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Synthesis of random and block copolymers of styrene and styrenesulfonic acid with low polydispersity using nitroxide-mediated living radical polymerization technique

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Abstract

Poly(styrene-*ran*-styrenesulfonic acid) and poly(styrene-*block*-styrenesulfonic acid) with low polydispersity were prepared using nitroxide-mediated living radical polymerization technique. Random or block copolymerization of styrene and neopentyl *p*-styrenesulfonate smoothly proceeded by AIBN/2,2,5,5-tetramethyl-4-diethylphosphono-3-azahexane-3-nitroxide initiating system. Transformation of the sulfonate ester to sulfonic acid was carried out by the reaction with trimethylsilyl iodide or by thermolysis at 150 °C. Those polymers showed amphiphilic characters.

Keywords: Living radical polymerization; Block copolymer; Styrenesulfonic acid

1. Introduction

Polymers having both hydrophilic units and hydrophobic units show amphiphilic characters. The control of self-organization of amphiphilic polymers has been great interest in the last decade [1]. Especially, polymers having sulfonic acid groups were extensively investigated by Morishma et al. [2]. They reported that random copolymers of hydrophobic monomers and comonomers containing sulfonic acid formed intrapolymer self-associations in a certain condition. Recently, micellization properties of block polymers having carboxylic acid with low polydispersity were investigated [3]. Dissociation degree of sulfonic acid to sulfonate anion shows little dependence on pH or temperature in the system, contrary to that of carboxylic acid to carboxylate. Thus, polymers having sulfonic acid groups with high molar ratio (>50% for monomer unit) is expected to be soluble in water at any pH. The polymer may also show amphiphilic characters. We consider that the amphiphilic character is strongly affected by the content and sequence (including random or block copolymes) of sulfonic acid groups in the polymer, in addition to the molecular weight and molecular weight distribution of the polymer. However, few reports can be seen for the synthesis of random or block polymers bearing sulfonic acid groups with low polydispersity [4–6].

This paper focuses on the new approach for preparation of amphiphilic polymers having sulfonic acid group with well-defined structures. For this purpose, we selected a living radical polymerization technique which afforded accurate control over molecular weight distribution, chain ends, and polymer architecture [7,8]. The pioneer work on the synthesis of polymers with sulfonic acid group with low polydispersity was carried out by Georges et al. [4]. They obtained poly(sodium *p*-styrenesulfonate) with low polydispersity using TEMPO/potassium persulfate initiating system. Arms et al. [5] reported the synthesis of novel acidic and zwitterionic block copolymers containing poly((sodium *p*-styrenesulfonate)-*block*-(*p*-(dimethylamino)methylstyrene)) via TEMPO-mediated living free-radical polymerization. Synthesis of poly(sodium styrenesulfonate-*block*-vinylnaphthalene) by nitroxide-mediated free radical polymerization was also reported by Nowakowska et al. [6].

Our strategy for the synthesis of random or block polymers with low polydispersity is (i) synthesis of precursor polymers using living radical polymerization, (ii) quantitative conversion of the precursor polymers into polymers having sulfonic acid groups. Advantages of our method are (i) easy characterization of precursor polymers and (ii) easy control of polymer structures compared to the method of direct polymerization of monomers having sulfonic acid.

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The synthesis of block copolymers of sodium 4-styrenesulfonate with hydrophobic monomers such as styrene is very difficult due to the inhomogeneity of the system. Whereas, our system is completely homogeneous during polymerization.

As a precursor monomer, styrenesulfonate esters were chosen. Although sulfonate esters are decomposed by thermolysis or the attack of nucleophiles, the reactivity of sulfonate esters with radical species is relatively low. The precursor polymers bearing sulfonate esters could be characterized precisely compared to the amphiphilic polymers having sulfonic acid previously reported [4,5], especially in terms of the molecular weight distribution.

In this paper, we report the synthesis of poly(styrene-*ran*-styrenesulfonic acid) and poly(styrene-*block*-styrenesulfonic acid) with low polydispersity. Random or block copolymerization of styrene (St) and neopentyl *p*-styrenesulfonate (SSPen) smoothly proceeded by nitroxide-mediated living radical polymerization using 2,2,5,5-tetramethyl-4-diethylphosphono-3-azahexane-3-nitroxide (DEPN) [9,10]. Transformation of the sulfonate ester units to sulfonic acid units was carried out by the reaction with trimethylsilyl iodide or by a thermal treatment. Amphiphilic characters of those polymers were also discussed in terms of the polymer structures.

