JOURNAL OF Applied Polymer SCIENCE

Synthesis of Sulfonated Polynaphthalene, Polyanthracene, and Polypyrene as Strong Solid Acids via Oxidative Coupling Polymerization

Kiyoshi Tanemura,[1] Tsuneo Suzuki,[1] Takaaki Horaguchi[2]

[1]School of Life Dentistry at Niigata, Nippon Dental University, Hamaura-cho, Niigata 951-8580, Japan
[2]Department of Chemistry, Faculty of Science, Niigata University, Ikarashi, Niigata 950-2181, Japan
Correspondence to: K. Tanemura (E-mail: tanemura@ngt.ndu.ac.jp)

ABSTRACT: Oxidative coupling polymerization of naphthalene, anthracene, and pyrene with $FeCl_3$ in nitrobenzene under nitrogen gave polynaphthalene (PNP), polyanthracene (PAT), and polypyrene (PPR) in good yields, respectively. PNP, PAT, and PPR were transformed into sulfonated PNP (S-PNP), S-PAT, and S-PPR by the treatment with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen, respectively. The activities of S-PPR were higher than those of S-PNP and S-PAT. For the hydrolysis of cyclohexyl acetate and oleyl acetate in water, activities of S-PPR, S-PAT, and S-PNP were considerably higher than those of the other conventional solid acids. Rate constants of S-PPR were *2.8 and 11.7 times larger* than those of the sulfonated condensed polynuclear aromatic (S-COPNA(PR)) resin (PR = pyrene) for the hydrolysis of cyclohexyl acetate and oleyl acetate, respectively. S-PPR, S-PAT, and S-PNP were reused without significant loss of activities. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: oxidation; polymerization; sulfonated polymers; acid catalysts; solid acids

Received 14 February 2012; accepted 13 May 2012; published online
DOI: 10.1002/app.38045

INTRODUCTION

Highly sulfonated polymers, which are used for acid catalysts, are of growing interest for many industrial applications.[1–14] For reactions in which water participates as a reactant such as hydrolysis, only a few solid acids involving sulfonated polymers are acceptable in terms of their activity, stability, and insolubility.[15,16] A difficulty is caused by the poisoning of the acid sites by water molecules, and in fact, most solid acids lose their catalytic activities in aqueous solutions.[15,16] Development of a new water-tolerant solid acids will have a major impact in industrial applications. Some sulfonated polyphenylenes[2,3,7,8] and sulfonated carbon materials prepared from naphthalene in sulfuric acid[17,18] have been prepared. However, these materials were less active or partially soluble to water and polar organic solvents such as methanol, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

We have reported the synthesis of the S-COPNA resins as strong protonic acids.[19,20] Although the S-COPNA resins were highly active than conventional solid acids, they would lose catalytic activity for the hydrolysis of esters in water because of the existence of hydrophilic terminal CH_2OH groups. We tried to synthesize more hydrophobic sulfonated polyarenes without terminal CH_2OH groups. We chose anthracene as the starting material which possessed the larger polynuclear aromatic skeleton than benzene and naphthalene. Effective polymerization was realized by the oxidative coupling reaction using $FeCl_3$ in nitrobenzene,[21–23] in which $FeCl_3$ acts as both a Lewis acid and an oxidant.[21,22,24–27] The obtained polyanthracene (PAT) was converted into sulfonated polyanthracene (S-PAT) by the treatment with chlorosulfonic acid. Furthermore, sulfonated polynaphthalene (S-PNP) and sulfonated polypyrene (S-PPR) were synthesized for comparison. These sulfonated polymers were more active than conventional solid acids not only for the esterification of carboxylic acids but also quite active for the hydrolysis of esters in water. In this article, we wish to report the synthesis and evaluation of S-PNP, S-PAT, and S-PPR.

EXPERIMENTAL

Methods

IR spectra were recorded on a JEOL FT/IR-620 spectrophotometer. UV spectra were recorded on a Shimadzu UV–Vis spectrophotometer UV-2550. XRD diffractograms were obtained with $Cu_{K\alpha}$ radiation over a 2θ range from 5 to 65°. Thermogravimetric analysis (TGA) in air atmosphere was carried out on a Rigaku Thermo Plus 2 station TG-DTA TG 8120 at a heating

© 2012 Wiley Periodicals, Inc.

rate of 10°C/min. All samples were evacuated at 150°C for 1 h under reduced pressure prior to the measurement of TGA.

Preparation of PAT

To a solution of anthracene (14.2 g, 80 mmol) in nitrobenzene (137 mL) was added $FeCl_3$ (28.6 g, 176 mmol) with vigorous stirring at room temperature under nitrogen. The solution was stirred at 60°C for 1 h and then at 150°C for 24 h. The mixture was poured into methanol (686 mL) containing a small amount of concentrated HCl (3 mL). The precipitate was filtered and washed with methanol. It was dispersed in chloroform (200 mL) to remove adsorbed nitrobenzene. The precipitate was filtered, washed with chloroform, and dried at 120°C for 3 h under reduced pressure. PAT (12.2 g, 87%) was obtained as the black powder. IR (KBr, cm^{-1}): 1578, 1561, 1492, 877, 812, and 753 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{14}H_{6.09}Cl_{0.60})_n$.

