Polymer 41 (2000) 5625–5631

polymer

Preparation of branched polymer by radical polymerization using polymerizable chain transfer agent

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Received 8 June 1999; received in revised form 12 October 1999; accepted 18 October 1999

Abstract

Methyl methacrylate was polymerized in the presence of a polymerizable addition–fragmentation chain transfer agent consisting of methacryloyl and α-(benzylthiomethyl)acryloyl groups as dual functionality. The copolymers containing up to 3.1 mol% of the units from the transfer agent were prepared. The polymerizable chain transfer agent can connect up to three polymer chains as a result of copolymerization followed by chain transfer or vice versa as one step branching. Furthermore, each branch could also involve branching points for secondary branching. The unsaturated moieties from the chain transfer agent were subjected to addition of poly(styrene) radical to yield hyperbranched block copolymer consisting of poly(methyl methacrylate) and poly(styrene) segments without gelation. A side reaction of the unsaturated moiety was also shown. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Radical polymerization; Addition–fragmentation chain transfer; End group

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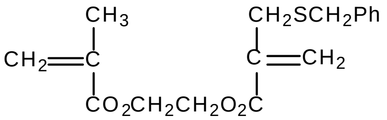
1. Introduction

Recent advances in free radical polymerization such as “living” free radical polymerization have been applied to synthesis of branched polymers as well as living ionic polymerizations [1–6]. The contribution of the bimolecular termination as the end stopping event is limited in the living radical polymerization because the activity of the propagating radical intermittently exhibits as a result of dissociation of the dormant species; otherwise premature mutual reaction of two or more propagating radicals in the branched polymer results in an intractable polymer. If an end-forming elementary reaction which can effectively minimize the contribution of the bimolecular termination is combined with branch formation, we are able to attain branched radical polymer without gelation. From such a point of view, addition–fragmentation chain transfer has drawn our attention because this type of chain transfer can quantitatively form a carbon–carbon bond between the polymer chain end and the moiety from the transfer agent to decrease M_n in competition with the bimolecular termination under appropriate conditions.

α-(Substituted methyl)acrylate type addition–fragmentation chain transfer agents such as α-(alkylthiomethyl)acrylate [7–9] and α-(bromomethyl)acrylate [10] have been studied extensively, and it has been shown that a small amount of chain transfer agent effectively reduces M_n of the polymers from methyl methacrylate (MMA) and styrene (St) in accord with their chain transfer constants (C_{tr}) close to unity. Similarly, methyl α-(benzylthiomethyl)acrylate could introduce SCH_2Ph and $CH_2C(CO_2CH_3){=}CH_2$ groups at the α- and ω-ends of the polymer, respectively [11]. Although addition of PMMA radical to the unsaturated end group has been evidenced by ESR detection of an adduct radical [12], it appeared that the $CH_2C(CO_2CH_3){=}CH_2$ group bound to PMMA chain end is not so reactive toward the PMMA radical to increase M_n [13] and the resultant adduct radical readily expels PMMA radical through β-cleavage [14,15].

In the present work, a polymerizable chain transfer agent (**1**) consisting of the methacryloyl and α-(benzylthiomethyl)acryloyl groups was synthesized to introduce the moiety arising from the addition–fragmentation chain transfer as a branching point bearing the resultant unsaturated group without gelation.



$CH_2{=}C(CH_3)CO_2CH_2CH_2O_2C(CH_2SCH_2Ph){=}CH_2$

1

It should be differentiated **1** from another type of

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PII: S0032-3861(99)00778-8

Table 1
Results of copolymerization of MMA with **1** for 40 h at 60°C ([MMA] = 2.00 mol/l, [AIBN] = 0.005 mol/l)

[**1**] in comonomer (mol%)	Conversion (%)	M_n	M_w/M_n	[**1**] in copolymer (mol%)
0.0	62	115000	2.0	–
0.2	86	42000	1.7	0.2
1.0	80	25000	1.6	0.9
2.9	85	15000	1.5	2.7
4.0	47	12000	1.5	3.2

polymerizable chain transfer agent such as methyl α-(chloromethyl)acrylate [16] and methyl α-(phenoxymethyl)acrylate [17]. In these cases, the respective carbon–carbon double bonds participate in propagation and chain transfer simultaneously, and formation of the respective homopolymers bearing the unsaturated end group have been confirmed.