2. Experimental

2.1. Measurements

^{1}H NMR spectra were observed at 400 MHz using a JEOL LA-400 or at 270 MHz using a JEOL GX-270 spectrometer. UV–Vis spectra were taken on a Shimadzu UV-2400 PC. FT-IR measurements were carried out using a JASCO IR-410. Thermal decomposition behavior was investigated with a Rigaku TAS 100 thermogravimetric analyzer (TGA) under nitrogen flow. Heating rate was 10 °C min^{-1} for measurements. Size exclusion chromatography (SEC) was carried out in THF on a JASCO PU-980 chromatograph equipped with polystyrene gel columns (Shodex GMNHR-$_H$ + GMNHR-$_N$; 8.0 mm i.d. × 30 cm each) and a differential refractometer JASCO RI1530. The number-average molecular weight (M_n) and molecular weight dispersion (M_w/M_n) were estimated on the basis of a polystyrene calibration.

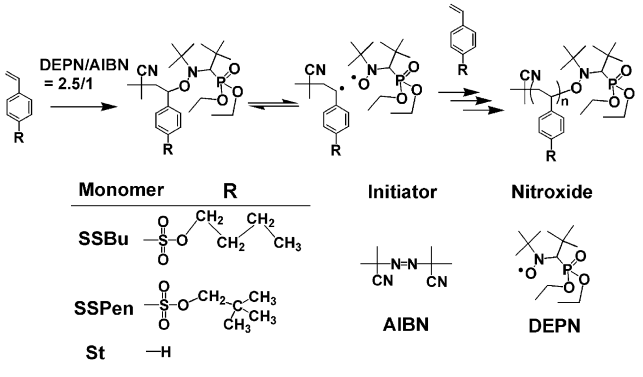
2.2. Materials

Commercially obtained styrene, benzoyl peroxide (BPO; Nacalai Tesque, Japan) and 2,2′-azobisisobutyronitrile (AIBN; Nacalai Tesque, Japan) were purified by the standard methods. Trimethylsilyl iodide (Tokyo Kasei, Japan) and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO; Aldrich) were used as received. 2,2,5,5-Tetramethyl-4-diethylphosphono-3-azahexane-3-nitroxide (DEPN) was prepared according to the literature [9]. *n*-Butyl *p*-styrenesulfonate (SSBu) [11] was prepared as follows. *p*-Styrenesulfonyl chloride [12] (5.0 g, 2.6×10^{-2} mol) was added dropwise to the mixture of *n*-butyl alcohol (1.9 g, 2.6×10^{-2} mol) and pyridine (11.7 ml, 1.3×10^{-1} mol) at 0 °C. After 5 h, chloroform was added to the resultant solution and washed with 1N HCl. The chloroform layer was dried over anhydrous sodium sulfate. SSBu was purified by column chromatography (silica gel, eluent: chloroform); yield 4.9 g (78%), pale yellow liquid. ^{1}H NMR: δ 7.85 (2H, d, aromatic), 7.55 (2H, d, aromatic), 6.75 (1H, dd, CH_2=C*H*–), 5.90 (1H, d, C*H*$_2$=CH–), 5.45 (1H, d, C*H*$_2$=CH–), 4.05 (2H, t, –S–O–CH_2–), 1.35–1.60 (4H, m, CH_2) 0.85 (3H, s, CH_3). Synthesis of neopentyl *p*-styrenesulfonate (SSPen) was carried out as follows. Neopentyl alcohol (3.6 g, 4.1×10^{-2} mol) was dissolved in pyridine (11.7 ml, 1.3×10^{-1} mol) and cooled to 0 °C. *p*-Styrenesulfonyl chloride (7.8 g, 3.8×10^{-2} mol) was added dropwise to the solution and kept at 0 °C for 2.5 h. Hexane was added to the reaction mixture and cooled to −15 °C to precipitate white solid. SSPen was purified by recrystallization from hexane:toluene (1:1, v/v). White crystal; yield 2.5 g (26%), m.p. 49 °C. ^{1}H NMR: δ 7.85 (2H, d, aromatic), 7.55 (2H, d, aromatic), 6.75 (1H, dd, CH_2=C*H*–), 5.90 (1H, d, C*H*$_2$=CH–), 5.45 (1H, d, C*H*$_2$=CH–), 3.70 (2H, s, –S–O–CH_2–), 0.90 (9H, s, $(CH_3)_3$).