Preparation of Less Crosslinked PAT

To a solution of anthracene (14.2 g, 80 mmol) in nitrobenzene (137 mL) was added $FeCl_3$ (28.6 g, 176 mmol) with vigorous stirring at room temperature under nitrogen. The solution was stirred at 60°C for 30 min, and poured into methanol (686 mL) containing a small amount of concentrated HCl (3 mL). The precipitate was filtered and washed with methanol. It was dispersed in dichloromethane (150 mL). The precipitate was filtered, washed with dichloromethane, and dried at 120°C for 3 h under reduced pressure. The less crosslinked PAT (5.1 g, 36%) was obtained as the brown powder. It was insoluble to hexane and MeOH, slightly soluble to dichloromethane, chloroform, benzene, ethyl acetate, and DMSO, and partially soluble to tetrahydrofuron (THF). IR (KBr, cm^{-1}): 3047, 1521, 1492, 882, 808, and 738 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{14}H_{7.17}Cl_{0.21})_n$.

The Sulfonation of PAT by Chlorosulfonic Acid

A solution of chlorosulfonic acid (3.9 mL, 60 mmol) in dichloromethane (24 mL) was slowly added to the mixture of the PAT (2.5 g, 15 mmol) in dichloromethane (60 mL) with stirring under nitrogen. The mixture was stirred at 25°C for 24 h. The precipitate was collected by filtration and washed with dichloromethane. The precipitate was dispersed in 0.5*M* NaOH solution (200 mL) and stirred at 80°C for 4 h. The mixture was filtered and the precipitate was washed with distilled water. The precipitate was dispersed in 2*M* sulfuric acid solution (200 mL) and stirred at room temperature for 1 h. The mixture was filtered and the precipitate was washed with distilled water. The precipitate was heated at 150°C for 3 h under reduced pressure. The precipitate was dispersed in distilled water (100 mL) and stirred at room temperature for 1 h. The mixture was filtered and the precipitate was washed with distilled water until the wash water reached a pH of 7. The precipitate was dried at 150°C for 3 h under reduced pressure to give the sulfonated polymer as the hygroscopic black powder. The yield was 2.4 g. IR (KBr, cm^{-1}): 1588 (ArH), 1168, 1033 (SO_3H), 817, 753 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{14}H_{6.61}Cl_{0.45}O_{2.56}S_{0.55})_n$.

Acid density was determined by titration using the following procedure. The sulfonated polymer (168 mg) was placed in 0.1*M* aqueous NaOH solution (20 mL) and the mixture was kept at room temperature for 1 day. The precipitate was filtered and the filtrate was then back titrated with 0.1*M* aqueous potassium hydrogen phthalate solution using phenolphthalein as an indicator.

Preparation of S-PAT by Sulfuric Acid

PAT (5.0 g) was added to concentrated sulfuric acid (40 mL). The mixture was stirred at 25°C for 24 h under nitrogen. The mixture was poured into distilled water (270 mL). The precipitate was collected by filtration and washed repeatedly with hot distilled water (>80°C) until the wash water reached a pH of 7. The precipitate was dried at 150°C for 3 h under reduced pressure. S-PAT (5.3 g) was obtained as the hygroscopic black powder. IR (KBr, cm^{-1}): 1589, 1558 (ArH), 1164, 1032 (SO_3H), 810, 753 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{14}H_{6.87}Cl_{0.28}O_{2.55}S_{0.46})_n$.

Preparation of PNP

To a solution of naphthalene (10.2 g, 80 mmol) in nitrobenzene (137 mL) was added $FeCl_3$ (28.6 g, 176 mmol) with vigorous stirring at room temperature under nitrogen. The solution was stirred at 90°C for 1 h and then at 150°C for 24 h. The mixture was poured into methanol (686 mL) containing a small amount of concentrated HCl (3 mL). The precipitate was filtered and washed with methanol. It was dispersed in chloroform (200 mL). The precipitate was filtered, washed with chloroform, and dried at 120°C for 3 h under reduced pressure. PNP (8.3 g, 83%) was obtained as the black powder. IR (KBr, cm^{-1}): 1491, 869, 808, 752 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{10}H_{4.33}Cl_{0.51})_n$.

Preparation of S-PNP by Chlorosulfonic Acid

S-PNP (3.3 g) was prepared from PNP (2.5 g) as the hygroscopic black powder in a manner similar to the sulfonation of PAT by chlorosulfonic acid. IR (KBr, cm^{-1}): 1552 (ArH), 1171, 1029 (SO_3H), 824, 764 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{10}H_{4.92}Cl_{0.30}O_{1.78}S_{0.36})_n$.

Preparation of PPR

To a solution of pyrene (16.2 g, 80 mmol) in nitrobenzene (137 mL) was added $FeCl_3$ (28.6 g, 176 mmol) with vigorous stirring at room temperature under nitrogen. The solution was stirred at 40°C for 24 h, and poured into methanol (686 mL) containing a small amount of concentrated HCl (3 mL). The precipitate was filtered and washed with methanol. It was dispersed in chloroform (200 mL). The precipitate was filtered, washed with chloroform, and dried at 150°C for 3 h under reduced pressure. PPR (16.0 g, 100%) was obtained as the reddish purple powder. IR (KBr, cm^{-1}): 3037, 1637, 1601, 1489, 1457, 902, 845, 815, 725, 682 (ArH). The nominal sample composition was determined by elemental analysis to be $(C_{16}H_{6.98}Cl_{0.14})_n$.