2. Experimental

For preparation of 2-(methacryloyloxy)ethyl α-(chloromethyl)acrylate as the precursor of **1**, α-(chloromethyl)acryloyl chloride [18] was added dropwisely to a benzene solution containing equimolar amounts of 2-hydroxymethyl methacrylate and triethylamine. The reaction mixture was refluxed for 4 h and then the product was obtained by distillation under reduced pressure. b.p. 120°C/1 mmHg. 2-(Methacryloyloxy)ethyl α-(chloromethyl)acrylate: ^{1}H NMR ($CDCl_3$): *δ*: 1.95 (s, 3H, CH_3), 4.29 (s, 2H, CH_2Cl), 4.41–4.48 (m, 4H, OCH_2), 5.60 (s, 1H, C*H*=CCH_3), 6.01 (s, 1H, C*H*=CCH_2Cl), 6.14 (s, 1H, C*H*=CCH_3), 6.41 (s, 1H, C*H*=CCH_2Cl); ^{13}C NMR ($CDCl_3$): *δ*: 18.1 (CH_3), 42.3 (CH_2Cl), 62.0 (CH_2=C(CH_3)CO_2*C*H_2), 62.8 (CH_2=C(CH_2Cl)CO_2*C*H_2), 126.1 (*C*H_2=CCH_3), 129.2 (*C*H_2=CCH_2Cl), 135.8 (CH_2=*C*CH_3), 136.5 (CH_2=*C*CH_2Cl), 164.6 (CH_2=C(CH_2Cl)*C*O_2), 167.0 (CH_2=C(CH_3)*C*O_2).

1 was synthesized by overnight reaction of 2-(methacryloyloxy)ethyl α-(chloromethyl)acrylate with benzylmercaptan in the presence of triethylamine at room temperature and was purified by the recycling preparative HPLC (Japan Analytical Industry LC-908). **1**: yield 47.6%; ^{1}H NMR ($CDCl_3$): *δ*: 1.95 (t, 3H, CH_3), 3.27 (s, 2H, CH_2=CC*H*$_2$S), 3.66 (s, 2H, SC*H*$_2$Ph), 4.39–4.45 (m, 4H, OCH_2), 5.59 (s, ^{1}H, C*H*=CCH_3), 5.61 (s, ^{1}H, C*H*=CCH_2S), 6.14 (s, ^{1}H, C*H*=CCH_3), 6.24 (s, ^{1}H, C*H*=CCH_2S), 7.22–7.31 (m, 5H, Ph); ^{13}C NMR ($CDCl_3$): *δ*: 18.2 (CH_3), 31.8 (CH_2=C*C*H_2S), 35.5 (S*C*H_2Ph), 62.2 (CH_2=C(CH_3)CO_2*C*H_2), 62.6 (CH_2=C(CH_2SCH_2Ph)CO_2*C*H_2), 126.1 (*C*H_2=CCH_3), 126.6, 128.5, 128.9, and 135.8 (Ph), 127.0 (*C*H_2=CCH_2S), 135.8 (CH_2=*C*CH_3), 137.7 (CH_2=*C*CH_2S), 165.8 (CH_2=C(CH_2SCH_2Ph)*C*O_2), 167.0 (CH_2=C(CH_3)*C*O_2).

Commercial MMA and St were distilled under reduced pressure before use. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Polymerizations and copolymerizations were carried out in sealed tubes and the polymeric product was precipitated in an excess amount of methanol. ^{1}H and ^{13}C NMR spectra were taken by a JEOL JNM a 400 spectrometer. M_n and M_w were measured by a Tosoh 8000 series HPLC equipped with columns for GPC, and standard PSts were used for calibration.