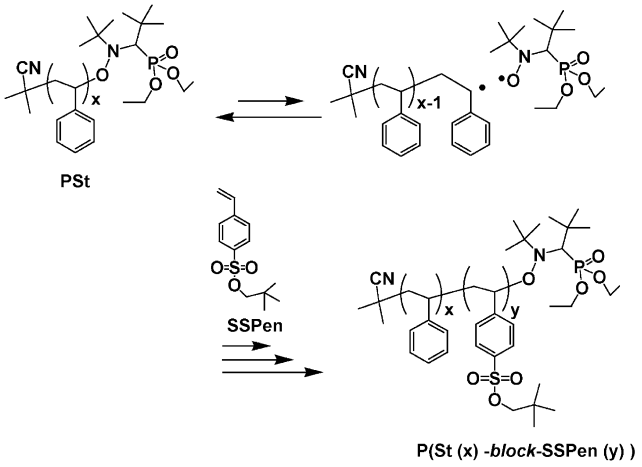
2.3. Polymerization

Polymerization of SSPen or SSBu was carried out using the reported method [9] Scheme 1. In brief, a mixture of SSPen (1.0 g, 3.9×10^{-3} mol), AIBN (27.3 mg, 1.7×10^{-4} mol), DEPN (122 mg, 4.2×10^{-4} mol), and benzene (1.0 ml) was charged in a glass tube, degassed with a several freeze–thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 120 °C for 6.5 h. The polymer was recovered as a precipitate from a large excess of hexane, purified by reprecipitation with a chloroform (solvent)/hexane (nonosolvent) system, and thoroughly dried (conversion: 28%). According to the PS-calibrated GPC, M_n and M_w/M_n were 5400 and 1.08, respectively.

Block copolymer P(St-*block*-SSPen) was prepared by the polymerization of SSPen with DEPN-terminated polystyrene



Scheme 1.



Scheme 2.

(PSt) Scheme 2. A mixture of SSPen (305 mg, 1.2×10^{-3} mol), DEPN-terminated PSt ($M_n = 2000$, 100 mg, 5.0×10^{-5} mol), and benzene (1.0 ml) was charged in a glass tube, degassed with a several freeze–thaw cycles, and sealed off under vacuum. Then, the mixture was heated at 120 °C for 2.5 h to yield a polymer. The polymer was recovered as a precipitate from a large excess of methanol, purified by reprecipitation with a chloroform (solvent)/hexane (nonosolvent) system, and thoroughly dried (conversion: 34%). According to the PS-calibrated GPC, M_n and M_w/M_n were 5900 and 1.10, respectively.

2.4. Transformation of sulfonate ester into sulfonic acid in polymer chain

Hydrolysis of sulfonate ester using trimethylsilyl iodide was accomplished based on the procedure reported previously [13]. A solution of poly(neopentyl styrenesulfonate) (PSSPen) in dichloromethane was mixed with trimethylsilyl iodide (2.5 equiv. to the ester units in the polymer) and the mixture was stirred at room temperature for 4 h. After removal of dichloromethane by evaporation, the precipitates were treated with an excess of methanol/1N HCl (1:1, v/v) mixture for 2 h with stirring. Finally the solution was concentrated to dryness to obtain polystyrenesulfonic acid (PSSA). PSSA was dissolved in 1N NaOH (excess molar of a hydroxyl anion) and the solution was dialyzed against deionized water for 2 days. The resulting solution was concentrated and freeze-dried to obtain poly (sodium styrenesulfonate) (PSSNa) in a quantitative yield.

Thermolysis of sulfonate ester was carried out as follows. PSSPen and random or block copolymer of St and SSPen were dissolved in chloroform and cast on silicon wafer. The sample film (~0.5 μm) was heated on a hot plate at 150 °C for a desired time. Decomposition degree of sulfonate ester was monitored by the peak at 1360 cm^{-1} ascribed to sulfonate ester. After sulfonate ester group in the film was completely decomposed, the film was dissolved in methanol or water, and characterized. Preparation method of PSSNa and random or block copolymer of St and sodium styrenesulfonate (SSNa) from thermally decomposed polymers containing SSPen was the same as described earlier.

2.5. Solubility of polymers in various solvents

All operations were conducted in an air-conditioned room at 25 °C. A 5 mg quantity of each polymer sample was mixed with 1 ml of solvents in a centrifuge tube. After 1 min of sonication (30 W), solubility of polymers was checked to be soluble, turbid or insoluble.

3. Results and discussion

3.1. Polymerization

Polymerization of SSPen was carried out using BPO/TEMPO system at 125 °C for 3 h. The color of the system turned red and precipitation formed during the polymerization. The obtained polymer was insoluble in chloroform and soluble in acetone, methanol and water. This result indicates that SSPen or PSSPen was decomposed during the polymerization and the sulfonic acid units produced. Polymerization of SSPen in the presence of TEMPO or AIBN/TEMPO as an initiating system did not occur at 120 °C within 30 h, and the monomer was recovered without decomposition. Although polymerization proceeded in PSSPen/BPO and PSSPen/BPO/DEPN systems, both obtained polymers were partially insoluble in THF and chloroform. The results indicate that thermal stability of SSPen decreased in the presence of BPO. Thus the BPO/TEMPO system and BPO/AIBN system were unsuitable for the polymerization of SSPen. Polymerization of SSBu using BPO/TEMPO system gave a similar result.