Preparation of S-PPR by Chlorosulfonic Acid

S-PPR (1.8 g) was prepared from PPR (2.5 g) as the hygroscopic black powder in a manner similar to the sulfonation of PAT by chlorosulfonic acid. IR (KBr, cm^{-1}): 1603, 1490 (ArH), 1198, 1042 (SO_3H), 834, 816 (ArH). The nominal sample

Table I. Polymerization of Anthracene by $FeCl_3$ in Nitrobenzene[a]

Entry	$FeCl_3$ (equiv.)	Insoluble in $CHCl_3$ (%)	Soluble in $CHCl_3$ (%)
1	0.2	2	90[b]
2	2.0	77	10
3	2.1	81	6
4	2.2	86	4
5	2.4	87	8

[a]Reagents and conditions: anthracene 14.2 g (80 mmol), $PhNO_2$ 137 mL, 60°C, 24 h, N_2, [b]Contains large amounts of anthracene.

composition was determined by elemental analysis to be $(C_{16}H_{8.03}Cl_{0.30}O_{2.88}S_{0.62})_n$.

Determination of the Rate Constant (k) for the Esterification of Carboxylic Acids and the Hydrolysis of Esters

Esterification of acetic acid with ethanol was typically carried out at 80°C in the mixture of ethanol (56.80 mL, 1.0 mol), acetic acid (5.71 mL, 0.1 mol), and the catalyst (200 mg). The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min was analyzed by titration with 0.1*M* aqueous NaOH solution. In the actual experiment, a blank sample containing EtOH (62.51 mL) and the catalyst (200 mg) without acetic acid was also titrated. From the difference in titrant volume required to reach the endpoint for the blank, the concentration of acetic acid was calculated. Rate constants were determined by the plots between time vs. $[1/(a - b)]\ln[b(a - x)/a(b - x)]$ (the second-order reaction) using the method of least squares. The rate constant of sulfuric acid was determined in the early stage of the reaction (10 min). S-PAT and S-PNP were dried at 150°C for 1 h under reduced pressure prior to the reaction.

Esterification of benzoic acid with ethanol was carried out in the mixture of ethanol (56.80 mL, 1.0 mol) and benzoic acid (12.2 g, 0.1 mol) at 80°C. The reaction mixture at 10, 20, 40, 60, 100, 140, 180, 220, 260, 300, 340, and 380 min was analyzed by titration with 0.1*M* aqueous NaOH solution.

The hydrolysis of cyclohexyl acetate was carried out in the mixture of cyclohexyl acetate (0.64 mL, 4.4 mmol) and distilled water (59.40 mL, 3.3 mol) at 90°C. The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min was analyzed by titration with 0.005*M* aqueous NaOH solution.

The hydrolysis of oleyl acetate was carried out in the mixture of oleyl acetate (1.57 mL, 4.4 mmol) and distilled water (59.40 mL, 3.3 mol) at 100°C. The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, 140, 160, and 180 min was analyzed by titration with 0.005*M* aqueous NaOH solution.

Recycle Experiments for the Formation of Ethyl Acetate Catalyzed by S-PPR

After esterification of acetic acid with ethanol for 4 h, the catalyst was recovered by filtration. The conversion of acetic acid was determined by acid titration of remaining AcOH with 0.1*M* aqueous NaOH solution. The catalyst was reused repeatedly for the next reaction.

Table II. The Results for Elemental Analyses of PAT

Entry	Temp. (°C)	Time (h)	Chemical composition
1	60	0.5	$(C_{14}H_{7.17}Cl_{0.21})_n$
2	60	24	$(C_{14}H_{6.69}Cl_{0.52})_n$
3	150	24	$(C_{14}H_{6.09}Cl_{0.60})_n$

Recycle Experiments for the Hydrolysis of Cyclohexyl Acetate Catalyzed by S-PPR

After the hydrolysis of cyclohexyl acetate for 1 h, the catalyst was recovered by filtration. The conversion of cyclohexyl acetate was determined by acid titration of AcOH with 0.005*M* aqueous NaOH solution. The catalyst was reused repeatedly for the next reaction.

RESULTS AND DISCUSSION

Synthesis of PAT

Anthracene was polymerized by oxidative coupling polymerization with $FeCl_3$ in nitrobenzene at 60°C for 24 h under nitrogen to give PAT as the black powder. PAT was separated into chloroform-soluble and -insoluble fractions. The chloroform-insoluble fraction is the higher molecular weight part of PAT. When 2.2 equivalents of $FeCl_3$ were employed, chloroform-insoluble PAT was obtained in the good yield (86%) (Table I, entry 4). It was insoluble to water and many organic solvents such as hexane, benzene, Et_2O, acetone, CH_3CN, MeOH, DMSO, and DMF, and slightly soluble to nitrobenzene, chloroform, and THF.