3. Results and discussion

3.1. Copolymerization of MMA with 1

Attempted homopolymerization of **1** at 60°C for 40 h using AIBN did not form any polymeric product. MMA polymerization in the presence of a small amount of **1** yielded soluble copolymers as shown in Table 1 and Fig. 1. Polydispersity (M_w/M_n) of the resulting copolymers remained almost constant irrespective of comonomers composition confirming that a significant increase in M_n arising from the binding of PMMA chain to the unsaturated group did not occur.

Copolymerization of **1** with MMA or chain transfer to **1** may yield **2** or **3** as shown by Scheme 1. **2** and **3** are the PMMA incorporating the monomeric unit bearing a chain transferable pendant group and that bearing the unsaturated end group, respectively. Further reactions of **2** as the chain transfer agent and **3** as a monomer can form **4** which retains the carbon–carbon double bond exhibiting extremely low reactivity toward PMMA radical. Based on the results in Table 1, the apparent value of C_{tr} for **1** was calculated from the Mayo equation: $C_{tr} = 0.24$. This value is smaller than the C_{tr} values for methyl α-(benzythiomethyl)acrylate (0.62) and ethylene bis[α-(benzylthiomethyl)acrylate] (0.67) [11], which are comparable to those for ethyl α-(*tert*-butylthiomethyl)acrylate (0.74) [7–9,19] and methyl α-(bromomethyl)acrylate (0.93) [10]. A decrease in M_n by the chain transfer to **1** seems to be partly compensated by binding of PMMA branch as in **4**.

3.2. Assignment of ^{1}H NMR resonances

Fig. 1 shows the ^{1}H NMR spectrum of the MMA/**1** copolymer prepared from monomer mixture containing 2.9 mol% of **1**. The resonances due to the methylene protons of the MMA unit bound to the PhCH_2S group were readily detected at 2.6–2.8 ppm as totally eight lines (2.3–2.8 ppm, **j** in Fig. 1) [11] arising from the diad tacticity and configuration of the asymmetric carbon of the MMA unit [10]. Hatada et al. [20] showed the resonances of the allylic

