 ($\delta_{\mathrm{C-H}}$), 1278 and 1133 [$\nu_{\mathrm{C-O}}$(ester)], and 1092 ($\nu_{\mathrm{C-O}}$) (Figure S2).

Preparation of RAFT Gel. All operations were carried out under dry N_2 conditions. In a round-bottom flask, poly[(butylene thiomalate)-*co*-(butylene adipate)] (0.81 g, 2.0 mmol), TCDI (0.36 g, 2.0 mmol), and tributylphosphine (24.6 μL, 0.1 mmol) were dissolved in 10 mL of THF. The reaction mixture was stirred for 6 h. When the reaction was completed, the gel was washed with an excess amount of THF and dried under reduced pressure (see also Figure S3). FT-IR (KBr disk, cm^{-1}): 3460 ($\nu_{\mathrm{O-H}}$), 2958 ($\nu_{\mathrm{C-H}}$), 1733 ($\nu_{\mathrm{C=O}}$, ester), 1461 ($\delta_{\mathrm{C-H}}$), 1255 ($\nu_{\mathrm{C=S}}$, trithiocarbonate), 1173 [$\nu_{\mathrm{C-O}}$, (ester)], and 1078 ($\nu_{\mathrm{C-O}}$) (Figure S2).

PET-RAFT Polymerization Using RAFT Gel under Blue LED Irradiation. All operations were carried out under dry N_2 conditions. RAFT gel (42.6 mg, 0.05 mmol), styrene, and $Ir(ppy)_3$ (0.16 mg, 2.5×10^{-4} mmol) were prepared in a round-bottom flask and sealed with a rubber septum. After the RAFT gel was swollen with styrene monomer, the polymerization was carried out under blue LED irradiation (456.1 nm, 15.04 lm/W, D160 series 24 V 10 mm LED dot tape, JW-system CO., Ltd., see also Figure S4) at room temperature for a predetermined time. The reaction was quenched by shutting down the blue LED irradiation, and the product was filtered through an excess amount of chloroform to separate the gel and sol components. The synthesized gel component was thoroughly dried by vacuum drying under reduced pressure. Conversion was calculated by the gravimetric yield. Grafting efficiency was also calculated by gravimetric yield and ^{1}H NMR spectra of the sol component according to the formula in Figure 2.

RAFT Polymerization Using RAFT Gel Using AIBN as an Initiator. All operations were carried out under dry N_2 conditions.

$$G_{eff} = \frac{100\Delta g}{\Delta g + \frac{s_p}{s_m + s_p}(M_o - \Delta g)}$$

G_{eff} : Grafting efficiency (%)
Δg : Weight increase of gel component (g)
s_m : Integral value of the monomer peak from ^{1}H NMR measurement of the sol component
s_p : Integral value of the homopolymer peak from ^{1}H NMR measurement of the sol component
M_o : Weight of monomer before the polymerization (g)

Figure 2. Formula for calculating grafting efficiency.

RAFT gel (42.6 mg, 0.05 mmol), styrene, and AIBN (4.1 mg, 0.025 mmol) were prepared in a round-bottom flask and sealed with a rubber septum. After the RAFT gel was swollen with styrene monomer, polymerization was carried out at 110 °C for a predetermined time. The product was filtered through an excess amount of chloroform to separate the gel and the sol components. The synthesized gel component was thoroughly dried by vacuum drying under reduced pressure. Conversion was calculated by gravimetric yield. Grafting efficiency was also calculated by gravimetric yield and ^{1}H NMR spectra of the sol component according to the formula in Figure 2.

Aminolysis Reaction of RAFT Gel after Polymerization of Styrene. All operations were carried out under an air atmosphere. RAFT gel after polymerization of styrene (100 mg), THF (4.0 mL), TEA (1.0 mL), and *n*-propylamine (0.50 mL) was prepared in a round-bottom flask. The mixture was stirred at 60 °C and refluxed for 24 h. As the reaction progressed, we observed that the gel had turned into a solution. The solution was washed with an excess amount of *n*-hexane. The recovered poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene)s were dried under reduced pressure.