Although much work with dehydrogenative condensation has been done with naphthalene,[28–31] a less degree of attention has been paid to higher members such as anthracene[31–41] and pyrene.[36,42–44] It has been briefly mentioned that anthracene reacted with $FeCl_3$ in a fused mixture or in carbon tetrachloride to yield the chlorinated polymer.[45] Table II summarizes the results for elemental analyses of PAT. PAT obtained by the reaction at 60°C for 30 min was the partially crosslinked polymer (entry 1). PAT obtained in our study also resulted in the

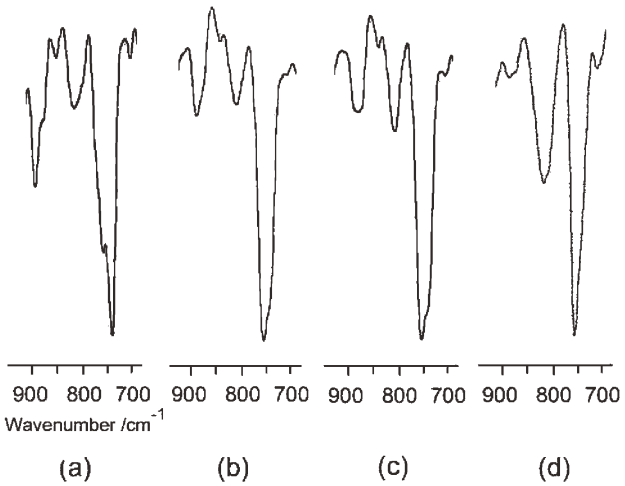

Figure 1. IR spectra of PAT prepared by the reactions (a) at 60°C for 30 min, (b) at 60°C for 24 h, (c) at 100°C for 24 h, and (d) at 150°C for 24 h.

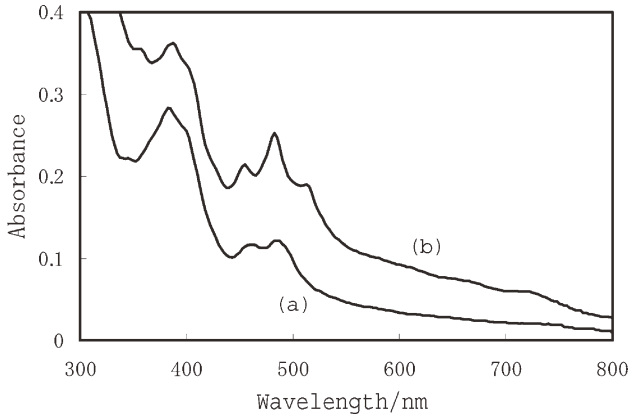

Figure 2. UV/Vis absorption spectra of PAT ($6.8 \times 10^{-5}M$) in $CHCl_3$ prepared by the reactions at 60°C for (a) 30 min and (b) 24 h (only in the soluble division).

incorporation of the chlorine atom. Further crosslinking and chlorination occurred as the reaction proceeded (entries 2 and 3).

The IR spectrum of PAT showed characteristic absorptions at 882, 808, 753, and 738 cm^{-1} assigned to out-of-plane carbon–hydrogen vibration for one, three, four, and four adjacent hydrogen atoms of the benzene ring, respectively [Figure 1(a)]. The absorptions at 882 and 738 cm^{-1} decreased and the absorption at 808 cm^{-1} increased as the reaction proceeded [Figure 1(b–d)]. Figure 2 shows the UV/Vis absorption spectra of PAT in chloroform prepared by the reactions at 60°C for 30 min and 24 h. We employed the soluble division for the measurement of the polymer prepared by the reaction for 24 h, because it was hardly dissolved in chloroform. The absorptions at 384, 462, and 487 nm increased and new absorptions at 514 and 719 nm appeared after 24 h. These facts obtained by IR and UV/Vis spectroscopy suggest the increase of the conjugated system by crosslinking. The ^1H NMR spectrum of the soluble division of PAT in DMSO-d_6 obtained by the reaction for 30 min is shown in Figure 3. No peak was observed in the aliphatic region. Many complex signals appeared at 7.30–9.59 ppm. Signals observed at 7.30–7.88, 8.08–8.44, and 8.58–9.59 ppm may be assigned to the protons of (2,3,6,7)-, (1,4,5,8)-, and (9,10)-positions of the

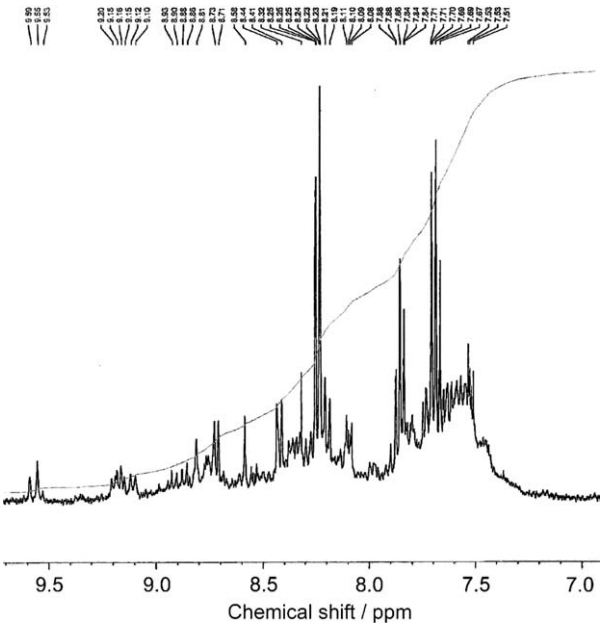

Figure 3. The ^1H NMR spectrum (400 MHz) of PAT in DMSO-d_6.

