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A Polyester/Polystyrene Hybrid Connected by Dynamic Covalent Bonds Prepared via Radical Polymerization of Styrene in a "RAFT Gel"

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Abstract

We demonstrate a new method for hybridization of an aliphatic polyester-based gel with a vinyl polymer via dynamic covalent bonds. First, we synthesized poly[(butylene thiomalate)-*co*-(butylene adipate)] ($M_n = 1.1 \times 10^4$; $M_w/M_n = 1.5$) containing pendent mercapto groups by chemoselective dehydration polycondensation of 1,4-butanediol, thiomalic acid, and adipic acid. Next, we cross-linked the polyester chains with 1,1-thiocarbonyldiimidazole to form a reversible addition fragmentation chain-transfer (RAFT) gel, in which trithiocarbonate moiety acted as cross-linker as well as chain transfer agent. The "RAFT gel" was then swollen in vinyl monomers including styrene, methyl methacrylate, *N*-isopropylacryl amide, and methyl acrylate, and styrene was radically polymerized within the gel. A transparent hybrid film was thereby prepared after drying under reduced pressure. Differential scanning calorimetry and dynamic mechanical analysis measurements confirmed that the polyester and polystyrene segments were miscible at segment level (50 μm level). Subsequent aminolysis of the trithiocarbonate moieties of the hybrid gel afforded poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene) ($M_n = 5.7 \times 10^4$, $M_w/M_n = 5.2$). We characterized the molecular weight of the branches ($M_n = 0.57 \times 10^4$, $M_w/M_n = 1.6$) after saponification of the polyester backbone, which was a narrower molecular-weight distribution than that in the absence of the RAFT gel ($M_n = 3.4 \times 10^4$, $M_w/M_n = 3.8$). The results indicate that the trithiocarbonate cross-links in the gel had acted as the chain-transfer agent.

Introduction

Aliphatic polyesters are currently being widely investigated owing to their potential as biomaterials, biodegradable polymers, and environmentally benign materials and as replacements for poly(ethylene) and poly(styrene) (PSt) because of their mechanical strengths and comparable softening temperatures.[1] Additionally, the availability of hybridized aliphatic polyester/vinyl polymers should further increase the number of potential practical use, aiming at coating and adhesive material including biological application. However, because most aliphatic polyesters do not contain pendent reactive centers and polar functional groups, post-polymerizational chemical modification and their miscibility with other types of polymers are difficult.[1]

We have developed methods for the direct polycondensations of dicarboxylic acids with diols at moderate temperatures and catalyzed by rare-earth metals with electron-withdrawing ligands to afford specific aliphatic polyesters with number-average molecular weight (M_n) values $>2.0 \times 10^4$.[2] We have also reported on the kinetically controlled chemoselective polycondensation of monomers with carbon-carbon double bonds,[3] pendant bromo,[3] or hydroxyl[4] groups and on the facile one-step chemoselective polycondensation of diols and the dicarboxylic acid thiomalic acid (TMA) that yield polyesters having pendant mercapto groups ($M_n = 1.4 \times 10^4$, $M_w/M_n = 1.5$) under mild conditions catalyzed by scandium trifluoromethanesulfonate [$Sc(OTf)_3$],[5] for which subsequent cross-linking of the mercapto groups by thiocarbonyldiimidazole (TCDI) produces a "reversible addition fragmentation chain-transfer (RAFT) gel" with trithiocarbonate cross-links as a solid-support RAFT agent.[5] Because aliphatic polyesters are not miscible with vinyl polymers,[6] we developed and report herein a new procedure for the hybridization using dynamic covalent bond of aliphatic polyesters with vinyl polymers via radical polymerization of the vinyl monomer using a RAFT gel as the reaction medium.

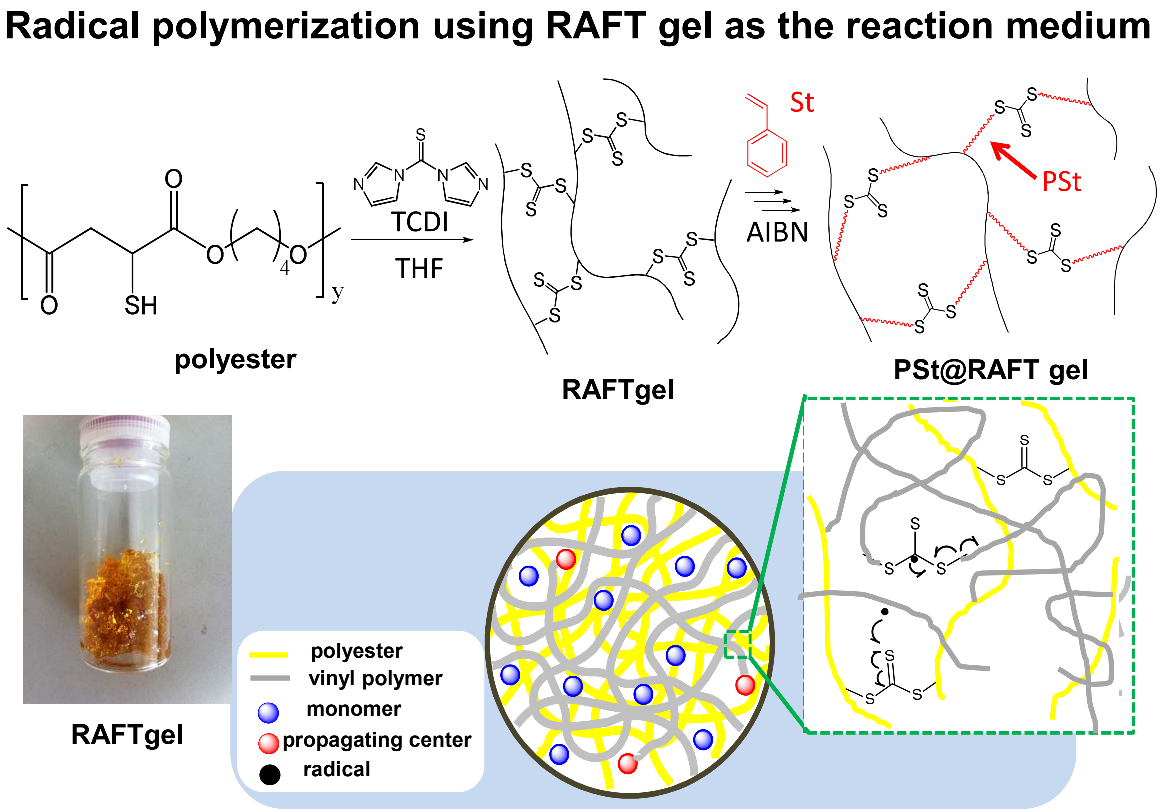


Fig. 1. Preparation of the “RAFT gel” and a schematic showing the radical polymerization of vinyl monomers in the gel, which acts as the reaction medium.