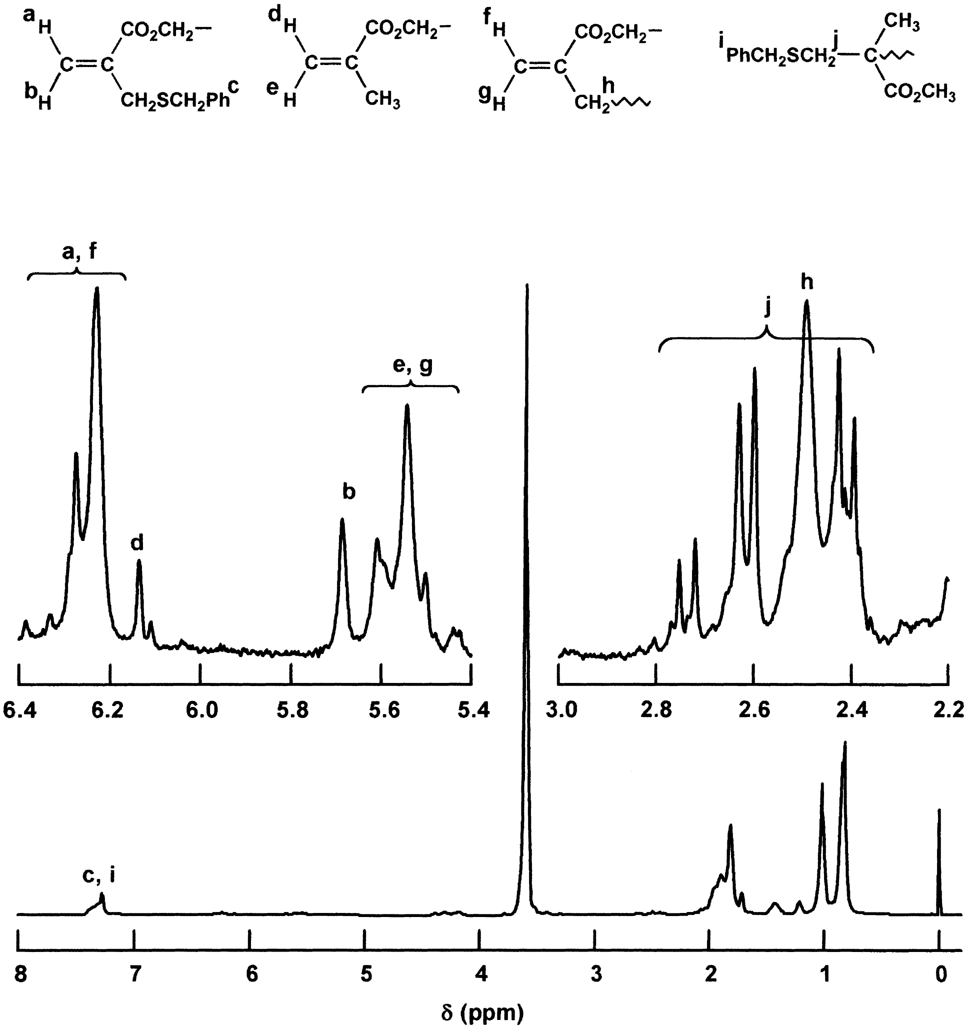
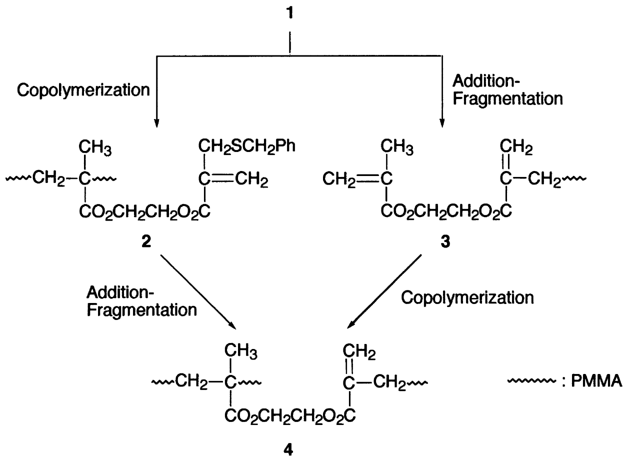


Fig. 1. ^{1}H NMR spectrum of MMA/**1** copolymer containing 3.5% of **1** unit.

methylene protons of the unsaturated end group in *racemo-* and *meso-* configurations at 2.47, and 2.45 and 2.60 ppm, respectively, using a 750 MHz ^{1}H NMR spectrometer. However, the resonances of the allylic methylene protons of the unsaturated end group of the MMA/**1** copolymer (**h**) overlapped with a part of the eight line spectrum as shown in Fig. 1. The sum of the intensities of **j** and **h** was confirmed to correspond to four protons.

The methoxy protons of the MMA units bound to the α- and ω-end groups and those of the unsaturated group would exhibit resonances at 3.6–3.8 ppm [10,20]. The methoxy protons of the MMA repeating unit were observed as much more intense resonance at 3.60 ppm. The total intensity of the resonances at 3.55–3.70 ppm was consistent with the structure of **2**, **3**, and **4** if the resonance due to the methylene protons of the SCH_2Ph group also appeared in the same chemical shift range [11]. The resonances at 6.13–6.34 ppm were readily assigned to the *cis*-olefinic protons of **2** (**a**), **3** (**d** and **f**), and **4** (**f**) because the chemical shifts of the respective resonances are quite similar to those of the corresponding protons of **1** and the unsaturated end group [10].



Scheme 1.