Saponification Reaction of Polymers after Aminolysis Reaction. All operations were carried out under an air atmosphere. Poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene)s (50 mg) after aminolysis of RAFT gel, NaOH (250 mg), THF (5.0 mL), and H_2O (5.0 mL) were prepared in a round-bottom flask. The mixture was then stirred at 60 °C for 24 h. Next, HCl aq. was added into the flask until pH = 2−3. After neutralization, the mixture was dried under reduced pressure. The polymers were dissolved in chloroform, and the insoluble part was removed by filtration. After filtration, the polymers were dried under reduced pressure (65% recovery yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 6.76−6.28 (br, aromatics), 7.20−6.87 (br, aromatics), 3.80−3.59 (br, $-CH_2C\mathit{H}_2OH$), 3.74−3.56 (br, $-OCOC\mathit{H}CH_2$), 3.10−2.94 (br, $-OCOCHC\mathit{H}_2$), 2.57−2.14 [br, $-CH_2CHS\mathit{H}$, $-CH_2C\mathit{H}_2COOH$], 2.00−1.78 (br, methine of PSt), 1.75−1.60 (br, $-C\mathit{H}_2CH_2OH$, $-C\mathit{H}_2CH_2COOH$), 1.57−1.28 [br, methylene of poly(styrene)].

Synthesis of TTC-I as a Low-Molecular-Weight Model. First, we synthesized dimethyl thiomalate. TMA (1.5015 g, 10 mmol), methanol (30 mL), and Sc(OTf)$_3$ (0.5 mmol, 246.1 mg) were prepared in a round-bottom flask. The mixture was then stirred and heated to 70 °C and refluxed for 8 h. Then, the mixture was evaporated to remove water and unreacted methanol and washed with brine three times. The solution was dried with dehydrated $MgSO_4$ and evaporated. The product was a colorless syrup (89% yield). Next, under N_2, dimethyl thiomalate (3.0 mmol, 534.6 mg), TCDI (1.4 mmol, 249.5 mg), and THF (5.0 mL) were prepared in a round-bottom flask. The mixture was then stirred for 4 h. After the reaction, the reaction mixture was evaporated and washed with brine three times. The solution was dried with dehydrated $MgSO_4$ and evaporated to afford a yellow solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 5.27−5.23 (m, $-SC\mathit{H}$), 3.77 (s, $-SCHCOOC\mathit{H}_3$), 3.72 (s, $-CH_2COOC\mathit{H}_3$), 3.07−3.05 (m, $-SCHC\mathit{H}_2-$). ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 218.80 ($-SCS_2-$), 170.63 ($-SCHCOOCH_3$), 169.53 ($-SCHCH_2COOCH_3$), 53.31 ($-CHCOOCH_3$), 52.26 ($-CH_2COOCH_3$), 48.27, 48.23 ($-SCS_2CH-$), and 35.89, 35.85 ($-SCHCH_2-$).

PET-RAFT Polymerization Using TTC-I. All operations were carried out under dry N_2 conditions. TTC (0.05 mmol), styrene, and Ir(ppy)$_3$ (0.16 mg, 2.5×10^{-4} mmol) were prepared in a round-bottom flask with a rubber septum. Polymerization was carried out under blue LED irradiation (456.1 nm) at room temperature for a predetermined time. The reaction was quenched by shutting down blue LED irradiation.

Compression Tests. Compression tests were performed on 1.0 cm square cubes of gels, which were fully swollen with chloroform, using an AG-20kNXDplus (Shimazu Co., Kyoto, Japan) system. The test rate was 0.50 mm min^{-1} and was terminated when the strain reached 90%.

Instrumentation. ^{1}H NMR (400 MHz) spectra and ^{13}C NMR (100 MHz) spectra were measured using Bruker Analytik DPX400 equipment at 27 °C with $CDCl_3$ as the deuterated solvent. The number of averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the parent polyesters were determined with Shodex KD803 and KD804 columns using a size exclusion chromatography (SEC) system composed of a pump (JASCO PU-2028), differential refractometer (JASCO RI-2031), and an Intelligent column oven (JASCO co-2065 Plus). *N*,*N*-Dimethylformamide (DMF) containing lithium bromide (0.05 wt%) was used as the eluent, in which the flow rate was 0.5 mL/min and the temperature was 40 °C. The calibration of M_n and M_w/M_n was performed using a series of poly(methyl methacrylate)s as the standard samples. The M_n and M_w/M_n values of the poly(styrene) linkers were determined using another SEC system including a JASCO PU4185 pump system, a JASCO RI-4035 differential refractometer, and a JASCO CO-2065 Plus Intelligent Column Oven (eluent, tetrahydrofuran (THF), flow rate, 0.35 mL/min, temperature, 40 °C), and Tosoh TSK-gel [SuperMultipore HZ-M (particle size: 4 μm)] (Tosoh, Tokyo, Japan), and poly(styrene) standards were used for calibration. FT-IR spectra (KBr disk) were measured using a JASCO FT-IR-430 spectrometer.