In addition to the recent progress made for other controlled radical polymerizations,[7] the RAFT process has been shown to be quite versatile in that different monomers and reaction conditions can be used. Indeed, with the use of a thiocarbonylthio reactant (S=C(Z)S-R), a reversible chain transfer radical polymerization can be successfully applied to different vinyl monomers.[8] We expected that that will be used to incorporate a vinyl polymer into a “RAFT gel”. For this article, we investigated the radical polymerization of St in a RAFT gel, which served as the gelatinous chain-transfer agent (environment) as a means of hybridizing the two parent polymers, which are otherwise immiscible. In addition, we characterized the morphology (miscibility) and swelling properties of the PSt/polyester hybrid (“PSt@RAFT gel”). Moreover, we transformed to a graft copolymer composed of polyester backbone with one or more branches (graft) composed of PSt by aminolysis of the trithiocarbonante cross-links in the PSt@RAFT gel. Notably, a variety of techniques for synthesizing graft copolymers, have been studied and categorized, i.e., grafting from, grafting onto, and grafting through.[9] We expanded the “grafting from” method using this RAFT gel to synthesize graft copolymers with well-defined structure. We also characterized the molecular weight of the branches after saponification of the polyester backbone, which also confirmed that the trithiocarbonate moiety in the RAFT gel acted as the chain transfer agent.

Although radical polymerizations can be carried out in heterogeneous and homogeneous systems, some studies dealing with radical polymerization used very viscous conditions to accelerate the polymerization rates so as to decrease the extent of the termination reactions.[10] Perrier et al.[10a] were the first to report the use of a polymerization solvent [poly(ethylene glycol) (PEG)]. They assumed that the polarity and metal-coordinating ability of PEG would promote the copper-catalyzed living radical polymerization of methyl methacrylate (MMA) and St. During free radical polymerization, propagating radicals usually terminate via bimolecular reactions. Such terminations are under diffusion control, so that termination is inversely proportional to the viscosity of the polymerization system.[10b,10c] There are many examples to prepare gels using RAFT radical polymerization of bifunctional vinyl monomers,[11-17] in which the simultaneous cross-linking copolymerization[11] or the sequential or step-wise polymerization followed by end-linking,[12-17] and yet, only a few report dealing with "gel-first" strategy.[18,19] J. He et al. reported amphiphilic polymer network by controlled radical polymerization using a nitroxide cross-linker as the “gel-first” strategy.[19] However, the gel consisting of framework and linkers prepared by vinyl monomers. There is no reported case of polymerized vinyl monomer in the polyester gel (frame work) to make polyester/vinyl polymer composites using polymer gels.

Materials and methods

Materials

1,4-Butanediol (1,4-BD), TMA, triethylamine, TCDI, tributylposphine, St, MMA, *N*-isopropylacrylamide (NIPAM), methyl acrylate (MA), and Sc(OTf)$_3$ were purchased from Tokyo Kasei

Co. (Tokyo, Japan). 2,2'-Azobisisobutyronitrile (AIBN), adipic acid (AdA), 1,1-carbonyldiimidazole (CDI), hydrochloric acid (HCl), sodium hydroxide (NaOH) and *n*-propylamine were purchased from Nacalai Tesque (Kyoto, Japan). Chloroform, *n*-hexane, *N,N*-dimethylformamide (DMF), toluene, tetrahydrofuran (THF), 1,4-butanediol, NIPAM, AdA, MMA, MA, and St were purified by distillation or recrystallization before use.

Sc(OTf)$_3$-Catalyzed Ternary Polycondensation of TMA, AdA, and 1,4-BD to Yield Poly[(butylene thiomalate)-*co*-(butylene adipate)]

AdA (7.0 mmol), TMA (1.0 mmol), 1,4-BD (8.0 mmol), and Sc(OTf)$_3$ (8.0×10^{-2} mmol, 0.5 mol%) were stirred at 80 °C (760 mmHg) in a 50-mL round bottom flask until a homogeneous state was observed. The pressure was then gradually decreased to 0.3–3 mmHg until polycondensation commenced (we observed that water was evaporated from the reaction mixture). When the reaction was finished, the polyester percentage yield (>99%) was calculated after subtracting the weight of the catalyst from the total weight of the solid. After precipitating the product from chloroform into *n*-hexane, the yield was 97%. ^{1}H NMR (200 MHz, CDCl$_3$, δ, ppm): 1.65–1.84 (m, -OCH$_2$CH_2, -COCH$_2$CH_2), 2.24–2.44 (br, -SH, -COCH_2CH$_2$), 2.77 [dd, -CH(SH)CH_AH$_B$, J_1 = 16.9 Hz, J_2 = 6.0 Hz], 3.02 [dd, -CH(SH)CH$_A$$H_B$, J_1 = 17.0 Hz, J_2 = 8.9 Hz], 3.67-3.83 [m, -CH(SH)CH$_A$H$_B$], 4.10–4.22 [br, -CH$_A$H$_B$COOCH_2, -CH_2OOCCH(SH)]. FT IR (KBr disk, cm^{-1}): 3456 ($\nu_{\text{O-H}}$), 2926 ($\nu_{\text{C-H}}$), 1739 [$\nu_{\text{C=O}}$(ester)], 1469 ($\delta_{\text{C-H}}$), 1278 and 1133 [$\nu_{\text{C-O}}$(ester)], and 1092 ($\nu_{\text{C-O}}$). In addition to the polycondensation of 1,4-BD, AdA, and TMA, bulk polycondensations of TMA and a diol (*n* = 4, 5, 6, 7, 8, 9, or 10) were performed under the same conditions.[5]

Preparation of the RAFT Gel

Next, poly[(butylene thiomalate)-*co*-(butylene adipate)] (0.81 g, 1.0 mmol), TCDI (0.18 g, 1.0 mmol), and tributylphosphine (24.6 µL, 0.1 mmol) were dissolved into 10 mL of THF contained in a 50-ml round bottom flask. Under nitrogen, the mixture was refluxed for 2 h. When the reaction was finished, the gel was washed with THF by Soxhlet extraction for 12 h to remove unreacted cross-linker and polyester. The purified gel (58% yield) was dried under reduced pressure. FT IR (KBr disk, cm^{-1}): 3460 ($\nu_{O\text{-}H}$), 2958 ($\nu_{C\text{-}H}$), 1733 ($\nu_{C=O}$, ester), 1461 ($\delta_{C\text{-}H}$), 1255 ($\nu_{C=S}$, trithiocarbonate), 1173 [$\nu_{C\text{-}O}$, (ester)], and 1078 ($\nu_{C\text{-}O}$).

