Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 8519–8523 **8519**
DOI: 10.1021/ma101501r

Preparation of Gelatinous Reversible Addition−Fragmentation Chain Transfer Agents "RAFT Gel" via Chemoselective Polycondensations of a Dicarboxylic Acid Containing a Mercapto Group and Diols

Ken Yamamoto and Akinori Takasu*

Department of Frontier Materials, Graduate School of Engineering, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan

Received July 6, 2010; Revised Manuscript Received September 5, 2010

ABSTRACT: The results of the model reactions with ethanol or 2-propanethiol and acetic acid showed that the dehydration condensation of the ethanol reaction was chemoselective and that thioesterification did not occur under the conditions used. We synthesized polyesters with pendant mercapto groups by dehydration polycondensations of diols and TMA, and as with the model reactions, esterification proceeded chemoselectively and thioesterification did not occur. The pendant mercapto-containing polyesters had M_ns $> 1.0 \times 10^4$. We also demonstrated that the pendant mercapto groups could be chemically modified by glycosylation or cross-linked by TCDI to synthesize a gelatinous RAFT agent as a first example, which acted as a RAFT agent in a radical polymerization to afford poly(methyl methacrylate) with a narrow molecular weight distribution ($M_n = 8.5 \times 10^4$, $M_w/M_n = 1.47$). These procedures could be used to produce new types of polyesters from monomers that differ in chirality and functionality and also nanoscale-reactive media containing RAFT agent as a cross-linker for controlled radical polymerization of vinyl monomers.

Introduction

Among the available chain polymerization methods,[1] the RAFT (reversible addition−fragmentation chain transfer) process is quite versatile in that different monomers and reaction conditions can be used. Indeed, with the appropriate choice of the thiocarbonylthio reactant (S=C(Z)S−R), the reversible chain transfer polymerization can be successfully applied to many different vinyl monomers.[2]

The development of step polymerization reactions has lagged in comparison with the remarkable progress made for chain polymerizations. For example, although the synthesis and properties of aliphatic polyesters have been widely investigated in recent years because they have potential as biomaterials, biodegradable polymers, and environmentally benign materials,[3] their synthetic procedures require severe reaction conditions (200−250 °C),[4] which prevents the use of thermally labile functionalized monomers. Additionally, because most aliphatic polyesters are hydrophobic, they cannot be functionally modified after polymerization as they lack the necessary reactive centers.

We have reported the direct polycondensation of dicarboxylic acids and diols at moderate temperatures catalyzed by rare-earth metals ligated to electron-withdrawing groups that afforded aliphatic polyesters with number-average molecular weights (M_ns) $> 1.0 \times 10^4$.[5] This polycondensation system can use thermally unstable monomers that contain a carbon−carbon double bond and a bromine.[6] Furthermore, we have also shown that chemoselective polycondensation of diols and dicarboxylic acids that contain secondary hydroxyl groups afford hydrophilic polyesters with pendant secondary hydroxyl groups under kinetic control.[7]

Recently, others have examined the potential of mercapto-containing compounds (thiol−enes and thiol−ynes click reactions) as synthetic tools[8] because mercapto moieties are highly reactivity, and their work prompted us to attempt the synthesis of macromolecules that contain pendant mercapto groups. Seabra et al. reported polycondensations of a dicarboxylic acid that contained a pendant mercapto group with diols that were catalyzed by concentrated hydrochloric acid at 120 °C.[9] However, they could not characterize the polyesters, e.g., by ^{1}H NMR spectroscopy, and they did not report polymer yields. Moreover, Matsumura et al. reported enzyme-catalyzed chemoselective polycondensations that gave polyesters with pendant mercapto groups via transesterification of dimethyl mercaptosuccinate.[10] However, the extent of polymerization for these polyesters was not satisfactory [molecular weights (M_w) $< 14\,000$ Da), molecular weight distributions (M_w/M_n) of 2.3−3.9, 48 h reaction time], and the types of monomers that can be used is limited by the enzymes' ability to recognize and react with the monomeric substrate.