Table 2
Structural analysis of MMA/**1** copolymers by ^{1}H NMR spectroscopy

Category	[**1**] in comonomer (mol%) 0.2	1.0	2.9	4.0
Number of **1** unit per chain	2.1	2.2	4.1	3.5
[**2**], [**3**], and [**4**][a] (%)	9, 33, 58	8, 30, 62	9, 24, 67	7, 22, 71
Number of branching point per chain	1.2	1.4	2.7	2.5
Number of arm	3.4	3.8	6.4	6.0
P_n of arm	121	64	21	18

[a] Calculated from intensity ratios of **h** and **j**, **d**, **a**, and **f** for (**3** + **4**), **3**, and (**2** + **3** + **4**), respectively.

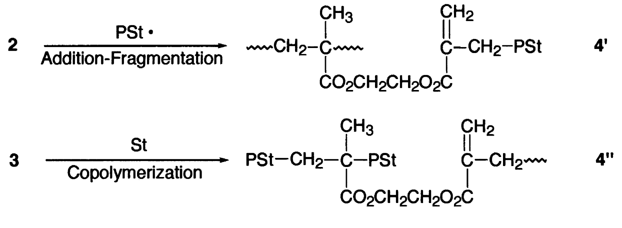
The resonances at 5.4–5.7 ppm (**b**, **e**, and **g**) were assigned to the *trans*-olefinic protons of **2**, **3**, and **4**.

*3.3. Structural analysis of MMA/**1** copolymer*

The content of (**2** + **3** + **4**) was calculated form the intensity ratio of the total of **a** and **f** to the resonances of the methoxy protons of the MMA repeating unit, and **d** was employed for calculation of the content of **3**. The content of (**3** + **4**) was calculated from the total intensity of **h** and **j**. The results of the structural analysis of the copolymers at different comonomer compositions are shown in Table 2. The number of **1** unit per chain increased with increasing content of **1** in comonomer except at 4 mol% of **1**. A shortest chain length of the PMMA arising from the highest **1** content in comonomer probably lead to a smaller amount of **1** unit per chain.

All the polymers were obtained free from gelation. According to the reactions shown in Schemes 1 and 2, the branching points may be involved in the branch to form a hyperbranched PMMA. For evaluation of the branch formation, M_n measured by GPC using standard PSt for calibration is not preferable. However, the M_n range of the polymers of the present work was found to be too small for a low angle laser light scattering detector of GPC. Consequently, the estimation of branching was based on M_n calibrated by standard PSt.

Among 4.1 units from **1** on the average per copolymer chain from the comonomer containing 2.9 mol% of **1**, 2.7 units of **4** were incorporated as branching points for one step branching. The mean number of the arms of the copolymer containing 4.1 units of **1** was calculated to be 6.4 because the polymer containing n branching points may have ($2n$ + 1) arms as show in Table 2. The M_n of this copolymer was 15000 as shown in Table 1 corresponds to 137 MMA units and the moieties from **1**, and each arm consists of 21 MMA units on the average.

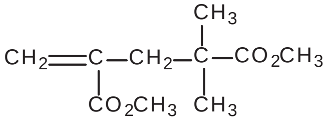


Scheme 2.

*3.4. St polymerization in the presence of MMA/**1** copolymer*

The MMA/**1** copolymer containing **2** (9%, 0.37 units per chain), **3** (24%, 0.98 units per chain), and **4** (67%, 2.75 units per chain) was added to the St polymerization ([**1** unit]/[St] < 0.05 molar ratio) in benzene. The results of the St polymerization are summarized in Table 3. PSt radical may be involved in addition–fragmentation chain transfer to **2** resulting in **4**′, and addition of PSt radical to **3** followed by coupling with the adduct radical can yield **4**″ (Scheme 2). **4**′ and **4**″ are structurally similar to **4**, and the PSt radical could further react with these carbon–carbon double bonds to bind up to four PSt chains as shown in Scheme 3.

The persistent character expected for the adduct radicals from **4** and **4**″ as well as the adduct radical from a MMA dimer (**8**) [12] and a low concentration of the $CH_2C(CO_2CH_3){=}CH_2$ group seem to prefer coupling of the adduct radical with the PSt radical to form branched structures such as **5** and **7** as shown by Scheme 3. The presence of small amounts of **3** and **4** did not suppress the polymerization of St in contrast to the effect observed for **8** at a higher concentration such as 10 mol% relative to St [12].