Radical Polymerization of St in the RAFT Gel

In a 10-mL round bottom flask, the gel (94 mg, 2.88×10^{-2} unit mmol of trithiocarbonate) was swollen in St (904 mg, 8.64 mmol) containing AIBN (2.36 mg, 1.44×10^{-2} mmol) (600/2/1, $[St]_0/[RAFT\ gel]_0/[AIBN]_0$). Under nitrogen, the RAFT gel swollen with St containing AIBN was held at 110 °C for 3 h, after which the gel was washed with hot THF using Soxhlet extractor to remove any non-crosslinked PSt and St and then dried under reduced pressure to give PSt-RAFT-gel hybrid ("PSt@RAFT gel") in 98 % yield. Conversions were calculated from the ^1H NMR measurements (in $CDCl_3$) after aminolysis of the trithiocarbonate cross-links.

Aminolysis of the "PSt@RAFT Gel" Prepared by Radical Polymerization of St

In a 10-mL round bottom flask PSt@RAFT hybrid (297 mg) was added into 4 mL of THF. To the swollen gel, excess amount of triethylamine (1 mL), and propylamine (0.5 mL) were also added. The mixture was then stirred at room temperature for 12 h, after we observed that the swollen gel turned to be sol which the solution was poured into an excess amount of *n*-hexane to precipitate the product. The graft copolymer was dried under reduced pressure (93% yield; grafting efficiency, 68%). ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.20-1.55 (br, methylene of PSt), 1.56-1.77 (br, $\text{-COOCH}_2\text{C}H_2$, $\text{-OCOCH}_2\text{C}H_2$), 1.78-1.97 (br, methine of PSt), 2.22-2.39 [br, $\text{-OCOC}H_2$, $\text{-CH}_2\text{CHS}H$ (terminus)], 2.94-3.10 (br, -$\text{OCOCHC}H_2$), 3.56-3.74 (br, $\text{-OCOC}H\text{CH}_2$) 3.97-4.17 (br, $\text{-COOC}H_2\text{CH}_2$) 6.28-6.76 (br, aromatic protons) 6.87-7.2 (br, $\text{-CC}H$, aromatic protons).

Saponification of the Graft Copolymer Prepared from PSt@RAFT Gel

The graft copolymer (275 mg) prepared by aminolysis of PSt@RAFT gel was soluble in THF (5.6 g), 1 N $NaOH_{(aq)}$ (0.32 g, 8 mmol), and H_2O (1.00 g), and were stirred together at room temperature for 12 h in a 30-mL round bottom flask. Next, sufficient HCl was added into the flask to neutralize the mixture, after which it was poured into an excess amount of *n*-hexane to precipitate the product. The polymers were isolated by filtration and dried under reduced pressure (60% recovery). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.28-1.57 (br, methylene of PSt) 1.6-1.75 (br, $-CH_2CH_2OH$, $-CH_2CH_2COOH$), 1.78-2.00 (br, methine of PSt), 2.14-2.57 [br, $-CH_2CHSH$ (terminus), $-CH_2CH_2COOH$], 2.94-3.10 (br, $-OCOCHCH_2$), 3.56-3.74 (br, $-OCOCHCH_2$), 3.59-3.80 (br, $-CH_2CH_2OH$), 6.28-6.76 (br, aromatic protons), 6.87-7.2 (br, aromatic protons).

Preparation of the CDI-Crosslinked Gel ("CDI Gel")

In a manner analogous to the preparation of the RAFT gel, poly[(butylene thiomalate)-*co*-(butylene adipate)] (0.81 g, 1.0 mmol), CDI (0.16 g, 1.0 mmol), tributylphosphine (24.6 µL, 0.1 mmol), and 10 mL THF were mixed in a 50-mL round bottom flask and refluxed under nitrogen for 2 h. When the reaction was finished, the gel was washed with THF in a Soxhlet extractor for 12 h. The gel was dried under reduced pressure.

Preparation of the Model RAFT Agent 1

TMA (2.70 g, 18 mmol), methanol (28.8 g, 0.9 mol), and $Sc(OTf)_3$ (442 mg, 0.9 mmol) in a 50-mL round bottom flask at 40 °C for 24 h. Then, the volatile compounds were evaporated under reduced pressure to afford dimethyl thiomalate. Next, we refluxed a mixture of dimethyl thiomalate, TCDI (641.56 mg, 3.6 mmol), THF (12.25 mL), and tributylphosphine (24.6 µL, 0.1 mmol) in a 50-mL round bottom flask at 60 °C for 6 h. The mixture was subjected to reduced pressure, and then **1**, which remained, was purified by column chromatography (eluent, ethyl acetate: hexane = 3/7, vol/vol). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 2.74–2.93 [m, $-CH(SH)CH_AH_B$], 3.00–3.17 [m, $-CH(SH)CH_AH_B$], 3.70 (s, $-CH_2COOCH_3$), 3.79 (s, $-SCHCOOCH_3$), 3.82–3.92 (m, $-SCH$).

Measurements

FT IR spectra were recorded using polymer-containing KBr disks and a JASCO FT/IR-430 spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded at 27 °C using a Bruker DPX200 (200 MHz) spectrometer. The tetramethylsilane resonance was set to 0 ppm, and all other resonances are reported relative to that resonance. The number average molecular weight (M_n) and the polydispersity index (M_w/M_n) of each polymer were determined by size exclusion chromatography (SEC) using a Tosoh DP8020 pump system, an RI (Tosoh RI-8020) detector, a TSK-GEL SUPERMULTIPOREHZ-M column (eluent, chloroform; flow rate, 0.35 mL/min; temperature, 40 °C) or a TSK-GEL α-3000 column (eluent, 0.05% (w/v) LiBr/DMF; flow rate, 0.5 mL/min; temperature, 40 °C; Tosoh Corp.). The columns were calibrated with polystyrene standards. Differential scanning calorimetry (DSC) used a DSC6220S calorimeter (Seiko Instruments Inc., Chiba, Japan), was performed at 10 °C/min, in which a complete temperature cycle, –80 °C to 180 °C to −80 °C, was obtained. The instrument was calibrated using indium and tin samples. Each polyester sample weighted between 5 and 7 mg and was contained in an aluminum pan that was covered with a lid within the calorimeter. The glass-transition temperature (T_g) was taken as the inflection point of the DSC heat-capacity jump. The melting temperature (T_m) was defined as the minimum point in the endothermic trough. The dynamic mechanical properties, the storage modulus (E') and the loss factor (tanδ) of the composites were measured as a function of temperature. The dynamic mechanical analyses were carried out using a DMS200 instrument (SEIKO Electronic Ltd), with the tension mode recorded, a sample size of 40 mm × 5 mm × 0.5 mm, a heating rate of 3˚C /min, a temperature range of –80 ˚C to 120 ˚C, a measuring frequency of 1 Hz, a chuck distance of 20 mm, and an atmospheric air flow rate of 150 ml/min.