AIBN/DEPN initiating system was effective for the synthesis of PSSPen. The GPC curves of PSSPen and PSSBu are shown in Fig. 1. Polymerization was carried out at 120 °C for both samples. PSSPen showed low polydispersity ($M_w/M_n = 1.09$), compared to PSSBu ($M_w/M_n =$

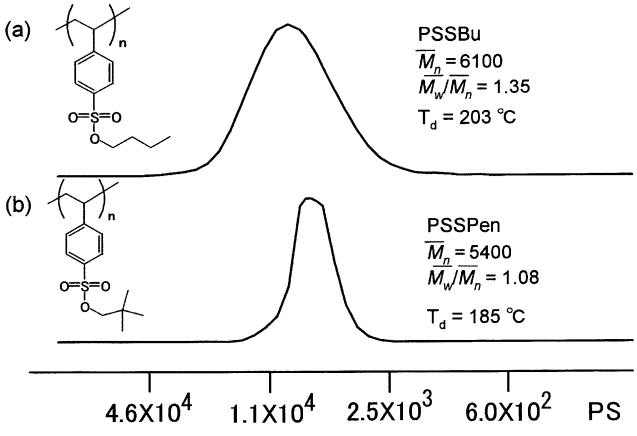


Fig. 1. GPC curves of (a) PSSBu and (b) PSSPen.

Table 1
Polymerization conditions and properties of polymers (Solvent: benzene. Reaction temperature: 100 °C except for PSSPen (120 °C))

Polymer	Feed ratio (mol) AIBN/DEPN/ SSBu or SSPen/St	Reaction time (h)	Content[a] of SSBu or SSPen in polymer (mol%)	$\overline{M}_n$[b]	$\overline{M}_w/\overline{M}_n$[b]	Yield (%)
PSSBu	1/2.5/50/0	22.0	100	6100	1.35	40
P(SSBu(33)-*ran*-St(67))	1/2.5/18/72	9.0	33	6300	1.23	42
PSSPen	1/2.5/24/0	6.5	100	5400	1.08	28
P(SSPen(86)-*ran*-St(14))	1/2.5/40/20	3.0	86	4900	1.11	36
P(SSPen(74)-*ran*-St(26))	1/2.5/33/33	12.0	74	6800	1.11	45
P(SSPen(43)-*ran*-St(57))	1/2.5/26/52	7.0	43	4900	1.16	68
P(SSPen(35)-*ran*-St(65))	1/2.5/26/52	4.0	35	6000	1.14	16

[a] Determined by elemental analysis.
[b] Determined by GPC. Eluent: THF.

1.35). Molecular weight of PSSPen increased with conversion and with decrease of quantity of initiators. PSSPen with high molecular weight (~12000) could be prepared with low polydispersity ($M_w/M_n < 1.2$). The decomposition temperatures of PSSPen and PSSBu were 185 and 203 °C, respectively. Thus, both polymers were thermally stable during the polymerization.

The polymerization conditions and characterization of PSSPen and P(St-*ran*-SSPen) are summarized in Table 1. The copolymerization of styrene with SSPen smoothly proceeded to generate random polymer having low polydispersity. To study the solubility of the polymers, the molecular weight of polymers was adjusted to 4900–6800.

Block copolymer of St and SSPen could be prepared with two methods. One was the polymerization of SSPen using DEPN-terminated PSt macroinitiator, and the other was the polymerization of St with DEPN-terminated PSSPen as a macroinitiator. The polymerization conditions and characterization of P(St-*block*-SSPen) are summarized in Table 2. For the polymerization of styrene, AIBN/DEPN ratio of 1/2.5 has been known to give polystyrene with high molecular weight and low polydispersity [7]. The polymerization of St was attempted using initiating system of DEPN-terminated PSSPen/DEPN with a ratio of 1/2.5 at 120 °C for 18 h. A desired block polymer was not obtained. When the ratio of DEPN to DEPN-terminated PSSPen was reduced from 2.5:1 to 1:0, the polymerization of St proceeded. Fig. 2(a) shows the GPC curves of the obtained polymer together with the PSSPen macroinitiator. The peak top of the curve moved from ca. 4800 to ca. 7000, which indicates the initiation of DEPN-terminated PSSPen. However, the obtained block polymer showed somewhat high polydispersity (M_w/M_n = 1.23). The leading was observed in the GPC curve of the block polymer. This may be due to the slow initiation rate of DEPN-terminated PSSPen compared to the propagation rate of St.

As shown in Fig. 2(b), chain extension of PSt macroinitiator smoothly proceeded. The polydispersity of the block polymer was kept low (M_w/M_n = 1.10). The composition of SSPen in the block polymer was increased with a decrease of a molar quantity of PSt macroinitiator added and with reaction time (high conversion).