■ RESULTS AND DISCUSSION

Preparation of RAFT Gel. First, a direct dehydration polycondensation reaction was performed using TMA, BD, and ADA as monomers, with Sc(OTf)$_3$ as a catalyst,[22−27] at 80 °C under reduced pressure, in which BD is a ternary segment in order to control the interval of cross-linkings (Figure 1). As polymerization progressed, an increase in viscosity was observed, but no gelation occurred. The purified polyester had a molecular weight (M_n) of approximately 8500 and a molecular weight distribution of about 1.3, estimated by SEC measurements (eluent, DMF + 0.1 wt % of LiBr, PMMA standards). As IR measurements confirmed the presence of pendant mercapto groups, gelation was achieved by cross-linking them with TCDI. Figure S3 shows a picture of the polyester before and after cross-linking. After the reaction, IR measurements of the resulting gel showed the complete consumption of mercapto groups and the new vibration of C═S at 1255 cm^{-1} assigned to the thiocarbonyl groups. The resultant gel generally swelled in various solvents and vinyl monomers, including styrene and MMA, as reported in previous studies.[15,16] However, in the case of poly(TMA-*alt*-BD) used as the parent polyester, the expected radical polymerization did not work (Table S1), because the cross-linking density became extremely high. It seems that it is essential for polymerization to be swollen enough with the vinyl monomer.

PET-RAFT Polymerization of Styrene Using RAFT Gel. In all experiments, polymerization was initiated after swelling of the RAFT gel with the styrene monomer. Blue LED light was used for PET-RAFT polymerization, and Ir(ppy)$_3$ was used as a photoredox catalyst (Figure S4) (entries 1, 3, and 6−8). RAFT radical polymerization was also performed using a previously reported procedure with AIBN as the initiator at 110 °C (entries 4 and 5). When the polymerization was performed at 70 °C, the conversion was ca. 30%. It revealed that heat fusion inside the gel inhibited the smooth initiation at 70 °C. It seems that the polymerization proceeded even without using Ir(ppy)$_3$, but it was extremely slowed down, and an unexpected side reaction caused the increase in M_w/M_n (entry 2). In order to investigate the molecular weight between cross-linking points, that is, linkers, the gels were degraded by the aminolysis reaction according to Scheme S1 and subsequent saponification reaction for all experiments. SEC measurements were used to characterize the M_n. In both the thermal and photoinduced methods, the expected radical polymerization occurred, but the thermal method (entries 4 and 5) resulted in a relatively large molecular weight distribution, and the grafting efficiency (Figure 2), which is a ratio of the monomers incorporated into the RAFT-gel against the consumed (polymerized) monomers, was not satisfactory (48−55%) because of contamination by polys(styrene) homopolymers initiated by AIBN, similar to observations in our previous reports.[15] The lower grafting efficiency makes it more difficult to control the molecular weight between cross-linking points because styrene monomers are also consumed by AIBN to give the corresponding homopolymers.

In contrast, the grafting efficiency was dramatically improved by using the PET-RAFT method. The efficiency was also calculated using an equation as shown in Figure 2. This result was ascribed to the prohibition of undesired free radical polymerization of styrene, by which it seems that initiation necessarily occurred by the RAFT agents, thereby keeping the cross-linking intact. As a result, the molecular weight between cross-linking points could be relatively controlled. In the PET-RAFT polymerization of styrene in the RAFT gel, the conversion showed a linear increase as a function of time (Figure 3). However, plots of M_n of the polystyrene cross-linkers against the conversion ratio were not linear (Figure 4), revealing that M_n of the poly(styrene) cross-linker was roughly controlled (M_w/M_n = 1.4−1.6).