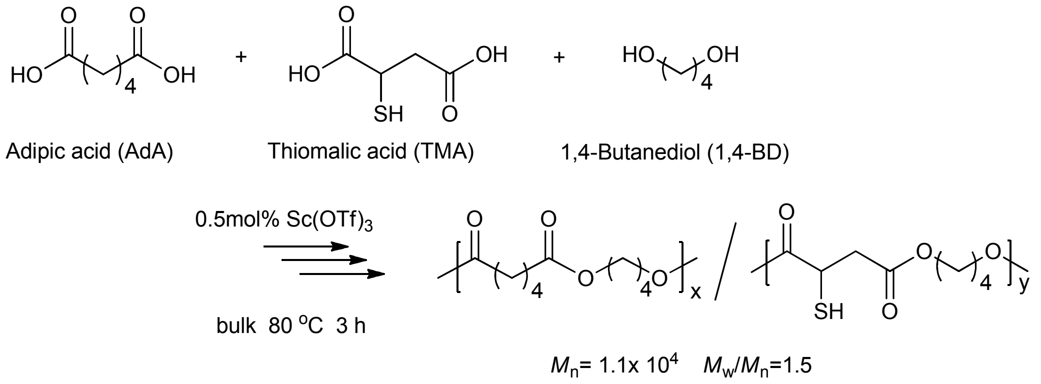
Results and discussion

Preparation of the RAFT Gel. Initially, polycondensations of TMA and a diol, HO-$(CH_2)_n$-OH ($n = 4$, 5, 6, 7, 8, 9, or 10) were performed under reduced pressure (0.3–3.0 mmHg) with $Sc(OTf)_3$ as the catalyst at 80 °C.[5] These polymers were probably formed via step polymerization because their M_n and

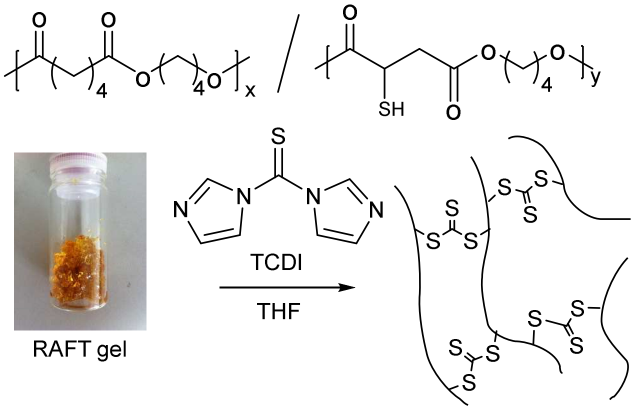
M_w/M_n were those predicted by Flory's theory.[20] All of these polyesters prepared in the presence of $Sc(OTf)_3$ could be cross-linked by TCDI to produce the corresponding RAFT gels, which were swollen in chloroform and DMF but not swollen in some vinyl monomers including St, NIPAM (1,4-dioxane solution), and MMA. For example, bulk polymerization of TMA and 1,4-butanediol (1,4-BD) gave poly(butylene thiomalate). The poly(butylene thiomalate) product had an M_n of 1.39×10^4. After cross-linking using TCDI, because no pendent mercapto groups were found in the IR spectrum of the cross-linked poly(butylene thiomalate), we concluded that all mercapto groups had participated in the cross-linking and that the cross-linking density was too high to allow the gel to be swollen in the presence of any of the vinyl monomers.

Therefore, to decrease the extent of cross-linking, AdA was added as a third component in polycondensation of TMA and 1,4-BD (Scheme 1; $[AdA]_0$: $[TMA]_0$:$[1,4\text{-BD}]_0$=7:1:8; product $M_n = 1.1 \times 10^4$, $M_w/M_n = 1.5$). Given the ^{1}H- and ^{13}C-NMR spectra of poly[(butylene thiomalate)-*co*-(butylene adipate)] (Supporting Information Fig. S1), this polycondensation was also chemoselective. In the ^{1}H-NMR spectrum of poly[(butylene thiomalate)-*co*-(butylene adipate)], peaks that could be ascribed to products of thioesterification or gelation were absent (Figures S1). We then cross-linked the pendent mercapto groups of poly[(butylene thiomalate)-*co*-(butylene adipate)] using TCDI (Scheme 2). The IR spectrum of the crosslinked polymer did not contain a band at 2558 cm^{-1} ascribable to SH stretching but did contain a band at 1255 cm^{-1} ascribable to C=S stretching (Fig. 2). Therefore most of the pendent mercapto groups had been chemically-modified (cross-linked), in which we consider mono functionalization of TCDI with mercapto group should have also occured.

Scheme 1. Ternary polycondensation of thiomalic acid, adipic acid, and 1,4-butanediol catalyzed by $Sc(OTf)_3$.



Scheme 2. Subsequent cross-linked to afford a gelatinous RAFT agent (RAFT gel).



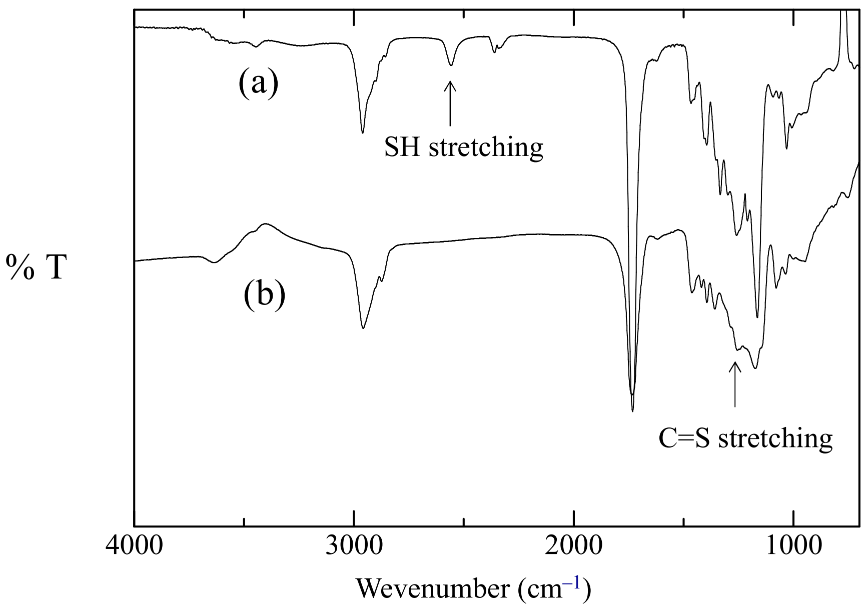


Fig. 2. IR spectra of poly[(butylene thiomalate)-*co*-(butylene adipate)] (a) before cross-linking and (b) after cross-linking to form the RAFT gel.