$CH_2{=}C(CO_2CH_3){-}CH_2{-}C(CH_3)_2{-}CO_2CH_3$

8

2 as the linear MMA/**1** copolymer was divided into two PMMA chains in the course of the reaction with PSt radical, because **2** was converted to **4**′ as a branched polymer. Totally three PSt chains can be involved in **6** through the reactions of **2** and **4**′ (see Scheme 3).

The maximum numbers of the PMMA and PSt chains per molecule of the resultant hyperbranched block polymers from the MMA/**1** copoloymer may be calculated from

Table 3
St polymerization in the presence of MMA/**1** copolymer for 40 h at 60°C (conversion of St = 66.3%)

Polymer (relative weight)	M_n	Number of C=C per chain	Number of arm	Type of polymer
MMA/**1** copolymer before St polymerization (1.0)	15000	4	6.4	MMA/**1** copolymer
Product of St polymerization (4.7)	11000	None	Mixture	Mixture
Cyclohexane soluble fraction (2.2)	8100	None	1.0	PSt
Cyclohexane insoluble fraction (2.2)	30000	None	17.3	Poly(MMA-*co*-**1**-*block*-St)

Eqs. (1) and (2). Eq. (1) shows the increase in branching point associated with the conversion of **2** to **4′**, and the number of the PSt chains incorporated in **5**, **6**, and **7** via **4**, **4′**, and **4″**, respectively, may be given by Eq. (2).

$$\text{Number of PMMA chain} = 6.4 + \text{number of } \mathbf{2} = 6.4 + 0.4 = 6.8 \qquad (1)$$

$$\text{Number of PSt chain} = 3 \times (\text{number of } \mathbf{2}) + 4 \times (\text{number of } \mathbf{3}) + 2 \times (\text{number of } \mathbf{4}) = 10.5 \qquad (2)$$

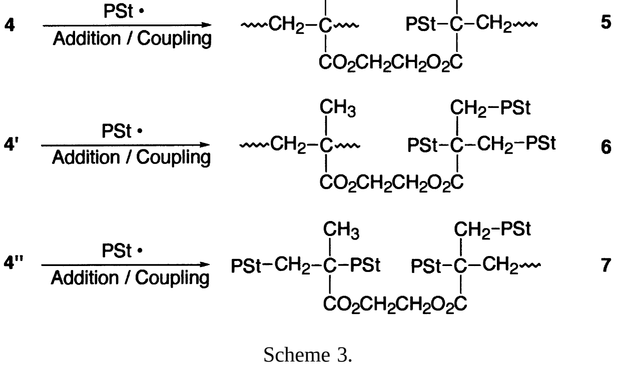
According to Eqs. (1) and (2), the hyperbranched polymer consisted of 17.3 (= 6.8 + 10.5) branches. All of the $CH_2C(CO_2CH_3)=CH_2$ groups in the original copolymer were completely consumed by the reaction with the PSt radical as confirmed by ^{1}H NMR spectroscopy. The total degree of polymerization (P_n) of PSt segments consisting of the resultant hyperbranched polymer as cyclohexane insoluble fraction was evaluated using Eq. (3).

$$\text{Total } P_n \text{ of PSt segment} = \frac{\text{Number of MMA unit in MMA/}\mathbf{1}\text{ copolymer}}{\text{[MMA unit]/[St unit] in hyperbranched copolymer}} = 137/(35/65) = \text{ca.}254 \qquad (3)$$

The average length of the PSt arms could be 24 (= 254/10.53). Based on the length of the PMMA and PSt segments, the M_n for the product copolymer from the MMA/**1** copolymer consisting of 137 MMA units and 4.1 units from **1** can be estimated using Eq. (4).

$$M_n = 13700 + (\text{molecular weight of St unit}) \times 254 + (\text{molecular weight of } \mathbf{1} \text{ unit}) \times 4.1 = 42600 \qquad (4)$$

where molecular weight of **1** unit is 320. The estimate of M_n is higher than the M_n measured by GPC, 30000. This discrepancy seems to support the formation of a highly branched copolymer, which may exhibit a smaller hydrodynamic volume. The formation of the hyperbranched PMMA and conversion to the hyperbranched poly(MMA-*co*-**1**-*block*-St) according to the results in Table 3 are schematically shown in Fig. 2. However, the homopolymerization of St is not avoidable in the second step to increase branching.