anthracene ring of PAT, referring to those of the anthracene monomer, respectively. This fact indicates that the anthracene unit would be combined with various positions. We cannot determine the coupling positions of anthracene from these spectroscopic observations at the present time. Several dimers with various coupling positions and more condensed materials have been reported to obtain by oxidative coupling of anthracene with $SbCl_5$.[35–37]

Synthesis of Sulfonated Polyanthracene (S-PAT)

PAT, obtained by oxidative coupling polymerization at 60°C for 24 h, was sulfonated by concentrated sulfuric acid to give S-PAT as the black powder. The results are summarized in Table III. Acid density was determined by acid titration. Rate constant (k) for the esterification of acetic acid with ethanol was determined by acid titration of remaining acetic acid included in the reaction mixture. When the reaction was performed in fuming sulfuric acid (SO_3, 15 wt %) at 25°C for 24 h under nitrogen, the catalyst with the highest acid density was obtained (entry 1).

Table III. The Sulfonation of PAT by H_2SO_4[a]

Entry	Temp. (°C)	Time (h)	Acid density ($mmol \cdot g^{-1}$)[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]
1[e]	25	24	6.87	3.61	++++
2	150	15	4.15	4.60	+++
3	100	15	3.53	6.68	+++
4	80	24	3.55	7.13	++
5[f]	80	24	3.02	6.06	++
6	60	24	3.20	4.95	++
7	25	24	2.83	5.97	-

[a]Reagents and conditions: PAT 5.0 g, H_2SO_4 40 mL, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ <++++ (partially soluble), [e]Fuming sulfuric acid (SO_3, 15 wt %) (40 mL) was used, [f]$(CH_3CO)_2O$ (120 mmol) was added.

Table IV. The Sulfonation of PAT by $ClSO_3H$[a]

Entry	Temp. (°C)	Acid density ($mmol \cdot g^{-1}$)[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]
1[e]	100	4.78	7.14	+++
2[f]	50	3.63	7.58	++
3	25	3.35	7.36	-

[a]Reagents and conditions: PAT 2.5 g, $ClSO_3H$ 3.9 mL (60 mmol), CH_2Cl_2 84 mL, 24 h, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ <++++ (partially soluble), [e]Solvent: 1,1,2,2,-Tetrachloroethane, [f]Solvent: chloroform.

However, it was partially soluble to boiling water. The results for sulfonation with sulfuric acid are summarized in entries 2–7. As the reaction temperature becomes higher, S-PAT possessed higher acid density and it was more soluble to boiling water. Although acetic anhydride was added to exclude water produced during the reaction, both acid density and rate constant k decreased (entry 5). S-PAT possessing the acetyl group was not detected by IR spectroscopy. The sulfonation of PAT by sulfuric acid at 25°C for 24 h under nitrogen afforded S-PAT insoluble to boiling water (entry 7). The results for the sulfonation of PAT by $ClSO_3H$ are summarized in Table IV. When PAT was treated with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen, S-PAT was insoluble to boiling water (Table IV, entry 3). It was more active than S-PAT sulfonated by sulfonic acid (Table III, entry 7 and Table IV, entry 3). It was insoluble to less polar hot organic solvents, but slightly soluble to hot MeOH and partially soluble to hot DMF and DMSO.

To prepare S-PAT with less solubility to organic solvents, we conducted polymerization of anthracene at higher temperature (150°C). The obtained PAT was treated with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen to give S-PAT (Table V, entry 3). S-PAT was insoluble to boiling water and hot MeOH, but slightly soluble to hot DMSO. S-PAT possessed the composition of $(C_{14}H_{6.61}Cl_{0.45}O_{3.19}S_{0.55})_n$. The decrease of the chlorine atom during sulfonation was observed (Table II, entry 3). The chlorine atom might be eliminated for substitution by the OH group or crosslinking between benzene rings. The IR spectrum showed characteristic absorptions at 1588, 817, and 753 cm^{-1} owing to the benzene ring and 1168 and 1033 cm^{-1} owing to the SO_3H group.

Figure 4 shows the XRD patterns of (a) PAT and (b) S-PAT. The broad diffraction peaks (2θ = 5–15 and 15–35°) can be attributed to the amorphous structure. Existence of the broad diffraction peak (2θ = 5–15°) suggests that PAT indeed consists of the anthracene repetitive units.[46–48] The weak broad diffraction peak (2θ = 35–50°) is owing to the a axis of the graphite structure.[11,17,18,49] There was not a large difference in the XRD patterns between PAT and S-PAT, suggesting that the sulfonation process did not affect the microstructure of PAT so much.