Radical Polymerization of St in the RAFT Gel to Produce "PSt@RAFT Gel" Hybrid. We next examined if a miscible hybrid of PSt and the RAFT gel via covalent bond ("PSt@RAFT gel") could be established by radical polymerization of St, with AIBN as the initiator, in the RAFT gel (Table 2). After radical polymerization, we washed PSt@RAFT gel using chloroform and we confirmed that homo polystyrenes were not obtained in the filtrate. This result indicated that most St monomers were inserted into the RAFT gel framework. The ratio of the final gel dry mass after polymerization divided by that before the polymerization (run 4 in Table 2) is 3.9. The RAFT gel swelled in the presence of vinyl monomers including St, MMA, NIPAM dioxane solution, and MA as well as organic solvents, THF, chloroform, and toluene (Table 1). The equilibrium swollen state for a given solvent/RAFT gel mixture was defined as W_s/W_0, where W_s and W_0 are the weights of the swollen and dry states of the gel, respectively. The W_s/W_0 values are 6 (THF), 11 (chloroform), 4 (toluene), 5 (MMA), and 5 (St; Table 1). After radical polymerization of St at 110 °C for 3 h in the RAFT gel, the W_s/W_0 values of the PSt@RAFT gel hybrid were 8 (THF), 22 (chloroform), 7 (toluene), 7 (MMA), and 10 (St) (Table 1). These results indicate that the trithiocarbonate moiety, acting as a chain-transfer agent, promoted the covalent insertion of PSt segments into the RAFT gel, which thereby decreased the overall density of cross-link in the gel.

Scheme 3. Preparation of the polyester/PSt Hybrid (PSt@RAFT Gel) by radical polymerization of St with the RAFT gel acting as the reaction medium.

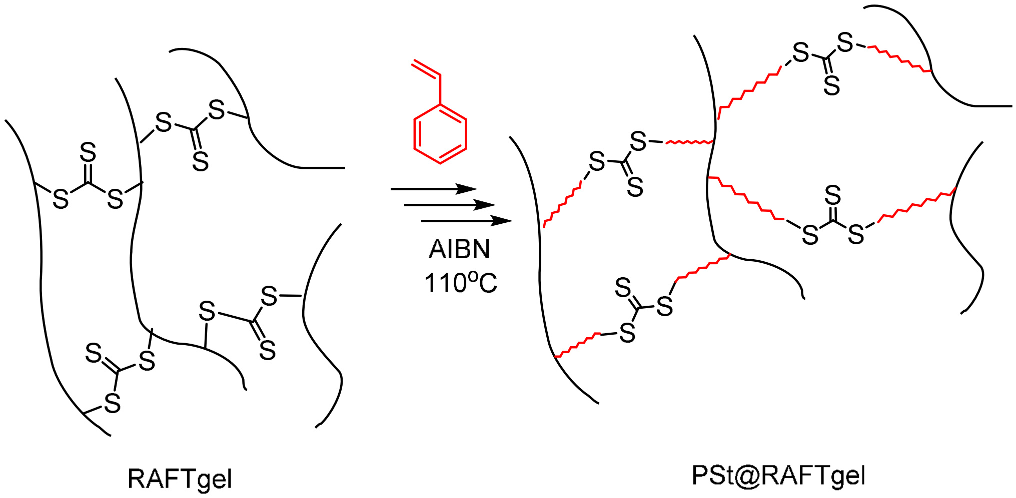


Table 1. Swelling Ratios of the RAFT and CDI Gels before and after Radical Polymerization of Styrene.[a]

Sample	Solvent			Monomer	
	THF	$CHCl_3$	Toluene	MMA	St
RAFT gel	6	11	4	5	5
PSt@RAFT gel	8	22	7	7	10
CDI gel	3	9	3	3	6
PSt@CDI gel	4	9	3	3	5

[a] The swelling ratio is defined as W_s/W_0 with W_0 and W_s the weight of the gel before and after swelling, respectively.

After drying the PSt@RAFT gel under vacuum, a transparent polymeric hybrid was obtained (Fig. 3, left), indicating that the polystyrene segments were dispersed within the polyester matrix and that phase separation had not occur on the 500–700-nm scale. To investigate the miscibility of PSt@RAFT gel hybrid, dynamic mechanical measurements were acquired (Fig. 4). The tanδ-temperature profile of the RAFT gel hybrid contains a unimodal peak centered at –40 °C reflecting the T_g of poly[(butylene thiomalate)-*co*-(butylene adipate)]; whereas, that of PSt@RAFT gel hybrid is centered at 1.0 °C. In the DSC measurement, the T_g value for the RAFT gel is –49 °C and is –3 °C for PSt@RAFT gel hybrid, in which T_m was not observed, although the parent RAFT gel showed a endothermic peak at 42 °C (Fig. 5). In the Figure 5 (red line), as a trace inflection point around –50 °C was also confirmed, we can conclude that micro domain consisting of polyester segments exists, which also induced unimodal but broad tan δ curve of PSt@RAFT gel hybrid (red line in Fig. 4). The calorimetry results support the dynamic mechanical measurements with both types of measurements indicating the excellent miscibility of PSt in the RAFT gel. Conversely, a physical blend (50/50, w/w) of poly[(butylene thiomalate)-*co*-(butylene adipate)] and poly(styrene) ($M_n = 3.4 \times 10^3$, $M_w/M_n = 3.8$) prepared by radical polymerization was turbid (Figure 3, right) and has two separate T_g values (–40 °C and 103 °C), indicating that RAFT gel is essential to form a miscible polyester/polystyrene hybrid (Fig. S2).

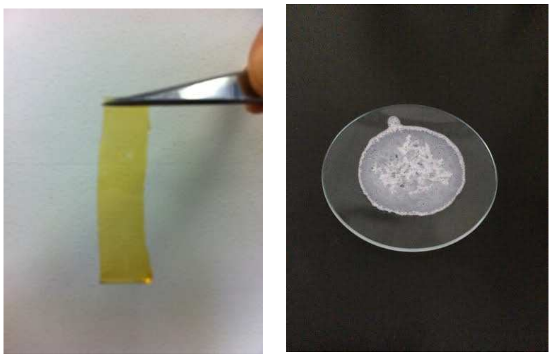


Fig. 3. Photographs of PSt@RAFT gel hybrid (left) and the physical blend (50/50, w/w) of poly[(butylene thiomalate)-*co*-(butylene adipate)] and poly(styrene) ($M_n = 3.4 \times 10^3$, $M_w/M_n = 3.8$) (right).