3.2. Transformation of sulfonate esters into sulfonic acid

Although hydrolysis of PSSPen with NaOH (20 wt%) or HCl (35 wt%) was attempted in 1,4-dioxane at ambient temperature for 1 day, only partially hydrolyzed polymer was obtained. This is due to the formation of the precipitation of polymers during hydrolysis. On the other hand, the trimethylsilyl iodide (TMSI) method [11] gave good results. A reaction scheme is shown in Scheme 3. The reaction occurred homogeneously during the reaction. The quantitative conversion of PSSPen into PSSNa was confirmed by ^1H, ^{13}C NMR and IR measurements. Fig. 3 shows the ^1H NMR spectra of (a) PSSPen in $CDCl_3$, (b) PSSPen after the reaction with TMSI in $CDCl_3$, and (c) PSSNa in D_2O. In Fig. 3(b), unassignable weak peaks (0.6–1.6 and 4.6–6.3 ppm) due to decomposed products from ester moiety were observed. The peaks at 0.9 and 3.7 ppm ascribed to neopentyl group in PSSPen disappeared after the treatment with TMSI, suggesting a complete transformation of neopentyl

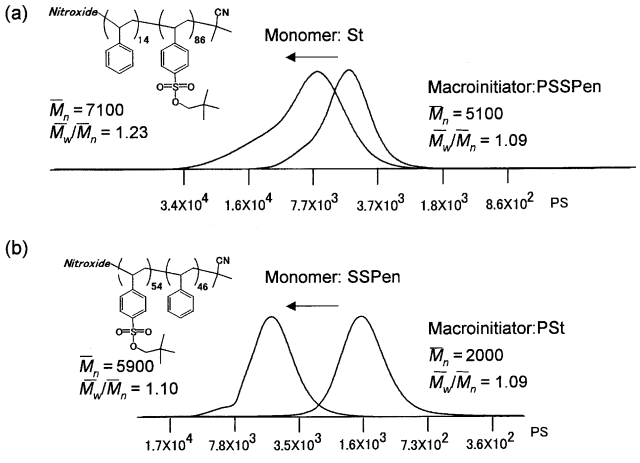
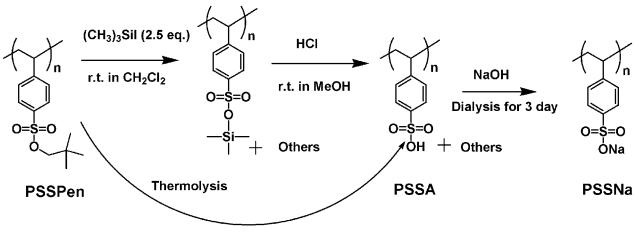


Fig. 2. GPC curves of (a) P(St(14)-*block*-SSPen(86)) using PSSPen (M_n = 5100) as a macroinitiator and (b) P(St(46)-*block*-SSPen(54)) using PSSPen (M_n = 2000) as a macroinitiator.

Table 2
Polymerization conditions and properties of P(St-*block*-SSPen) (Polymerization temperature: 120 °C)

P(St(*x*)-*block*-SSPen(*y*))	Macroinitiator			Monomer	Feed ratio (mol%) macroinitiator/DEPN/monomer	Reaction time (h)	Block polymer			Conversion (%)
	Macroinitiator	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]				Content[b] of SSPen (mol%)	$\bar{M}_n$ [a]	$\bar{M}_w/\bar{M}_n$ [a]	
P(St(*x*)-*block*-SSPen(*y*))	PSSPen	5100	1.09	St	1/2.5/250	18	0	5100	1.09	0
P(St(*x*)-*block*-SSPen(*y*))	PSSPen	11200	1.17	St	1/1.25/125	20	0	11200	1.17	0
P(St(86)-*block*-SSPen(14))	PSSPen	5100	1.09	St	1/0/48	3.5	14	7100	1.23	– [c]
P(St(70)-*block*-SSPen(30))	PSt	2000	1.09	SSPen	1/0/13	1.5	33	4300	1.13	16
P(St(62)-*block*-SSPen(38))	PSt	2000	1.09	SSPen	1/0/24	1.5	38	5400	1.11	23
P(St(46)-*block*-SSPen(54))	PSt	2000	1.09	SSPen	1/0/24	2.5	54	5900	1.10	34

[a] Determined by GPC. Eluent: THF.
[b] Determined by ^{1}H NMR.
[c] Not determined.



Scheme 3.

ester to trimethylsilyl esters (ca. 0 ppm in (b)). After subsequent treatment with 2N HCl, NaOH, and dialysis, the peak at ca. 0 ppm ascribed to trimethylsilyl esters completely disappeared (Fig. 3(c)). The spectrum was almost identical to commercially available PSSNa.

Although transformation of block or random polymers of SSPen with St proceeded by the reaction with TMSI, the reaction did not always proceed quantitatively, especially for the polymer with high St content. The optimization of the reaction conditions is now under investigation.