For this article, we describe a facile one-step synthesis of polyesters that have pendant mercapto groups that relies on chemoselective polycondensation and uses diols and the pendant mercapto-containing dicarboxylic acid, thiomalic acid (TMA), as reactants. The syntheses proceeded under mild conditions with scandium trifluoromethanesulfonate [Sc(OTf)$_3$] as the catalyst. We were able to chemically modify (glycosylation) or, using thiocarbonyldiimidazole (TCDI), cross-link the polymers.

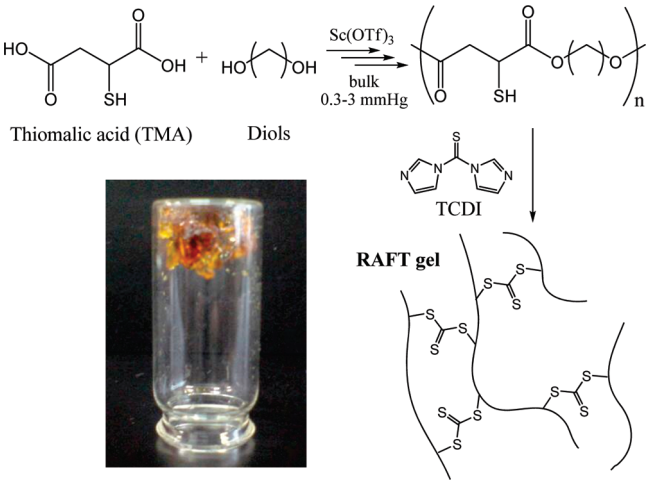
Experimental Section

Materials. Thiomalic acid (TMA), adipic acid (Ada), 1,4-butanediol (1,4-BD), 1,5-pentanediol (1,5-PD), 1,6-hexanediol (1,6-HD), 1,7-heptanediol (1,7-HD), 1,8-octanediol (1,8-OD), 1,9-nonanediol (1,9-ND), 1,10-decanediol (1,10-DD), 3-methyl-1,5-pentanediol (MPD), 2-propanethiol, scandium trifluoromethanesulfonate [Sc(OTf)$_3$], and 3-butene-1-ol were purchased from Tokyo Kasei Co. (Tokyo, Japan). 2,2′-Azodiisobutyronitrile (AIBN) was purchased from Nacalai Tesque (Kyoto, Japan). Chloroform, *n*-hexane, *N,N*-dimethylformamide (DMF),

*To whom correspondence should be addressed: Tel +81-52-735-7159; Fax +81-52-735-5342; e-mail takasu.akinori@nitech.ac.jp.

Published on Web 09/24/2010

Scheme 1. Direct Polycondensation of Thiomalic Acid and Diols Catalyzed by $Sc(OTf)_3$ and Subsequent Cross-Linking to Afford Gelatinous RAFT Agents ("RAFT Gels")



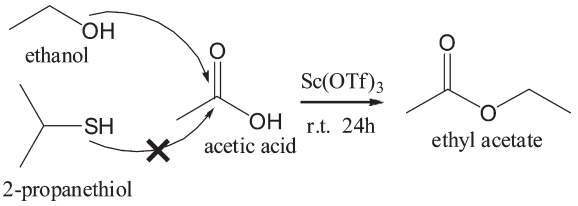
acetic acid, ethanol, toluene, tetrahydrofuran (THF), methyl methacrylate (MMA), and styrene (St) were purified by distillation before use.

Model Chemoselective Esterification of Acetic Acid and Ethanol in the Presence of 2-Propanethiol. In a 10 mL round-bottom flask, acetic acid (2.0 mmol), ethanol (2.0 mmol), 2-propanethiol (1.0 mmol), and $Sc(OTf)_3$ (0.025 mmol) were added and stirred at room temperature for 24 h. The esterification of ethanol and chemoselectivity in the reaction determined by ^{1}H NMR were 54.9% and >99%, respectively.