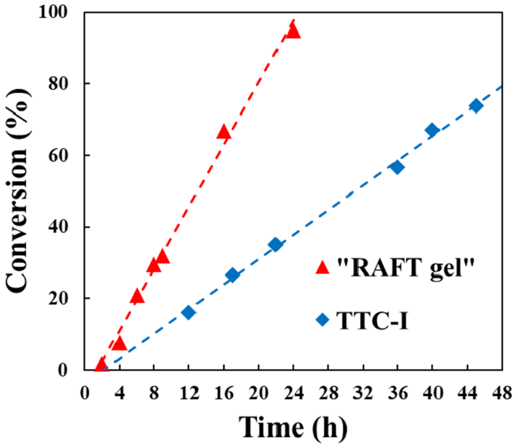

Figure 3. Time vs. conversion plot of polymerization using the RAFT gel and TTC-I.

Comparison of Polymerization with a Modeled Low-Molecular-Weight RAFT Agent (TTC-I). It is known that the viscosity of the reaction medium influences radical polymerizations.[28,29] To evaluate the effects of gel as the reaction medium and viscosity in polymerization, we synthesized a model RAFT agent: TTC-I (Figure 5), which mimics the cross-linking points of the RAFT gel (please see also entries 9−14 in Table 1). The structure was confirmed by ^{1}H (Figure S5) and ^{13}C (Figure S6) spectra. This RAFT agent was used as a chain transfer agent, and the polymerization was carried out under similar conditions. Similar to polymerization using a RAFT gel, the conversion increased linearly with reaction time. In both results, there was also an induction period of about 2 h in the initiation. Interestingly, whereas with RAFT gel, the conversion reached more than 90% within 24 h, and in the case of polymerization using TTC-I, the conversion did not reach 80% even after 45 h (see Figure 6). The results indicated that the polymerization rate of the RAFT gel was much faster than that with TTC-I (see Figure 6). This result agrees with radical polymerization in other viscous media (e.g., ethylene glycol or poly(ethylene glycol)), as reported by Matsuoka et al.[29] in which both the suppression of bimolecular termination reactions, that is, recombination or disproportionation, due to limited fusion of growing polymer chains and restricted monomer diffusion encapsulated in the gel, accelerated the apparent chain growth. Recently, Chou et al. reported fast PET-RAFT polymerization of MMA in deep eutectic solvents consisting of tetrabutylammonium chloride and ethylene glycol to afford ultra-high-molecular-weight poly(MMA), in which the kinetic plot showed two-step kinetics, that is, polymerization rate was accelerated when the conversion exceeded over 50%.[30] As shown in Figure 6, in this study, the polymerization rate in RAFT gel was also accelerated when the conversion exceeded 50%. The results suggested that the termination and RAFT-gel-mediated propagation were both diffusion-controlled.

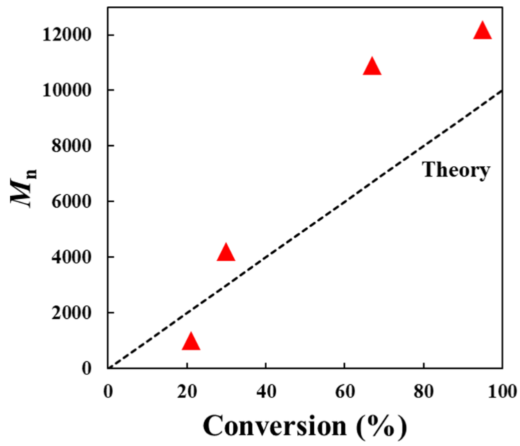

Figure 4. Conversion vs. M_n plot of polymerization using RAFT gel.

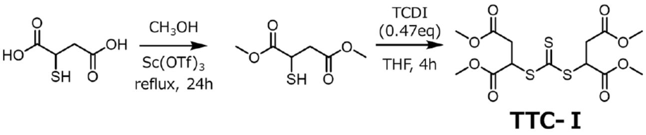

Figure 5. Synthesis and chemical structure of TTC-I.

Compression Tests of RAFT Gel after Polymerization of Styrene and Self-Healing Properties Mediated by PET-RAFT Mechanisms. As a sample of self-healing polyacrylamide gel mediated with trithiocarbonates was recently reported,[31] the described RAFT gels prepared by irradiating blue LED for 24 h (Table 1 entry 8, trithiocarbonate units: 0.68 wt% to the gel) were cut into cubes for compression tests. The gel samples were then swollen in chloroform as a solvent for 24 h and subjected to compression tests. The red line in Figure 7 shows a stress−strain curve of the virgin gel.