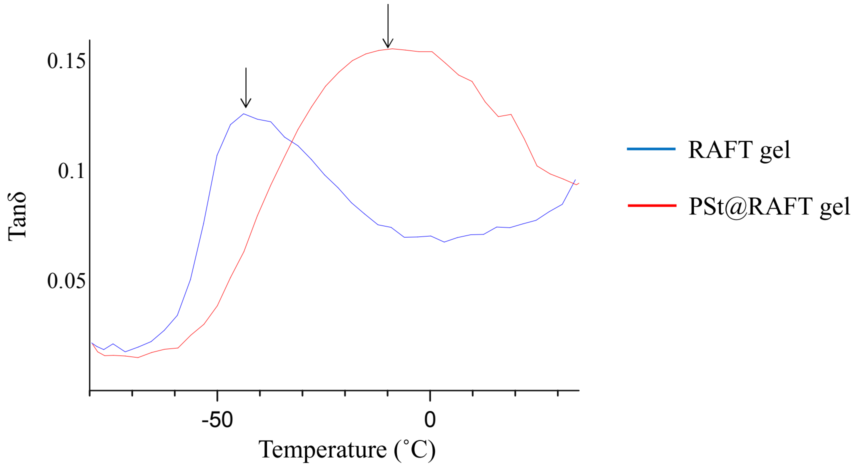


Fig. 4. Temperature dependence of tanδ for RAFT gel (blue) and for PSt@RAFT gel (red). Heating rate, 2 °C /min.

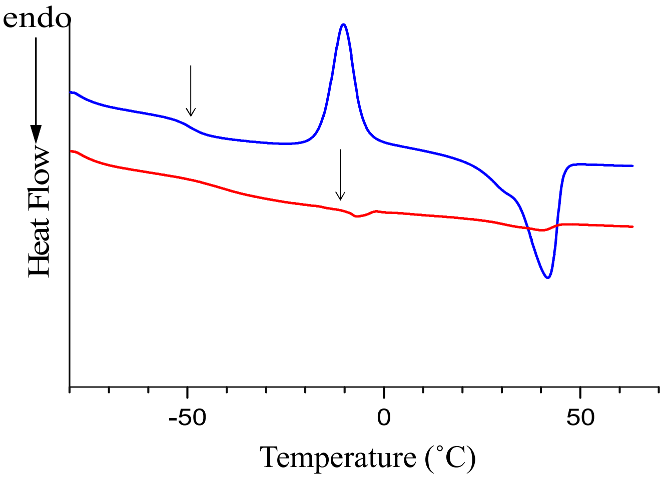


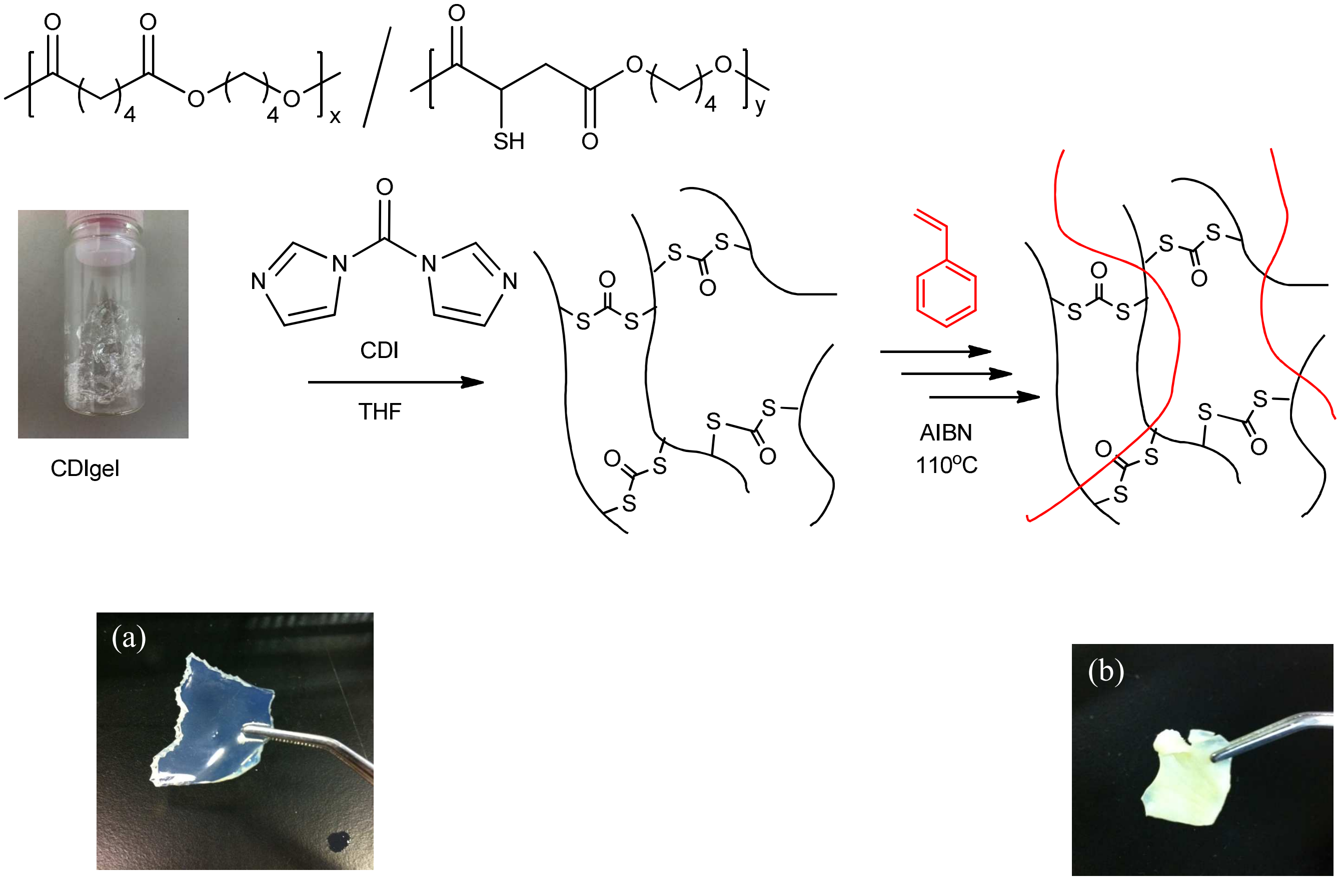
Fig. 5. DSC traces of PSt@RAFT gel hybrid (red line) and RAFT gel (blue line). Heating rate, 10 °C/min.