$Sc(OTf)_3$-Catalyzed Chemoselective Polycondensation of TMA and 1,4-BD. A typical polycondensation procedure is as follows. In a 10 mL round-bottom flask, TMA (2.0 mmol), 1,4-BD (2.0 mmol), and $Sc(OTf)_3$ (0.01 mmol) were stirred at 80 °C (760 mmHg) until a homogeneous state was observed. The pressure was gradually decreased to 0.3−3 mmHg, at which point polycondensation commenced. When the reaction was finished, the yield of the polyester was calculated by subtracting the known weight of the catalyst from the total weight of the solid present (<99%). After precipitating the product from $CHCl_3$ into *n*-hexane, the yield was (97%). ^{1}H NMR (200 MHz, $CDCl_3$, δ, ppm): 1.65−1.84 (4H, m, $-OCH_2CH_2$), 2.22 (1H, d, 9.6 Hz, $-SH$), 2.77 (1H, dd, $-CH(SH)CH_ACH_B$, J_1 = 16.9 Hz, J_2 = 6.0 Hz), 3.02 (1H, dd, $-CH(SH)CH_ACH_B$, J_1 = 17.0 Hz, J_2 = 8.9 Hz), 3.67−3.83 (1H, m, $-CH(SH)CH_ACH_B$), 4.10−4.16 (2H, m, $-CH_ACH_BCOOCH_2$), 4.16−4.22 (2H, br, $-CH_2OOCCH(SH)$). ^{13}C NMR (150 MHz, $CDCl_3$, ppm): 25.2 ($-OCH_2CH_2$), 36.2 ($-CH(SH)CH_2$), 39.8 ($-CH(SH)CH_2$), 64.6 ($-CH_2OOCCH(SH)$), 65.2 ($-CH_2COOCH_2$), 170.5 ($-OOCCH(SH)$), 172.5 ($-CH_2COO$). FT IR (KBr disk, cm^{-1}): 3456 (ν_{O-H}), 2926 (ν_{C-H}), 1739 [$\nu_{C=O}$(ester)], 1469 (δ_{C-H}), 1278 and 1133 [ν_{C-O}(ester)], and 1092 [ν_{C-O}].

Glycosidation of Poly(buthylene thiomalate) Having Pendant Mercapto Groups. In a 10 mL round-bottom flask, poly(buthylene thiomalate) (0.06 g, 0.27 mmol), GlcNAc(Ac)$_3$-β-D-*n*-butenyl (0.16 g, 0.41 mmol), and AIBN (4.5 mg, 0.027 mmol) were dissolved in 1 mL of THF. Under nitrogen, the mixture was stirred at 60 °C for 3 h. The reaction mixture was poured into an excess of *n*-hexane to precipitate out the product. The purified polymer was dried under reduced pressure. ^{1}H NMR (200 MHz, $CHCl_3$, δ, ppm): 1.64−1.75 ($-OCH_2CH_2$), 1.75−1.84 (sugar$-OCH_2CH_2$), 1.84−1.90 ($-SCH_2CH_2$), 1.90−2.13 ($OCOCH_3$), 2.60−2.77 ($-CH(SH)CH_ACH_B$ and $-SCH_2$), 2.89−3.11 ($-CH(SH)CH_ACH_B$), 3.47−3.63 (H-5), 3.66−3.81 (H-2 and $-CH(SH)CH_ACH_B$), 3.83−4.00 (sugar$-OCH_2$), 4.06−4.40 ($-CH_ACH_BCOOCH_2$, $-CH_2OOCCH(SH)$ and $-CH_2OCOCH_3$), 4.67−4.74 (H-1), 4.99−5.15 (H-4), 5.24−5.37 (H-3), 5.52(1H, d, 8.1 Hz, $-NHCOCH_3$).

Scheme 2. Model Esterification of Acetic Acid and Ethanol in the Presence of 2-Propanethiol, Catalyzed by $Sc(OTf)_3$ at Room Temperature



Preaparation of RAFT Gels. First, we prepared ternary polyester of AdA and TMA ($[AdA]_0/[TMA]_0$ = 3/1) with 1,4-BD. In a 10 mL round-bottom flask, 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 in 10 mL of THF. Under nitrogen, the mixture was refluxed for 2 h. When the reaction was finished, gels were washed with THF by a Soxhlet extractor for 12 h. The purified gels were dried under reduced pressure (57.8% yield). FT IR (KBr disk, cm^{-1}): 3460 (ν_{O-H}), 2958 (ν_{C-H}), 1733 [$\nu_{C=O}$(ester)], 1461 (δ_{C-H}), 1255[$\nu_{C=S}$(trithiocarbonate)] and 1173 [ν_{C-O}(ester)], and 1078 [ν_{C-O}].