After the first compression test, the gels were reswollen in toluene under a nitrogen atmosphere, again using a photoredox catalyst, and irradiated with a blue LED for 24 h to prepare the first-healed gel. The blue line in Figure 7 shows that the broken gels were recombined (healed). Under the same conditions, the gels were left in the dark for 24 h without light irradiation,

Table 1. Polymerization of Styrene Using RAFT Gel or TTC-I

entry[a]	radical trigger	[St]/[RAFT agent]	time (h)	conv.[b] (%)	grafting efficiency[c] (%)	M_n[d] (kg/mol)	M_w/M_n[d]
1	blue LED[e]	100/1	8	66	>99	3.30	1.61
2[i]	blue LED[e]	100/1	8	48	>99	4.50	1.93
3	blue LED[e]	200/1	8	30	>99	4.20	1.78
4	AIBN[f]	100/1	3	38	55	2.99	1.92
5	AIBN[f]	200/1	8	40	48	7.54	2.19
6	blue LED[e]	200/1	9	32	>99	2.85	1.50
7	blue LED[e]	200/1	16	71	99	10.9	1.44
8	blue LED[e]	200/1	24	95	99	12.2	1.66
9[g]	blue LED[e]	200/1	12	16	NA[h]	2.96	1.15
10[g]	blue LED[e]	200/1	17	27	NA[h]	4.50	1.14
11[g]	blue LED[e]	200/1	22	35	NA[h]	5.85	1.12
12[g]	blue LED[e]	200/1	36	57	NA[h]	8.34	1.13
13[g]	blue LED[e]	200/1	40	67	NA[h]	9.37	1.12
14[g]	blue LED[e]	200/1	45	74	NA[h]	10.3	1.14

[a]Bulk polymerization. [b]Determined by gravimetric yield. [c]Determined by gravimetric yield and ^{1}H NMR spectra. [d]Determined by SEC (THF) using PS standard for branched poly(styrene) samples after aminolysis and saponification of RAFT gel. [e]Room temperature, [RAFT agent]/[Ir(ppy)$_3$] = 1/0.005. [f][RAFT agent]/[AIBN] = 1/0.5, 110 °C. [g]TTC-I as a RAFT agent. [h]NA = Grafting efficiency was not available for TTC-I. [i]Without Ir(ppy)$_3$.

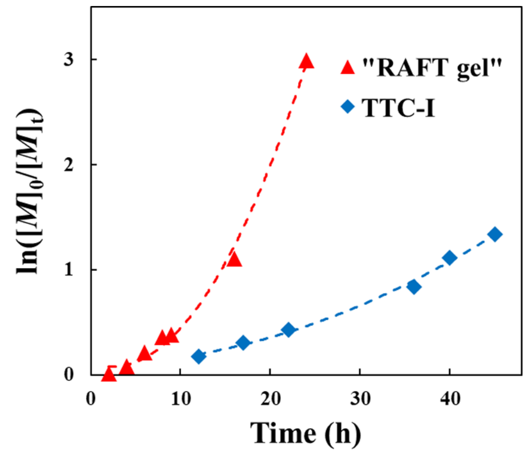

Figure 6. Kinetic studies of polymerization using the RAFT gel and TTC-I as RAFT agents.

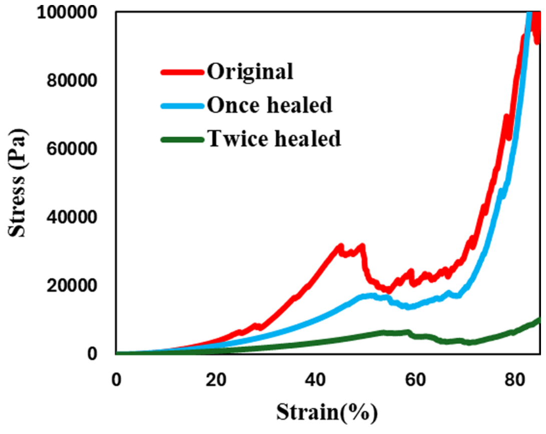

Figure 7. Stress−strain curves of RAFT gel after polymerization of styrene (entry 6) after being swollen in chloroform.

and the gels were not healed. This suggests that the gels showed self-healing properties in response to blue LED irradiation. This self-healing property is thought to be due to dynamic covalent bonding exchanges of the trithiocarbonate as a cross-linking point, triggered by blue LED irradiation, shown schematically in Figure 8.