The thermolysis was an easy and simple method to transform SSPen into styrene sulfonic acid (SSA) units. It is known that cyclohexyl *p*-toluenesulfonate [14] generates *p*-toluenesulfonic acid quantitatively by thermolysis in solid state. The thermal decomposition of PSSPen was carried out at 150 °C in film to prevent further reaction of sulfonic acid produced. Decomposition degree could be monitored by IR measurements. Fig. 4 shows the IR spectra of PSSPen (a) before and (b) after thermal treatments. The characteristic peak at 1360 cm^{-1} ascribed to sulfonate esters completely disappeared after the thermal treatment for 20 min. The O–H stretching in Fig. 4(b) was observed due to the formation of sulfonic acid. Thermolysis of sulfonate esters was known to be auto-accelerated [15,16]. Decomposed degree of sulfonate ester was estimated by the

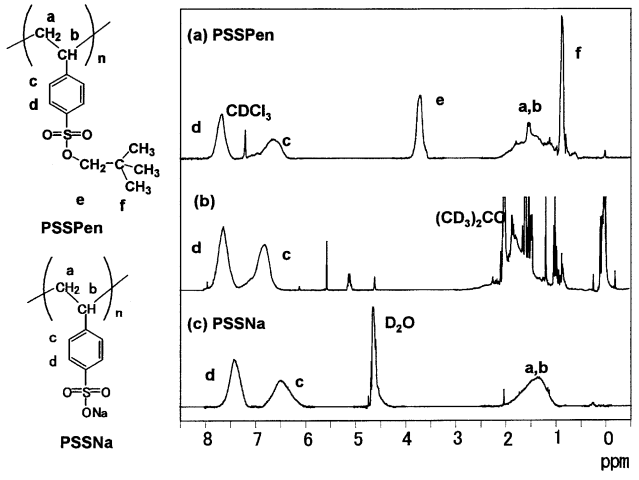


Fig. 3. ^{1}H NMR spectra of (a) PSSPen in $CDCl_3$ and (b) PSSPen after the reaction with TMSI in $(CD_3)_2CO$ and (c) PSSNa in D_2O at 270 MHz. Assignments are shown in the figure.

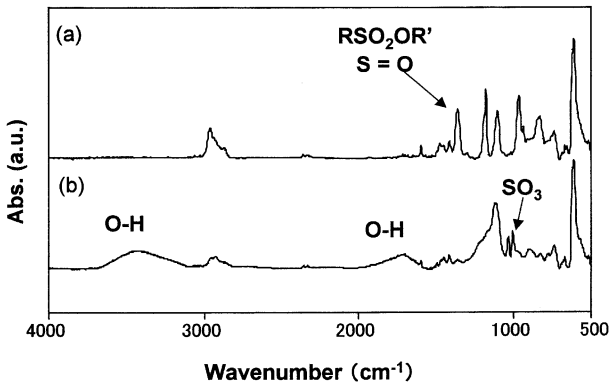


Fig. 4. FT-IR spectra of (a) PSSPen and (b) PSSPen after the thermal treatment at 150 °C for 20 min.

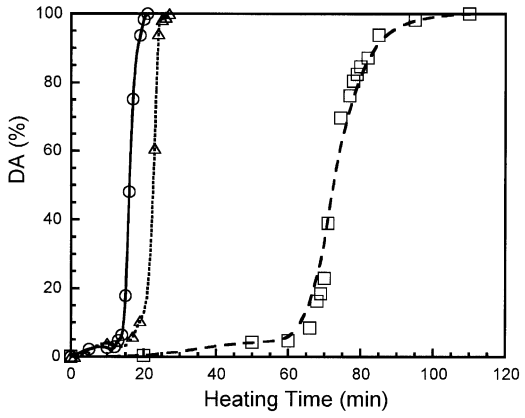


Fig. 5. Decomposition properties of sulfonate esters in PSSPen (○), P(St(62)-*block*-SSPen(38)) (△), and P(St(57)-*ran*-SSPen(43)) (□) on thermal treatment at 150 °C.

following equation:

$$\mathrm{DA}(\%) = (\Delta A_t(1360\ \mathrm{cm}^{-1})/\Delta A_{t=\infty}(1360\ \mathrm{cm}^{-1})) \times 100 \quad (1)$$

where DA is degree of decomposition of sulfonate ester in the film, $\Delta A_t(1360\ \mathrm{cm}^{-1})$ is the difference of the absorbance at 1360 cm^{-1} before and after heating for a certain period, and $\Delta A_{t=\infty}(1360\ \mathrm{cm}^{-1})$ is the difference of the absorbance at 1360 cm^{-1} before and after prolonged heating where the peak disappeared.

Thermal decomposition property of PSSPen, P(St(57)-*ran*-SSPen(43)), and P(St(62)-*block*-SSPen(38)) is shown in Fig. 5. The decomposition of SSPen units in PSSPen started after heating for 15 min and completed after 20 min. Decomposition time for the polymer was defined as the time where DA was 50% on heating. Decomposition time for PSSPen, P(St(57)-*ran*-SSPen(43)), and P(St(62)-*block*-SSPen(38)) was 15, 20, and 70 min, respectively. Table 3 summarizes the decomposition time for PSSPen, block or random compolymers of St and SSPen with different SSPen content. Decomposition time increased with the content of SSPen in polymer. Decomposition properties were largely affected not only by the content of PSSPen but also by the difference of copolymer type. Decomposition time of block copolymers of St and SSPen was shorter than that of random copolymers. It is suggested that a sulfonic acid unit produced by the decomposition of a certain sulfonate ester unit catalyzes the decomposition of the adjacent sulfonate ester units.