Radical Polymerization of MMA Using RAFT Gels. In a 10 mL round-bottom flask, RAFT gels (42.35 mg, 0.05 mmol) were swollen to THF (2.0 mL). MMA (1.06 mL, 10.0 mmol) and AIBN (4.1 mg, 0.025 mmol) were added in the mixture. Under nitrogen, the swollen gel was heated at 60 °C for 2 h. When the reaction finished, the gel was washed with THF, and then the filtrate was poured into an excess of methanol to precipitate out the product. The purified polymer was dried under reduced pressure (80% yield).

Radical Polymerization of St Using RAFT Gels. In a 10 mL round-bottom flask, RAFT gels (24.56 mg, 0.03 mmol) were swollen to St (1.0 mL, 8.64 mmol). AIBN (2.4 mg, 0.015 mmol) was added in the mixture. Under nitrogen, the mixture was heated at 110 °C for 2 h. When the reaction was finished, the polymer was extracted from the gel by washing with chloroform and successive evaporation.

Measurements. FT IR spectra were recorded in KBr disks using a JASCO FT/IR-430 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured at 27 °C using a Bruker DPX200 (200 MHz) or Bruker DRX600 (600 MHz) spectrometer. All chemical shifts were expressed as a downfield from tetramethylsilane (TMS). The number-average molecular weights (M_n) and the polydispersity index (M_w/M_n) of the polymers were estimated by size exclusion chromatography (SEC) calibrated with polystyrene standards using a pump system of Tosoh DP8020 with an RI (Tosoh RI-8020) detector TSK-GEL SUPERMULTIPOREHZ-M column (eluent, chloroform; flow rate, 0.35 mL/min; temperature, 40 °C) or TSK-GEL α-3000 column [eluent, DMF + LiBr (0.05 wt %); flow rate, 0.5 mL/min; temperature, 40 °C; Tosoh Corp.]. These solvents were purified by distillation before use. Differential scanning calorimetry (DSC), using a DSC6220S calorimeter (Seiko Instruments Inc., Chiba, Japan), was performed from −80 to 180 °C, with the temperature increased or decreased at a rate of 10 °C/min. The instrument was calibrated using indium and tin samples. For all experimental samples, a complete temperature heating cycle from −80 to 180 °C and back to −80 °C was obtained. Each sample weighted between 4 and 6 mg and was placed into 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 corresponding heat capacity jump of the DSC trace. The melting temperature (T_m) was defined as the minimum point of the endothermic trough.

Results and Discussion

As a model for polyesterification, the direct esterification of ethanol by acetic acid (1 mol equiv) was carried out in bulk using

Table 1. Direct Polycondensations of Thiomalic Acid and Diols under Reduced Pressure[a]

run	diol	catalyst	mol %	time (h)	yield[b] (%)	$M_n \times 10^{-4}$ [c] (M_w/M_n)[c]	T_g (°C)
1	1,4-butanediol	none	0.25	3	*d*		
2	1,4-butanediol	$Sc(OTf)_3$	0.25	3	97	1.39 (1.5)	−21
3	1,5-pentanediol	$Sc(OTf)_3$	0.25	3	98	1.52 (1.5)	−25
4	1,6-hexanediol	$Sc(OTf)_3$	0.25	3	>99	1.42 (1.6)	−30
5	1,7-heptanediol	$Sc(OTf)_3$	0.25	3	>99	1.55 (1.6)	−35
6	1,8-octanediol	$Sc(OTf)_3$	0.25	3	99	1.32 (1.7)	−39
7	1,9-nonanediol	$Sc(OTf)_3$	0.25	3	>99	1.42 (1.6)	−42
8	1,10-decanediol	$Sc(OTf)_3$	0.25	3	>99	1.62 (1.8)	−43
9	3-methyl-1,5-pentanediol	$Sc(OTf)_3$	0.25	3	98	1.59 (1.7)	−22

[a] All runs are performed by bulk condensation under reduced pressure (0.3−3.0 mmHg) at 80 °C. [b] Without reprecipitation. [c] Determined by SEC measurement in DMF relative to poly(styrene)s. [d] No polymerization.