Preparation of a CDI-Crosslinked Gel ("CDI Gel") and the Radical Polymerization of St in the Gel. As a control, we cross-linked poly[(butylene thiomalate)-*co*-(butylene adipate)] using CDI to make not trithiocarbonate but carbonylthio cross-links [CDI-crosslinked gel ("CDI gel")]. The preparation of the CDI gel was otherwise the same as that of the RAFT gel. The IR spectrum of the CDI gel indicated that no free mercapto groups were present. The gel could be swollen in styrene, THF, chloroform, and toluene. The W_s/W_0 values for the CDI gel are: 3 (THF), 9 (chloroform), 3 (toluene), 3 (MMA), and 6 (styrene) (Table 2). After radical polymerization of styrene ($[St]_0/[RAFT\ gel]_0/[AIBN]_0$=600/2/1) at 60

°C for 3 h in the CDI gel, the W_s/W_0 values were not change from the parent CDI gel as follows: 4 (in tetrahydrofuran), 9 (in chloroform), 3 (in toluene), 3 (MMA), 5 (styrene) (Table 1).

After drying the CDI-PSt hybrid gel (PSt@CDI gel) under vacuum, a turbid polymeric hybrid was obtained (Scheme 4(b), right photograph), indicating that phase separation had occurred on the >500-nm scale. To investigate the morphology of this material, DSC measurements were made after extraction of the system with THF to remove PSt homopolymer (Figure S3), the T_g value of the CDI gel (–43 °C) did not shift to higher temperature (–48 °C). These results agree with the visual observation that the gel was turbid and indicate that PSt was not miscible in the CDI gel.

Scheme 4. Preparation of the CDI gel and radical polymerization of St in the CDI gel acting as the reaction medium to fabricate PSt@CDI gel hybrid [the pictures of CDI gel (a) before and (b) after polymerization of St].



Aminolysis of PSt@RAFT Hybrid Gel to Prepare the Graft Copolymer, Poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene). To determine if the trithicarbonate moiety in the RAFT gel had acted as the chain transfer agent, we subjected PSt@RAFT gel hybrid to propylamine-catalyzed aminolysis, which proceeded smoothly and afforded a graft copolymer as a sol-like material (93% yield; grafting efficiency, 68%). The structure of poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene) was confirmed by ^{1}H NMR spectrum (Fig. S4). The SEC chromatograph (Fig. 6) of the copolymer shows a remarkable broadening of its elution behavior compared with that of parent poly[(butylene thiomalate)-*co*-(butylene adipate)], suggesting that the trithiocarbonate moiety in the RAFT gel had acted as the chain transfer agent and that aminolysis had afforded poly[(butylene thiomalate)-*co*- (butylene adipate)]-*graft*-poly(styrene) ($M_n = 5.7 \times 10^4$, $M_w/M_n = 5.2$).

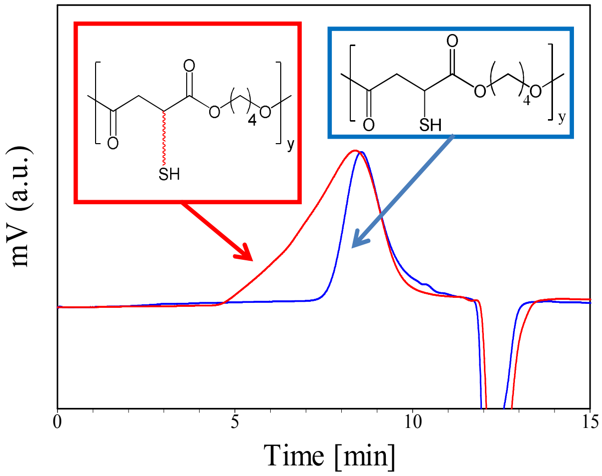
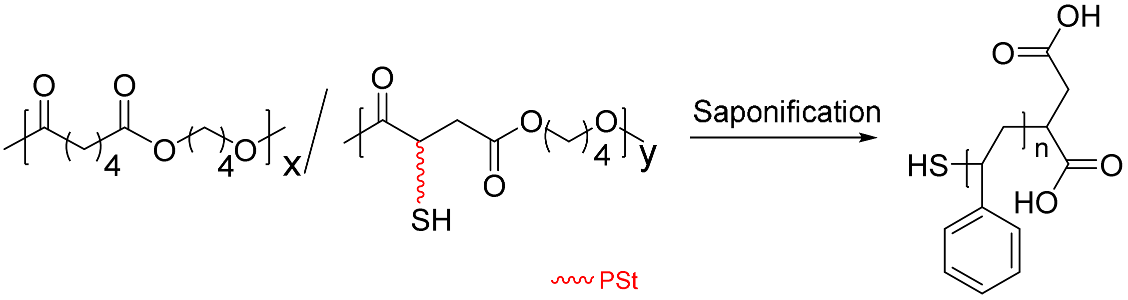


Fig. 6. SEC curves of poly[(butylene thiomalate)-*co*-(butylene adipate)]-*graft*-poly(styrene) prepared by aminolysis of PSt@RAFT gel (red) and of the parent poly[(butylene thiomalate)-*co*-(butylene adipate)] (blue).

Scheme 5. Saponification of the graft copolymer to characterize the PSt branches.



Characterization of the Graft Copolymer PSt Branches after Saponification. Finally, to characterize the graft copolymer PSt branches, the graft copolymer was subjected to saponification (Scheme 5; Table 2). The saponification was confirmed by ^{1}H NMR spectrum (Figure S5). In our previous paper,[5] we already tried radical polymerization of St but molecular weight control was difficult (M_n = 3.7 × 10^4, M_w/M_n = 3.0) because cross linking density of the RAFT gel was too high to be swollen with vinyl monomers including St. Therefore, the chain transfer occurred only on the solid RAFT-gel surface. In this paper, therefore, it was very important to characterize polystyrene (PSt) actually inserted in to the RAFT gel via -SCS_2 linkage, in which we did the saponification of the polyester back bone. The isolated PSt branches had a smaller molecular weight and a narrower molecular-weight distribution (run 2, M_n = 0.57 × 10^4, M_w/M_n = 1.6) than did those for a preparation in which the RAFT gel had been omitted (run 1, M_n = 3.4 × 10^4, M_w/M_n = 3.8), indicating that the gel had acted as the reaction platform and as a chain-transfer agent. Extension of the reaction time from 3 h to 6h increased the conversion to 46 % (run 3), but increase of the RAFT gel content ($[St]_0/[\text{chain transfer agent}]_0/[AIBN]_0$=600/7/1) did not show remarkable improvement (run 4, M_w/M_n = 1.5). For the PSt@CDI gel (run 5), the molecular weight of PSt was apparently more difficult to control as its polydispersity index was larger (run 5, M_n = 1.8 × 10^4, M_w/M_n = 3.0).