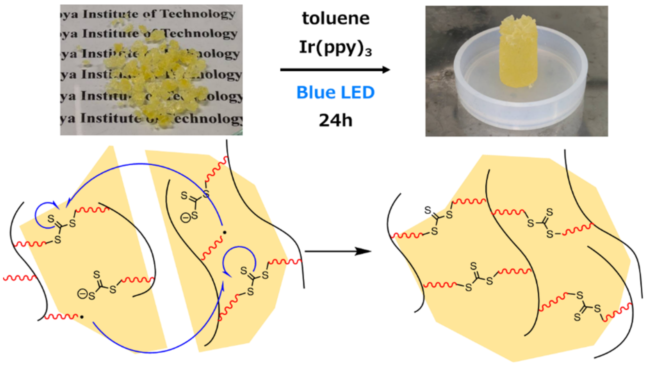

Figure 8. Schematic representation of the RAFT gel and the speculated mechanism of self-healing properties.

The repaired gels (healed first) were then compression-tested again until broken, and the subsequently broken gels were again healed under the same conditions as those described earlier. The repaired sample that had therefore been healed twice was compression-tested. The green line in Figure 7 shows that the initial elastic modulus of the gel was decreased, and the strength of the gel was also decreased after this second healing procedure was carried out. The results are also summarized in Table S2. The gel, after two cycles of compression tests and successive healing, had been degraded via aminolysis and saponification, confirmed by an SEC measurement, which showed a decrease of M_n and broadening of M_w/M_n. Therefore, the observed changes in mechanical properties could be attributed to the cleavage of nonhealable covalent bonding, that is, poly(styrene) chain, acting as dangling chains (Figure 8).

To investigate self-healing phenomenon rheologically, we examined the stress-relaxation tests with as well as without blue LED irradiation; strain = 4%, at 25 °C, using an AG-20kNXDplus (Shimazu Co., Kyoto, Japan) system (Figure S7). The gel was cut into 1 × 1 × 1 cm cubes after being swollen in a toluene solution of Ir(ppy)$_3$ for 1 day. According to the stress vs. time graph, the stress-relaxation phenomenon might be due to dynamic covalent bonding when blue LED was irradiated (blue line as shown in Figure S7). However, because the gel was very soft (σ_0 = 0.9 kPa), a remarkable difference in the relaxation speed from that without irradiation (red line as shown in Figure S7) was not observed in this time scale. Therefore, it was not possible to discuss the rheology in detail now, so we will discuss it in the forthcoming paper.

■ CONCLUSIONS

In this study, we improved the grafting efficiency of the RAFT gel significantly using PET-RAFT as a radical initiator compared with previous studies using AIBN-RAFT radical polymerization because contamination by poly(styrene) homopolymer was greatly suppressed. We also found that radical propagation of styrene in RAFT gel was accelerated compared to that of a conventional low-molecular-weight RAFT agent in solution, where the structure of the RAFT agent mimics the cross-linking points of RAFT gel. Radical polymerization inside the gels featured faster propagation because restricted molecular motion of polymer radical chains in the gel suppressed termination (recombination), and diffusion of styrene monomer to the outside of the gel was also restricted. This accelerated propagation under kinetic control indicates how the propagation of a monomer molecule is affected by its surroundings. In addition, we confirmed the self-healing property of the RAFT gel under blue light irradiation via dynamic covalent bonding of trithiocarbonates. This research has provided new insights into radical polymerization in the gelatinous state, making possible miscible hybridization of polyesters with vinyl polymers and control of molecular weights between cross-linking points. Such information should also prove useful in designing a new type of photosensitive glue for poly(styrene) foams.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c01490.

> Synthetic procedures, spectroscopic data, and results of control experiment and compression test of the healed material (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) McCleary-Petersen, K. C.; Wiegand, K. R.; Taleff, M. T.; Guironnet, D. Engineering Polymer Architecture Through Reaction Rates. *Macromolecules* **2025**, *58* (1), 18−31.