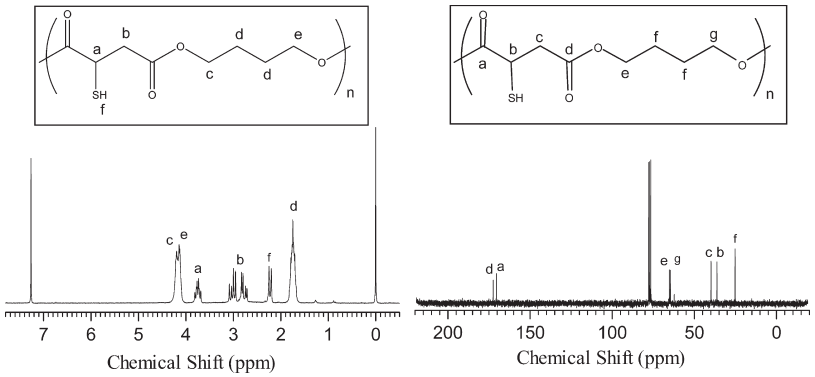


Figure 1. ^1H and ^{13}C NMR spectra of poly(buthylene thiomalate) (in $CDCl_3$, 27 °C, TMS, 200 MHz).

0.5 mol % $Sc(OTf)_3$ at room temperature for 24 h without removing residual water. The extent of the conversion, as determined by ^1H NMR spectroscopy, was 58%. Conversely, when 2-propanethiol was reacted with acetic acid, thioesterification scarcely took place. To determine which of the nucleophilic groups reacted more rapidly with acetic acid, we ran the reaction using a 1:1 (mol/mol) mixture of ethanol and 2-propanethiol in the presence of 2 mol equiv of acetic acid and 0.5 mol % $Sc(OTf)_3$. Interestingly, esterification of ethanol (55% conversion) proceeded chemoselectively as thioesterification of the mercapto group did not occur, even though the mercapto group is more nucleophilic than is the hydroxyl group. We assume that chemoselectivity occurred because the reactions were thermodynamically controlled.

Bulk polycondensations of TMA and diols (n = 4, 5, 6, 7, 8, 9, 10) were carried out under reduced pressure (0.3−3.0 mmHg) with $Sc(OTf)_3$ as the catalyst at 80 °C (Table 1). The results suggested that the polymers was formed via step polymerization because their molecular weight distributions were those predicted by Flory's theory.[11] For all runs made in the presence of $Sc(OTf)_3$, polymeric solids were obtained, which were soluble in chloroform and DMF. The first bulk polymerization that we performed used TMA and 1,4-butanediol (1,4-BD) to produce poly(butylene thiomalate) (run 2, Table 1). As for all the polyesters, the M_n of poly(butylene thiomalate) was determined using size exclusion chromatography (SEC) with DMF as the eluent. (The relationship between elution volume and M_n was calibrated with polystyrene standards.) The poly(butylene thiomalate) product had an M_n of 13.9×10^4. Notably, in the absence of catalyst, polycondensation did not occur (run 1, Table 1). Given the appearance of the ^1H and ^{13}C NMR spectra of poly(butylene thiomalate) (run 2), the polycondensation was chemoselective. In the ^1H and ^{13}C NMR spectra of poly(butylene thiomalate), peaks that could be ascribed to products of thioesterification or gelation were absent (Figures 1 and 2). Using the SEC data (M_n), the calculated turnover number for poly(butylenes thiomalate) is 388 (mol/mol), which is a larger value