Thermally decomposed polymers were characterized by NMR. Fig. 6 shows the ^{1}H NMR spectra of (a) PSSPen in $CDCl_3$ and (b) thermally decomposed PSSPen in D_2O. Thermally decomposed PSSPen was prepared by heating at 150 °C for 20 min on silicon wafer, followed by neutralization and dialyzed. The peak at 3.7 ppm ascribed to neopentyl group in PSSPen disappeared after thermolysis, suggesting a complete decomposition of neopentyl ester. The peak at 0.9 ppm (**f** in Fig. 6) did not disappear completely. The peak intensity was not reproducible and was 5–15% of the original peak estimated from the comparison of the peak intensity ascribed to phenyl proton of the polymer.

Further study was carried out by ^{13}C NMR measurements. Fig. 7 shows the ^{13}C NMR spectra of (a) PSSPen in $CDCl_3$ and (b) thermally decomposed PSSPen in D_2O. The peaks **a** to **i** are assigned as shown in the figure. The peaks **g**, **h**, and **i** in Fig. 7(a) ascribed to neopentyl group in PSSPen disappeared and new peaks **j** appeared. It is considered that thermolysis of sulfonate esters proceeded with the scission of S–O–C bonds followed by the generation of a sulfonate anion and a counter carbocation. In the case of the thermolysis of SSPen units, unstable neopentyl cation may be produced. It is supposed that the large fraction of the produced neopentyl cation reacted with water to generate neopentyl alcohol. Some neopentyl cations reacted directly to the adjacent aromatic ring by Freadel-Crafts reaction, or caused rearrangement to stable 1,1-dimethylpropyl cation. The produced 1,1-dimethylpropyl cation reacted with the adjacent aromatic ring by Freadel-Crafts reaction, or gave

Table 3
Decomposition time of sulfonate ester in polymers

Random copolymer	Decomposition time (min)[a]	Block copolymer	Decomposition time (min)[a]
PSSPen	15	PSSPen	15
P(St(14)-*ran*-SSPen(86))	30	P(St(46)-*block*-SSPen(54))	20
P(St(57)-*ran*-SSPen(43))	70	P(St(62)-*block*-SSPen(38))	20
P(St(65)-*ran*-SSPen(35))	70	P(St(70)-*block*-SSPen(30))	30

[a] The time at which DA is 50%. $\mathrm{DA}(\%) = \Delta A_t(1360\ \mathrm{cm}^{-1})/\Delta A_{t=\infty}(1360\ \mathrm{cm}^{-1}) \times 100$.

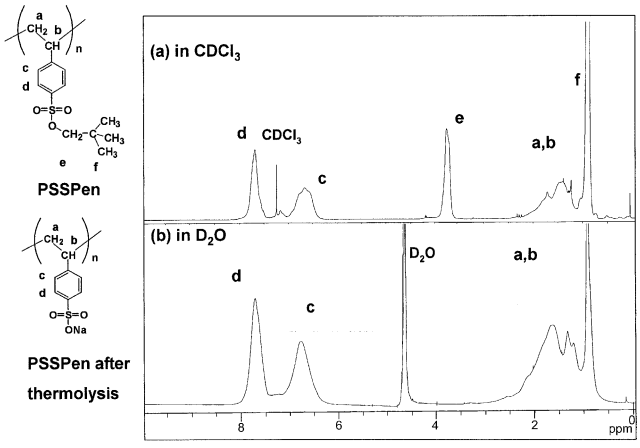


Fig. 6. ^{1}H NMR spectra (400 MHz) of (a) PSSPen in $CDCl_3$ and (b) thermally decomposed PSSPen in D_2O. Thermally decomposed PSSPen was prepared by heating at 150 °C for 20 min on silicon wafer followed by neutralization and dialyzed. Assignments are shown in the figure.