(2) Negim, E.; Shalash, M.; Mukatayeva, Z. S.; Baidullayeva, A. K.; Alferov, T. K.; Nurtazina, A. A.; Karabayeva, A. E.; Samy, M. Mini review polyurethane hybrids: preparation, characterization and applications. *Kompleks Ispol Miner* **2025**, *333* (2), 16−26.

(3) Andrzejewski, J.; Das, S.; Lipik, V.; Mohanty, A. K.; Misra, M.; You, X. Y.; Tan, L. P.; Chang, B. P. The Development of Poly(lactic acid) (PLA)-Based Blends and Modification Strategies: Methods of Improving Key Properties towards Technical Applications-Review. *Materials* **2024**, *17* (18), 4556.

(4) Jain, V.; Kumar, H.; Moona, G. A retrospective review of polymer blending for additive manufacturing polymer filament manufacturing: concept, present and trends. *Adv. Mater. Process. Technol.* **2024**, No. 2423493.

(5) Kim, S.; Chung, H. Y. Biodegradable polymers: from synthesis methods to applications of lignin-*graft*-polyester. *Green Chem* **2024**, *26* (21), 10774−10803.

(6) Getahun, M. J.; Kassie, B. B.; Alemu, T. S. Recent advances in biopolymer synthesis, properties, & commercial applications: a review. *Process Biochem* **2024**, *145*, 261−287.

(7) Belletti, G.; Ronconi, G.; Mazzanti, V.; Buratti, E.; Marchi, L.; Sotgiu, G.; Calosi, M.; Mollica, F.; Bertoldo, M. Morphology and Mechanical Properties of Poly(vinyl alcohol)/Poly(lactic acid) Blend Films Prepared from Aqueous Dispersions. *Macromol. Mater. Eng.* **2024**, *309* (1), No. 2300237.

(8) Vayshbeyn, L. I.; Mastalygina, E. E.; Olkhov, A. A.; Podzorova, M. V. Poly(lactic acid)-Based Blends: A Comprehensive Review. *Appl Sci-Basel* **2023**, *13* (8), 5148.

(9) Rahman, S. S.; Mahmud, M. B.; Monfared, A. R.; Lee, P. C.; Park, C. B. Achieving outstanding toughness of PMMA while retaining its strength, stiffness, and transparency using in situ developed TPEE nanofibrils. *Compos. Sci. Technol.* **2023**, *236*, No. 109994.

(10) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; et al. Living free-radical polymerization by reversible addition-fragmentation chain transfer: The RAFT process. *Macromolecules* **1998**, *31* (16), 5559−5562.

(11) Goto, A.; Sato, K.; Tsujii, Y.; Fukuda, T.; Moad, G.; Rizzardo, E.; Thang, S. H. Mechanism and kinetics of RAFT-based living radical polymerizations of styrene and methyl methacrylate. *Macromolecules* **2001**, *34* (3), 402−408.

(12) Monteiro, M. J.; Sjöberg, M.; van der Vlist, J.; Göttgens, C. M. Synthesis of butyl acrylate-styrene block copolymers in emulsion by reversible addition-fragmentation chain transfer: Effect of surfactant migration upon film formation. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (23), 4206−4217.

(13) Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Chong, Y. K.; Moad, G.; Thang, S. H. Living radical polymerization with reversible addition-fragmentation chain transfer (RAFT polymerization) using dithiocarbamates as chain transfer agents. *Macromolecules* **1999**, *32* (21), 6977−6980.

(14) Yamamoto, K.; Takasu, A. Preparation of Gelatinous Reversible Addition-Fragmentation Chain Transfer Agents 'RAFT Gel' via Chemoselective Polycondensations of a Dicarboxylic Acid Containing a Mercapto Group and Diols. *Macromolecules* **2010**, *43* (20), 8519−8523.

(15) Yoshimura, D.; Yamada, S.; Takasu, A. A polyester-polystyrene hybrid connected by dynamic covalent bonds prepared via radical polymerization of styrene in a 'RAFT gel'. *Polym Chem-Uk* **2014**, *5* (11), 3689−3696.

(16) Crescenzi, V.; Dentini, M.; Bontempo, D.; Masci, G. Hydrogels based on pullulan derivatives crosslinked via a "living" free-radical process. *Macromol Chem Physic* **2002**, *203* (10−11), 1285−1291.