Scheme 3.

3.5. β-scission of adduct radical

If the β-scission of the adduct radical formed by addition of the PSt radical to the unsaturated end group of PMMA could yield the PMMA radical and PSt bearing the unsaturated end groups as shown in Scheme 4, the PMMA radical is expected to readily initiate St polymerization followed by bimolecular termination or the addition to the unsaturated group to yield linear block or branched block copolymer [15].

The fate of the adduct radical was examined using the PMMA prepared by the polymerization in the presence of methyl α-(bromomethyl)acrylate: $M_n = 2500$ and $M_w/M_n = 1.42$. St (2 mol/l) was allowed to polymerize in the presence of the PMMA bearing the unsaturated end group (0.007 mol/l) in benzene using AIBN for 12 h at 60°C. The ^{1}H NMR spectrum of the resultant polymer exhibited the resonance assigned to the methylene protons of the unsaturated end group bound to PSt chain at 5.12 and 5.96 ppm (**d** and **c** in Fig. 3) unlikely to those of the same group bound to PMMA chain at 5.49 and 6.23 ppm (**b** and **a**) as shown in Fig. 3. The rate of the β-scission relative to the coupling with PSt radical was estimated to be 0.1–0.4 depending on initiator concentration, and the branched PSt arising from the reaction of the unsaturated end group bound to PSt with the PSt radical would be involved in the

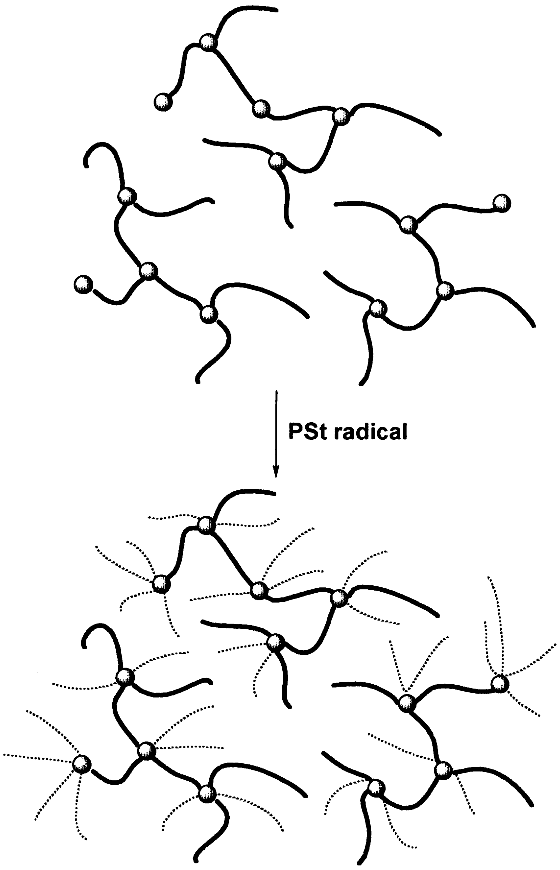
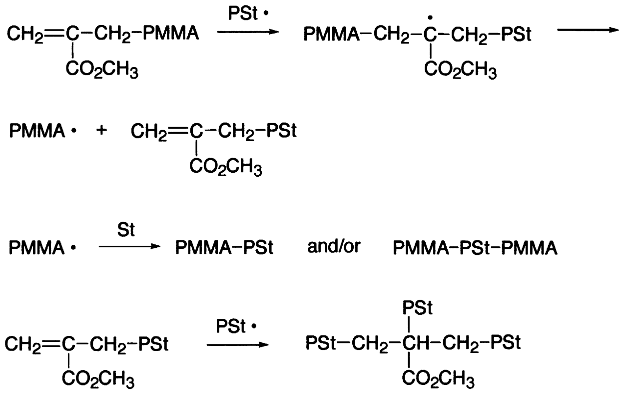