Synthesis of S-PNP

For the comparison, synthesis and evaluation of S-PNP were investigated. Polynaphthalene (PNP) was obtained as the black powder by oxidative coupling polymerization of naphthalene by $FeCl_3$ in nitrobenzene at 90°C for 48 h under nitrogen. PNP was insoluble to water and many organic solvents such as hexane, benzene, Et_2O, acetone, CH_3CN, MeOH, DMSO, and DMF, and slightly soluble to nitrobenzene, chloroform, and THF.

It has been reported that 1,4-polynaphthalene was prepared by electrochemical polymerization of naphthalene using a composite electrolyte of $AlCl_3$ and Cu_2Cl_2.[29] 1,1′-Binaphtyl and 1,4-di-α-naphthylnaphthalene were isolated by the reaction of naphthalene with $FeCl_3$-H_2O.[28] 1,4- or 1,2-Linked dihydropolynaphthalene was formed by $AlCl_3$ alone.[30] It has been mentioned that the treatment of naphthalene with $FeCl_3$ in a fused mixture afforded the chlorinated polymer.[45] Hydrogen chloride evolved during polymerization was employed for chlorination of the products.[35]

Table VI summarizes the results for elemental analyses of PNP obtained in our study. PNP obtained by the reaction at 60°C for 30 min was the partially crosslinked polymer (entry 1). PNP resulted in the incorporation of chlorine atoms. Further crosslinking and chlorination occurred as the reaction proceeded (entries 2 and 3).

The IR spectrum of PNP showed characteristic absorptions at 3047 cm^{-1} owing to the benzene ring. The weak absorption at 874 cm^{-1} and the strong absorptions at 818, 802, and 752 cm^{-1} were assigned to out-of-plane carbon–hydrogen vibration for one, two, three, and four adjacent hydrogen atoms of the benzene ring, respectively [Figure 5(a)]. The intensity of these absorptions was similar to that for 1,4-polynaphthalene reported by Hara and Toshima.[29] The absorptions at 874, 818, and 802 cm^{-1} increased as the reaction proceeded (Figure 5). It

Table V. The Sulfonation of More crosslinked PAT by H_2SO_4[a]

Entry	Acid density ($mmol \cdot g^{-1}$)[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]	Solubility to hot MeOH[d]	Solubility to hot DMSO[d]
1[e,f]	2.94	4.63	-	-	+++
2[f]	1.51	2.72	-	-	+
3[f,g]	2.33	3.26	-	-	+
4[g,h]	2.85	5.90	-	+	++

[a]Reagents and conditions: PAT 5.0 g, H_2SO_4 40 mL, 25°C, 24 h, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ <++++ (partially soluble), [e]Fuming sulfuric acid (SO_3, 15 wt %) (40 mL) was used, [f]Polymerization of anthracene was carried out at 150°C, [g]Sulfonated by $ClSO_3H$ in dichloromethane, [h]Polymerization of anthracene was carried out at 100°C.

Applied Polymer SCIENCE

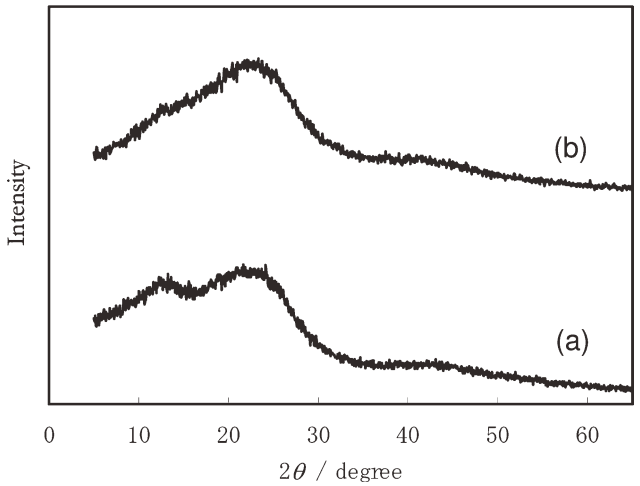

Figure 4. XRD patterns of (a) PAT and (b) S-PAT.

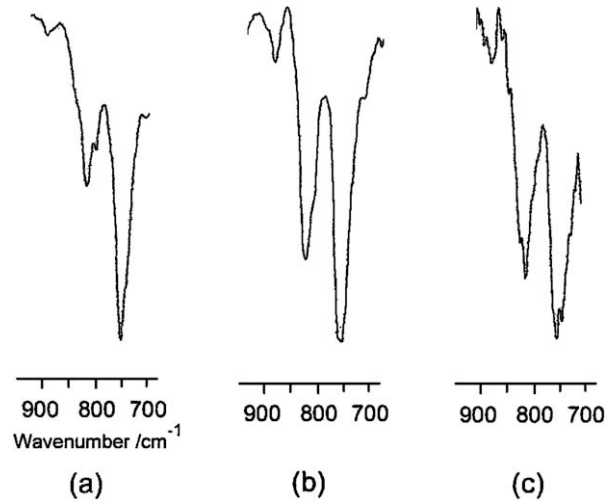

Figure 5. IR spectra of PNP prepared by the reactions (a) at 90°C for 30 min, (b) at 90°C for 48 h, and (c) at 150°C for 24 h.