(17) Feng, X. S.; Pan, C. Y. Synthesis of amphiphilic miktoarm ABC star copolymers by RAFT mechanism using maleic anhydride as linking agent. *Macromolecules* **2002**, *35* (13), 4888−4893.

(18) He, T.; Zou, Y. F.; Pan, C. Y. Controlled/'living' radical ring-opening polymerization of 5,6-benzo-2-methylene-1,3-dioxepane based on reversible addition-fragmentation chain transfer mechanism. *Polym J* **2002**, *34* (3), 138−143.

(19) Prescott, S. W.; Ballard, M. J.; Rizzardo, E.; Gilbert, R. G. Successful use of RAFT techniques in seeded emulsion polymerization of styrene: Living character, RAFT agent transport, and rate of polymerization. *Macromolecules* **2002**, *35* (14), 5417−5425.

(20) Stenzel, M. H.; Davis, T. P. Star polymer synthesis using trithiocarbonate functional β-cyclodextrin cores (Reversible addition-fragmentation chain-transfer polymerization). *J Polym Sci Pol Chem* **2002**, *40* (24), 4498−4512.

(21) Wang, A. R.; Zhu, S. P. ESR study on diffusion-controlled atom transfer radical polymerization of methyl methacrylate and ethylene glycol dimethacrylate. *Macromolecules* **2002**, *35* (27), 9926−9933.

(22) Takasu, A.; Oishi, Y.; Iio, Y.; Inai, Y.; Hirabayashi, T. Synthesis of aliphatic polyesters by direct polyesterification of dicarboxylic acids with diols under mild conditions catalyzed by reusable rare-earth triflate. *Macromolecules* **2003**, *36* (6), 1772−1774.

(23) Takasu, A.; Iio, Y.; Oishi, Y.; Narukawa, Y.; Hirabayashi, T. Environmentally benign polyester synthesis by room temperature direct polycondensation of dicarboxylic acid and diol. *Macromolecules* **2005**, *38* (4), 1048−1050.

(24) Takasu, A.; Iio, Y.; Mimura, T.; Hirabayashi, T. Room-temperature polycondensation of dicarboxylic acids and diols catalyzed by water-stable lewis acids. *Polym J* **2005**, *37* (12), 946−953.

(25) Takasu, A.; Narukawa, Y.; Hirabayashi, T. Direct dehydration polycondensation of lactic acid catalyzed by water-stable Lewis acids. *J Polym Sci Pol Chem* **2006**, *44* (18), 5247−5253.

(26) Takasu, A.; Tsuruta, H.; Narukawa, Y.; Shibata, Y.; Oshimura, M.; Hirabayashi, T. Dual catalytic system for combination of chain and step polymerizations: Ring-opening polymerization of ε-caprolactone and successive dehydration polycondensation with dicarboxylic acid using the same catalyst. *Macromolecules* **2008**, *41* (13), 4688−4693.

(27) Shibata, Y.; Takasu, A. Synthesis of Polyester Having Pendent Hydroxyl Groups via Regioselective Dehydration Polycondensations of Dicarboxylic Acids and Diols by Low Temperature Polycondensation. *J Polym Sci Pol Chem* **2009**, *47* (21), 5747−5759.

(28) Perrier, S.; Gemici, H.; Li, S. Poly(ethylene glycol) as solvent for transition metal mediated living radical polymerisation. *Chem Commun* **2004**, No. 5, 604−605.

(29) Matsuoka, S.; Kikuno, T.; Takagi, K.; Suzuki, M. Poly(ethylene glycol)-induced acceleration of free radical polymerization of methyl methacrylate: effects of highly viscous solvent and kinetic study. *Polym J* **2010**, *42* (5), 368−374.

(30) Chou, Y.-T.; Lee, W.-R.; Yu, S.-S. Efficient Synthesis of Ultrahigh Molecular Weight Poly(methyl methacrylate) via Visible Light-Induced RAFT Polymerization in Deep Eutectic Solvent. *Macromolecules* **2024**, *57* (19), 9241−9249.

(31) Ueno, Y.; Nakazaki, H.; Onozaki, H.; Tamesue, S. Adhesive Gel System Growable by Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization. *ACS Applied Polymer Materials* **2023**, *5* (1), 983−990.