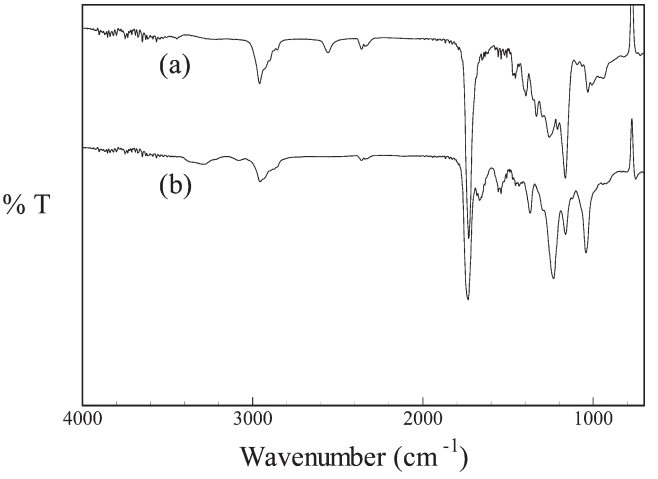
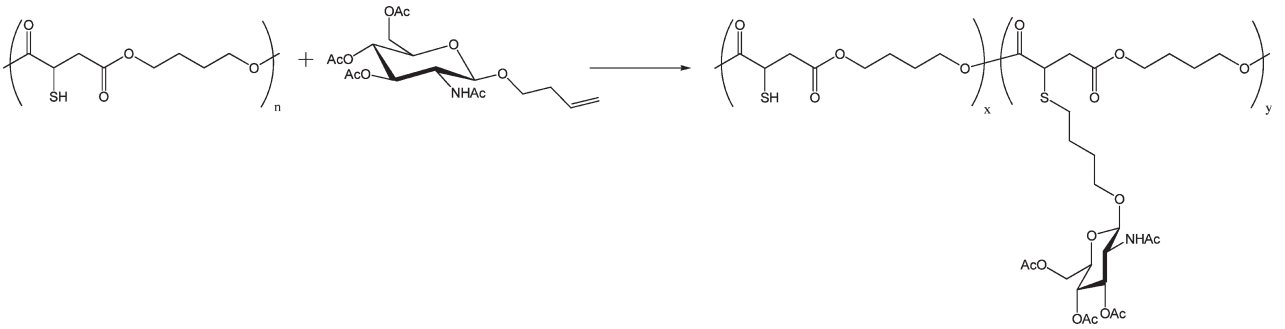


Figure 2. IR spectra of poly(buthylene thiomalate) (a) before glycosidation and (b) after glycosidation.

(294) than that found when 0.25 mol % $Sc(OTf)_3$ was used for polycondensation of methyl succinic acid with 1,4-BD.[5b] For 1,10-decanediol, the corresponding polyester had a larger M_n (1.6×10^4, run 8) than did poly(butylene thiomalate). The values of the M_w/M_ns for all the polymers spanned a relatively narrow range (1.5−1.8). Finally, as expected, the polyesterifications occurred in the absence of thioesterification or transesterification.

We next examined whether the mercapto groups of poly(butylene thiomalate) could be modified by glycosidation (Scheme 3). As a thiol−ene-type reaction, glycosidation of poly(butylene thiomalate) (M_n = 0.28×10^4, M_w/M_n = 1.61) was performed in acetonitrile at 60 °C under nitrogen with GlcNAc(Ac)$_3$-β-D-*n*-butenyl as the glycosyl donor and azobis(isobutyronitrile) (AIBN) as the initiator. We can confirm from IR spectra (Figure 2) that disappearance of free mercapto groups peak (2558 cm^{-1}) after reaction. The glycosidation proceeded smoothly and afforded a