Fig. 2. Schematic description of branch formation by copolymerization of polymerizable chain transfer agent and further reaction of the unsaturated group as **2**, **3**, or **4** (●) to form hyperbranched block copolymer consisting of PMMA (—) and PSt (– – –) chains.

homopolymer isolated as the cyclohexane soluble fraction in Table 3.

4. Conclusion

Using a polymerizable addition–fragmentation chain transfer agent, we successfully prepared a hyperbranched block copolymer by the bond formation through the addition–fragmentation reaction and subsequent reactions of the polymer radical with the unsaturated moiety from the chain transfer agent for secondary branching. The addition–fragmentation reaction, which is useful not only in chain transfer but also in quantitative introduction of the end group, has been shown to prevent gelation.



$$CH_2{=}\underset{CO_2CH_3}{C}{-}CH_2{-}PMMA \xrightarrow{PSt\bullet} PMMA{-}CH_2{-}\underset{CO_2CH_3}{\overset{\bullet}{C}}{-}CH_2{-}PSt \longrightarrow$$

$$PMMA\bullet + CH_2{=}\underset{CO_2CH_3}{C}{-}CH_2{-}PSt$$

$$PMMA\bullet \xrightarrow{St} PMMA{-}PSt \quad \text{and/or} \quad PMMA{-}PSt{-}PMMA$$

$$CH_2{=}\underset{CO_2CH_3}{C}{-}CH_2{-}PSt \xrightarrow{PSt\bullet} PSt{-}CH_2{-}\underset{CO_2CH_3}{\overset{PSt}{CH}}{-}CH_2{-}PSt$$

Scheme 4.

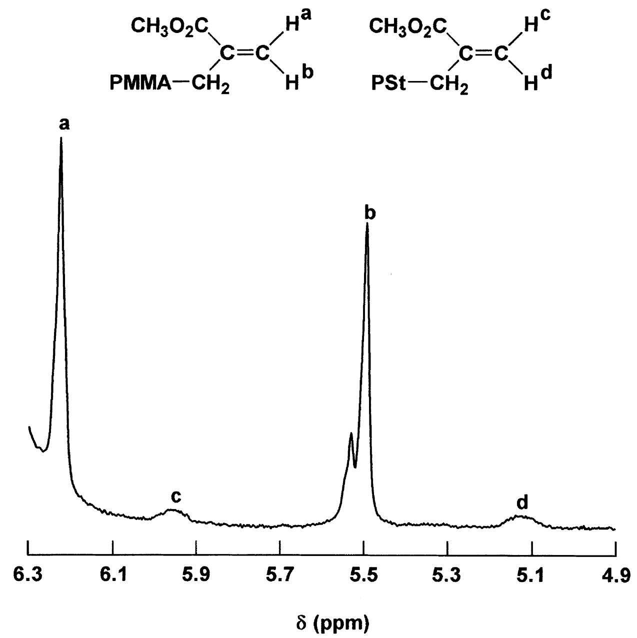


Fig. 3. ^{1}H NMR spectrum of the olefinic protons of the unsaturated end groups after polymerization of St for 12 h at 60°C in the presence of the PMMA ($M_n = 2500$) bearing the moiety from methyl α-(bromomethyl)acrylate: *cis*-olefinic protons ($CH_3O_2CC{=}CH$-*cis*) of the end groups bound to PMMA (a) and PSt (c), and *trans*-olefinic protons ($CH_3O_2CC{=}CH$-*trans*) of the end groups bound to PMMA (b) and PSt (d).

Acknowledgements

The authors are grateful to generous support by NEDO for the project on Technology for Novel High-Functional Material in Industrial Science and Technology Frontier Program, AIST (Agency of Industrial Science and Technology, Japan).

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