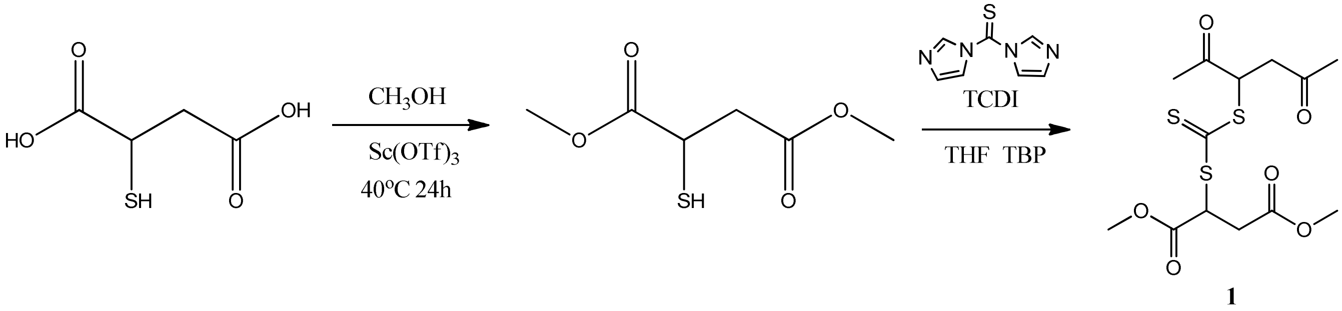
Table 2. Radical Polymerization of St in RAFT Gel and Characterization of Poly(styrene) Branches from Graft Copolymers after Saponification.[a]

run	chain transfer agent	$[St]_0/[\text{chain transfer agent}]_0/[AIBN]_0$ molar ratio	time h	conversion[b] %	$M_{n(\text{theory})} \times 10^{-4}$	after saponification $M_n{}^c \times 10^{-4}$ Da	after saponification $M_w/M_n{}^c$
1	RAFT gel	600/0/1	3	68	2.1	3.4	3.8
2	RAFT gel	600/2/1	3	35	0.55	0.57	1.6
3	RAFT gel	600/2/1	6	46	0.72	1.17	1.8
4	RAFT gel	600/7/1	3	43	0.2	0.31	1.5
5	CDI gel	600/2/1	3	60	0.94	1.8	3.0
6	**1**	600/10/1	3	45	0.15	4.5	2.6

[a] All radical polyesters were prepared by bulk polymerization at 110 °C. [b] As determined from the corresponding ^{1}H-NMR spectra. Solvent, $CDCl_3$. [c] Determined by SEC with $CHCl_3$ as the eluent. Values are reported relative to those of poly(styrene) standards.

In order to evaluate the ability of the trithiocarbonate moiety to act as a chain transfer agent, we prepared the model RAFT agent **1** using TCDI and dimethyl thiomalate (1/2, mol/mol) simulated for the structure of RAFT gel (Scheme 6). With **1** substituting for the original RAFT gel during the polymerization of St ($[St]_0/[[\mathbf{1}\text{ OR RAFT gel}]]_0/[AIBN]_0 = 600/10/1$), the M_n and M_w/M_n values of the recovered PSt were 4.5 × 10^4 and 2.6, respectively; therefore, it appears that the molecular weight of PSt is better controlled in the RAFT gel (runs 2–4) than the bulk state (run 6).

Scheme 6. Preparation of the Model RAFT Agent 1.



For this article, we demonstrated the chemoselective polycondensation and subsequent cross-linking of the polyester poly[(butylene thiomalate)-*co*-(butylene adipate)] to prepare a RAFT gel containing trithiocarbonate moieties as cross-linkers. We then performed the radical polymerization of

St using the RAFT gel as the reaction medium. In addition, we determined the miscibility and swelling properties in vinyl monomers as well as organic solvents of the PSt@RAFT gel. The fundamental results described herein can be used to synthesize other novel polyester/vinyl polymer hybrids.

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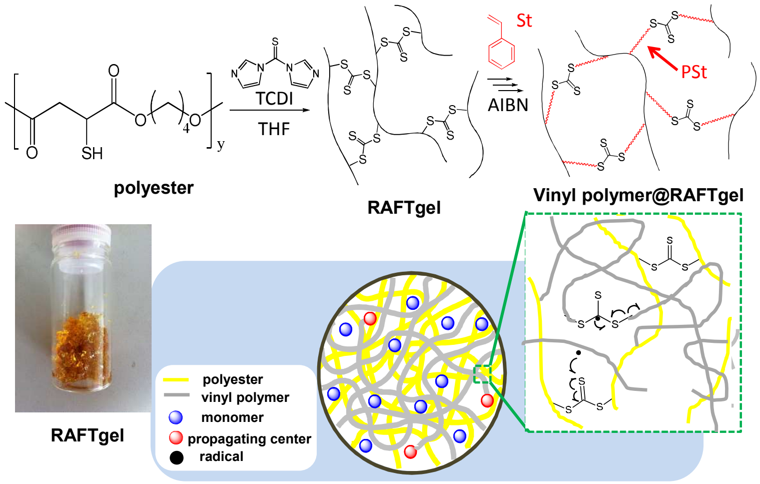
Graphical and Textual Abstract
for Polymer Chemistry

A Polyester/Polystyrene Hybrid Connected by Dynamic Covalent Bonds Prepared via Radical Polymerization of Styrene in a "RAFT Gel"

*Daiki Yoshimura, ShinjiYamada, Akinori Takasu**

Radical polymerization using RAFT gel as the reaction medium



We demonstrate a new method for hybridization of an aliphatic polyester-based gel with a vinyl polymer via dynamic covalent bonds. First, we synthesized polyester containing pendent mercapto groups by chemoselective dehydration polycondensation of 1,4-butanediol, thiomalic acid, and adipic acid. Next, we cross-linked the polyester chains with 1,1-thiocarbonyldiimidazole to form a reversible addition fragmentation chain-transfer (RAFT) gel, in which trithiocarbonate moiety acted as cross-linker as well as chain transfer agent. The "RAFT gel" was then swollen in vinyl monomers, and styrene was radically polymerized within the gel. Differential scanning calorimetry and dynamic mechanical analysis measurements confirmed that the polyester and polystyrene segments were miscible at segment level.