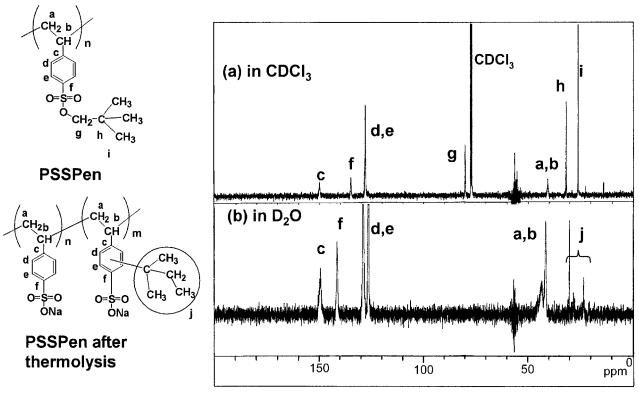


Fig. 7. ^{13}C NMR spectra (100 MHz) of (a) PSSPen in $CDCl_3$ and (b) thermally decomposed PSSPen in D_2O. Thermally decomposed PSSPen was prepared by heating at 150 °C for 20 min on silicon wafer followed by neutralization and dialyzed. Assignments are shown in the figure.

olefins by release of a proton. Thus, we can conclude that sulfonic acid was produced quantitatively in spite of the incomplete thermal transformation of SSPen units into styrenesulfonic acid (SSA) units.

3.3. Solubility characteristics of polymers

Polymers having sulfonic acid groups show amphiphilic characters. The solubility characteristics were briefly studied for the block or random copolymers of St and SSPen, St and SSA, and St and SSNa having different content and sequence. The solubility property of those polymers is summarized in Table 4. Effect of the content of SSA or SSNa on the solubility of the polymers was studied using methanol and water. Using methanol as a solvent, the solubility of the random and block copolymers of St and SSNa decreased with the increase of SSNa contents. On the other hand, random and block copolymers of St and SSA with any SSA contents were soluble in methanol. SSA content did not affect the solubility of the polymers in methanol.

Using water as a solvent, the solubility of the random and block copolymers of both St with SSNa and St with SSA increased with SSNa and SSA contents, respectively. The block copolymers showed slightly enhanced the solubility in water. This is due to easy formation of micelles of the block copolymers. It is known that micelle formation of diblock copolymers of styrene and sulfonated isoprene is observed in aqueous solution [17].

Significant effect of the monomer sequence in the block or random copolymers of St and SSA on the solubility was

Table 4
Solubility of polymers having sulfonate ester, sulfonic acid and sodium sulfonate (○, soluble; △, turbid, ×, insoluble; at 25 °C, ca. 0.5 wt%)

Polymer	Hexane	Tolune	Benzene	THF	Chloroform	Acetone	DMF	Methanol	Water
P(St(14)-*ran*-SSPen(86))	×	○	○	○	○	×	○	×	×
P(St(57)-*ran*-SSPen(43))	×	○	○	○	○	×	○	×	×
P(St(65)-*ran*-SSPen(35))	×	○	○	○	○	×	○	×	×
P(St(46)-*block*-SSPen(54))	×	○	○	○	○	×	○	×	×
P(St(62)-*block*-SSPen(38))	×	○	○	○	○	×	○	×	×
P(St(70)-*block*-SSPen(30))	×	○	○	○	○	×	○	×	×
P(St(14)-*ran*-SSA(86))[a]	×	△	△	△	×	×	○	○	○
P(St(57)-*ran*-SSA(43))[a]	×	△	△	○	×	○	○	○	△
P(St(65)-*ran*-SSA(35))[a]	×	△	△	○	×	○	○	○	×
P(St(46)-*block*-SSA(54))[a]	×	△	△	○	○	○	○	○	○
P(St(62)-*block*-SSA(38))[a]	×	△	△	○	○	○	○	○	○
P(St(70)-*block*-SSA(30))[a]	×	△	△	○	○	○	○	○	×
P(St(14)-*ran*-SSNA(86))[b]	×	×	×	×	×	×	○	×	○
P(St(57)-*ran*-SSNA(43))[b]	×	×	△	×	×	×	○	△	△
P(St(65)-*ran*-SSNA(35))[b]	×	×	△	×	×	×	○	○	×
P(St(46)-*block*-SSNA(54))[b]	×	×	△	×	×	×	○	×	○
P(St(62)-*block*-SSNA(38))[b]	×	×	△	×	×	×	○	△	○
P(St(70)-*block*-SSNA(30))[b]	×	×	△	×	×	×	○	○	△

[a] Transformed into sulfonic acid by thermolysis.
[b] Transformed into sodium sulfonate by the treatment of NaOH after thermolysis.

observed in chloroform. Although the random copolymers of St and SSA were not soluble in chloroform, the block copolymers of St and SSA were soluble in chloroform irrespective of SSA contents. Detailed studies on solubility behavior of those polymers are in progress.

4. Conclusions

P(St-*ran*-SSPen) and P(St-*block*-SSPen) with low polydispersity were prepared using nitroxide-mediated living radical polymerization technique. Random or block copolymerization of St with SSPen smoothly proceeded by a DEPN/AIBN initiating system. Transformation of the sulfonate ester to sulfonic acid was carried out by the reaction with trimethylsilyl iodide or thermolysis at 150 °C. Thermal degradation properties of sulfonate esters were affected by the composition and sequence of sulfonate esters in polymers. The random or block copolymers of St with SSA and St with SSNa showed amphiphilic characters.

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