suggests further crosslinking of PNP during the reaction. The UV/Vis absorption spectra of PNP in chloroform prepared by the reaction at 90°C for 30 min exhibited the absorptions at 487, 517, and 555 nm. We could not measure the UV/Vis spectrum of PNP after 48 h because it was quite insoluble to any tested solvents. The ^{1}H NMR spectrum of the soluble part of PNP in DMSO-d_6 obtained by the reaction at 90°C for 30 min gave the simple pattern in the aromatic region as shown in Figure 6. No peak was observed in the aliphatic region. These peaks could be attributed to the protons of 1,4-linked polynaphthalene (Figure 7). The peak c in Figure 6 is assigned to the protons of the peri-position of the naphthalene ring, referring to that of the naphthalene monomer. On the basis of these literatures, elemental analyses, IR, and ^{1}H NMR spectra, the polymer obtained in our study may possess the partially condensed structure of 1,4-linked polynaphthalene.

PNP polymerized at 90°C for 48 h was sulfonated with concentrated sulfuric acid to give S-PNP as the black powder. The results are summarized in Table VII. The treatment of PNP with sulfuric acid at 25°C for 24 h under nitrogen afforded S-PNP which was insoluble to boiling water (entry 3). PNP was sulfonated with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen to give S-PNP which was insoluble to boiling water (entry 4). It was more active than S-PNP sulfonated by sulfuric acid at 25°C for 24 h (entries 3 and 4). It was insoluble to less polar hot organic solvents, but partially soluble to hot MeOH, DMF, and DMSO.

As an attempt to suppress the solubility of S-PNP to organic solvents, an attempt to postcure PNP prior to sulfonation was carried out. PNP was heated at 300°C for 4 h under nitrogen.

Table VI. The Results for Elemental Analyses of PNP

Entry	Temp. (°C)	Time (h)	Chemical composition
1	90	0.5	$(C_{10}H_{4.91}Cl_{0.15})_n$
2	90	48	$(C_{10}H_{4.80}Cl_{0.24})_n$
3	150	24	$(C_{10}H_{4.33}Cl_{0.51})_n$

A large amount of hydrogen chloride was generated. Postcured PNP was treated with chlorosulfonic acid in dichloromethane at 25°C for 24 h. The obtained S-PNP was more active than the others, but partially soluble to hot DMSO (Table VIII, entry 4).

To synthesize S-PNP with less solubility to organic solvents, we conducted polymerization of naphthalene at higher temperature. Many impurities such as $FeCl_3$, $FeCl_2$, and nitrobenzene

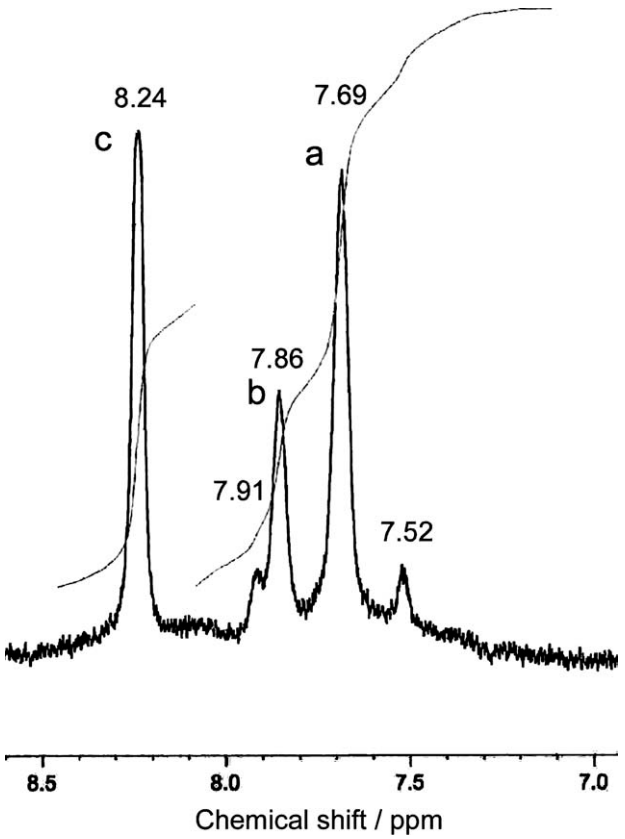

Figure 6. The ^{1}H NMR spectrum (400 MHz) of PNP in DMSO-d_6.

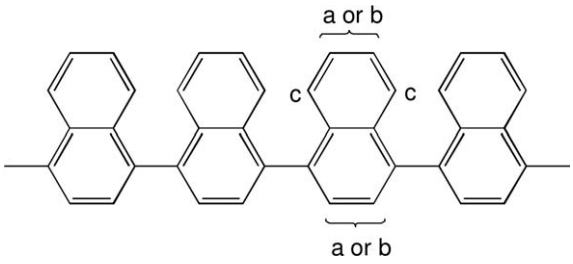

Figure 7. Plausible structure of PNP.

were incorporated when polymerization was carried out at 180°C. PAT polymerized at 150°C was treated with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen to give S-PNP. It was insoluble to boiling water and hot MeOH, but slightly soluble to hot DMSO (entry 3). It possessed the composition of $(C_{10}H_{4.92}Cl_{0.30}O_{1.96}S_{0.36})_n$. The decrease of the chlorine atom during sulfonation was observed (Table VI, entry 3). The IR spectrum showed characteristic absorptions at 824 and 764 cm^{-1} owing to the benzene ring and 1171 and 1029 cm^{-1} owing to the SO_3H group.