Scheme 3. Glycosidation of Pendant Mercapto Groups in Linear Polyester



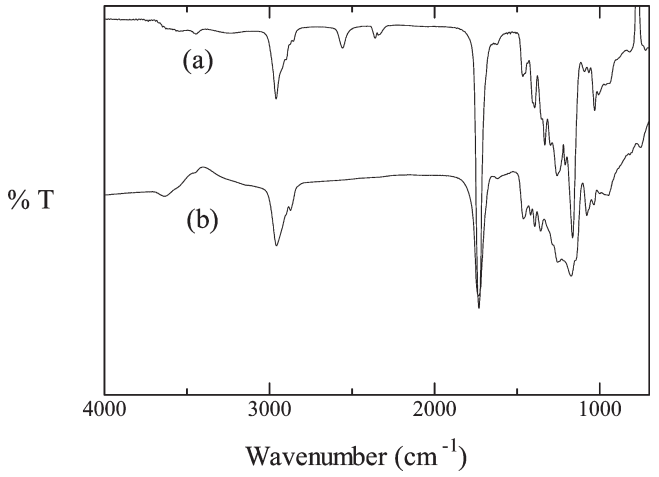


Figure 3. IR spectrum of (a) poly(butylene thiomalate-*co*-butylene adipate) before cross-linking and (b) RAFT gel.

sugar-containing polyester (99% glycosidation) in a good yield (80%), in which the glycosidation was estimated by ^{1}H NMR intensity ratio of peaks at 2.60−3.11 ppm (−CH(SH)CH_2) and at 2.60−2.77 ppm (−SCH_2).

We also demonstrated that the pendant mercapto groups of a polymer formed by reaction of adipic acid, TMA, and 1,4-BD (molar ratio of reactants, 3:1:4, M_n = 0.71 × 10^4, M_w/M_n 2.00) could be cross-linked by TCDI. After the cross-linking, the IR band at 2558 cm^{-1} ascribed to SH stretching disappeared, and a new band due to C═S stretching was observed at 1255 cm^{-1} (Figure 3). The results indicated that all of the pendant mercapto groups associate with the cross-linking.

This gelatinous chain transfer agent, which we call a "RAFT gel", swelled in tetrahydrofuran, chloroform, and toluene. The property in the equilibrium swollen state was evaluated by the W_s/W_0 value, in which W_s and W_0 are weights at swollen and dry state, respectively. The property in the equilibrium swollen state was evaluated by the W_s/W_0 value, in which W_s and W_0 are weights at swollen and dry state, respectively. The W_s/W_0 values are as follows: 3.8 (in tetrahydrofuran), 6.2 (in chloroform), 2.2 (in toluene), 2.8 (MMA), 2.9 (styrene). Succesively, radical polymerization was performed with methyl methacrylate and the RAFT gel ($[M]_0/[I]_0$ = 200). The poly(methyl methacrylate) product had a narrow molecular weight distribution (M_n = 8.5 × 10^4, M_w/M_n = 1.47) compared with the free radical polymerization (M_n = 8.2 × 10^4, M_w/M_n = 1.8), which indicated that the gel acted as a reaction platform and as a chain-transfer agent. ^{1}H NMR indicated the PMMA was composed of 59% syndiotactic, 35% heterotactic, and 6% isotactic, indicating that the microstructure was not influenced by the gel matrix because free radical polymerization showed the same tendency (62% syndiotactic, 33% heterotactic, and 5% isotactic). In order to check whether transfer reaction occurred or not, aminolysis was performed using propylamine as the reagents. The aminolysis proceeded completely in THF (at 27 °C); the remarkable change in the SEC trace of the polyester backbone was not observed, which revealed that chain transfer to polyester backbone was not predominate. Using styrene as the monomer, the control of molecular weight was difficult [free (M_n = 3.6 × 10^4, M_w/M_n = 4.04), RAFT gels (M_n = 3.7 × 10^4, M_w/M_n = 3.01)]. Finally, we could reuse the RAFT gel by simple filtration, in which a similar polymerization tendency was obtained.

In this article, we synthesized polyesters with pendant mercapto groups by dehydration polycondensations of diols and TMA, and as with the model reactions, esterification proceeded chemoselectively and thioesterification did not occur. The pendant mercapto-containing polyesters had M_ns > 1.0 × 10^4. We also demonstrated that the pendant mercapto groups could be chemically modified by glycosylation or cross-linked by TCDI to synthesize a gelatinous RAFT agent. These procedures can be used to produce new types of polyesters from monomers that differ in chirality and functionality and also nanoscale-reactive media containing RAFT agent as a cross-linker for controlled radical polymerization of vinyl monomers.

Acknowledgment. This work was funded by the Ministry of Education, Science, and Culture of Japan (Grant-in-Aid for Development Scientific Research, No. 22750104). The authors are also grateful to Mr. Suguru Seike of Nagoya City University, who were supported by the Initiative for Attractive Education in Graduate Schools "Nanomedicine" by Nagoya City University and Nagoya Institute of Technology for their technical help and fruitful discussions.

References and Notes

(1) (a) Matyjazewski, K.; Davis, T. P. In *Handbook of Radical Polymerization*; Wiley-Interscience: Hoboken, NJ, 2002. (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3746. (c) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990.

(2) (a) First reversible chain transfer polymerization reported: 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.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559–5562. (b) Trithiocarbonate: Mayadunne, R. T. A.; Rizzardo, E.; Chiefari, J.; Krstina, J.; Moad, G.; Postma, A.; Thang, S. H. *Macromolecules* **2000**, *33*, 243–245. (c) Review: Moad, G.; Rizzardo, E.; Thang, S. H. *Polymer* **2008**, *49*, 1079–1131.

(3) (a) Lenz, R. W. *Adv. Polym. Sci.* **1993**, *107*, 1–40. (b) Koeshak, V. V.; Vinogradora, S. V. *Polyester*; Pergamon Press: New York, 1995.

(4) (a) Carothers, W. H.; Dorough, G. L. *J. Am. Chem. Soc.* **1930**, *52*, 711–721. (b) Takiyama, E.; Niikura, I.; Hatano, Y. Japan Patent 189823, 1992. (c) Miura, M. Watanabe, H.; Fujiwara, M. Japan Patent 53695, 1995. (d) Ito, H.; Yamamoto, N.; Hiroji, F.; Jojima, M. Japan Patent 71641, 1997.

(5) (a) Takasu, A.; Oishi, Y.; Iio, Y.; Inai, Y.; Hirabayashi, T. *Macromolecules* **2003**, *36*, 1772–1774. (b) Takasu, A.; Iio, Y.; Oishi, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2005**, *38*, 1048–1050. (c) Takasu, A.; Takemoto, A.; Hirabayashi, T. *Biomacromolecules*

2006, *7*, 6–9. (d) Takasu, A.; Narukawa, Y.; Hirabayashi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5247–5253. (e) Takasu, A.; Shibata, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2007**, *40*, 151–153. (f) Takasu, A.; Narukawa, Y.; Hirabayashi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5247–5253. (g) Takasu, A.; Makino, T.; Yamada, S. *Macromolecules* **2010**, *43*, 144–149.

(6) Takasu, A.; Iio, Y.; Mimura, T.; Hirabayashi, T. *Polym. J.* **2005**, *37*, 946–953.

(7) (a) Takasu, A.; Shibata, Y.; Narukawa, Y.; Hirabayashi, T. *Macromolecules* **2007**, *40*, 151–153. (b) Shibata, Y.; Takasu, A. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5747–57.

(8) (a) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 627–645. (b) Hoyle, C. E.; Lee, T. Y.; Roper, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 5301–5338. (c) Campos, L. M.; Killops, K. L.; Sakai, R.; Paulusse, J. M. J.; Damiron, D.; Drockenmuller, E.; Messmore, B. W.; Hawker, C. J. *Macromolecules* **2008**, *41*, 7063–7070. (d) Semsarilar, M.; Ladmiral, V.; Perrier, S. *Macromolecules* **2010**, *43*, 1438–1443. (e) Shin, J.; Matsushima, H.; Chan, J. W.; Hoyle, C. E. *Macromolecules* **2009**, *42*, 3294–3301.

(9) Seabra, A. B.; Silva, R.; Oliveira, M. G. *Biomacromolecules* **2005**, *6*, 2521–2520.

(10) Kato, M.; Toshima, K.; Matsumura, S. *Biomacromolecules* **2009**, *10*, 366–37.

(11) (a) Flory, P. J. *J. Am. Chem. Soc.* **1936**, *58*, 1877–1885. (b) Flory, P. J. *Chem. Rev.* **1946**, *39*, 137–197.