Figure 8 shows the XRD patterns of (a) PNP and (b) S-PNP. The broad diffraction peaks (2θ = 5–15 and 15–35°) can be attributed to the amorphous structure. Existence of the broad diffraction peak (2θ = 5–15°) suggests that PNP indeed consists of the naphthalene repetitive units.[46,50] The weak broad diffraction peak (2θ = 35–50°) is owing to the *a* axis of the graphite structure.[11,17,18,49] There was not a large difference in the XRD patterns between PNP and S-PNP, suggesting that the sulfonation process did not affect the microstructure of PNP so much.

Synthesis of Sulfonated Polypyrene (S-PPR)

Polypyrene (PPR) was produced as the reddish purple powder by oxidative coupling polymerization of pyrene with $FeCl_3$ in nitrobenzene at 40°C for 24 h under nitrogen. PPR was insoluble to water and many organic solvents such as hexane, benzene, Et_2O, acetone, CH_3CN, MeOH, nitrobenzene, chloroform, THF, DMSO, and DMF.

Few reports on the synthesis of PPR exist because of the difficulty of polymerization. It has been reported that 1,1′-bipyrene was produced by the treatments of pyrene with $SbCl_3$–$AlCl_3$,[36] $AlCl_3$–$CuCl_2$,[44] and periodic acid in acetic acid.[42] Recently, PPR was synthesized by chemical oxidative polymerization of pyrene with $FeCl_3$ in hexane–nitromethane and the results indicated that PPR was formed mainly through dehydrocoupling between (2- or 1-) and (2′- or 1′-) positions on the pyrene ring.[46]

Table IX summarizes the results for elemental analyses of PPR obtained in our study. The polymer generated by the reaction at 40°C for 30 min may be partially crosslinked PPR (entry 1). Chlorine atoms were incorporated during the reaction. Further crosslinking and chlorination occurred as the reaction proceeded (entry 2).

The IR spectrum of PPR showed characteristic absorptions at 3037, 1601, and 1489 cm^{-1} owing to the benzene ring. The weak absorption at 902 cm^{-1}, the strong absorptions at 845 and 815 cm^{-1}, and the weak absorption at 725 cm^{-1} were assigned to out-of-plane carbon–hydrogen vibration for one, two, two, and three adjacent hydrogen atoms of the benzene ring, respectively (Figure 9). The weak absorption at 725 cm^{-1} suggested the lack of three adjacent hydrogen atoms of the benzene ring of PPR. The intensity of these absorptions was similar to that

Table VII. The Sulfonation of PNP by H_2SO_4[a]

Entry	Temp. (°C)	Time (h)	Acid density ($mmol \cdot g^{-1}$)[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]
1	150	15	8.65	6.37	++++
2	80	24	5.83	5.85	+++
3	25	24	2.39	4.24	-
4[e]	25	24	5.43	6.74	-

[a]Reagents and conditions: PNP 5.0 g, H_2SO_4 40 mL, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ <++++ (partially soluble), [e]Sulfonated by $ClSO_3H$ in dichloromethane.

Table VIII. The Sulfonation of More Crosslinked PNP by H_2SO_4[a]

Entry	Acid density ($mmol \cdot g^{-1}$)[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]	Solubility to hot MeOH[d]	Solubility to hot DMSO[d]
1[e,f]	3.12	4.52	-	-	+++
2[f]	1.54	1.76	-	-	+
3[f,g]	2.11	2.65	-	-	+
4[g,h]	1.63	3.12	-	-	++

[a]Reagents and conditions: PNP 5.0 g, H_2SO_4 40 mL, 25°C, 24 h, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ < ++++ (partially soluble), [e]Fuming sulfuric acid (SO_3, 15 wt %) (40 mL) was used, [f]Polymerization of naphthalene was carried out at 150°C, [g]Sulfonated by $ClSO_3H$ in dichloromethane, [h]PNP was postcured at 300°C for 4 h under N_2 prior to sulfonation.

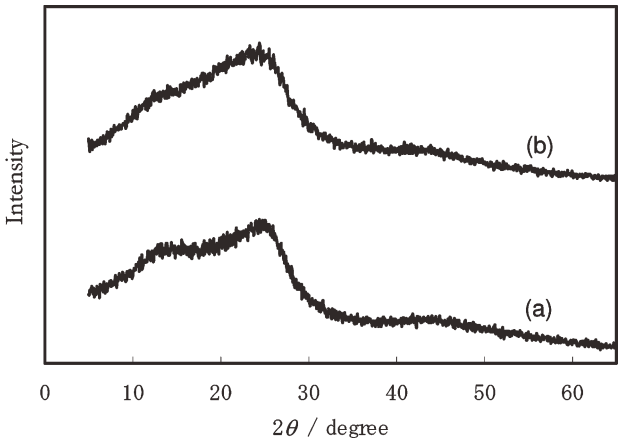

Figure 8. XRD patterns of (a) PNP and (b) S-PNP.

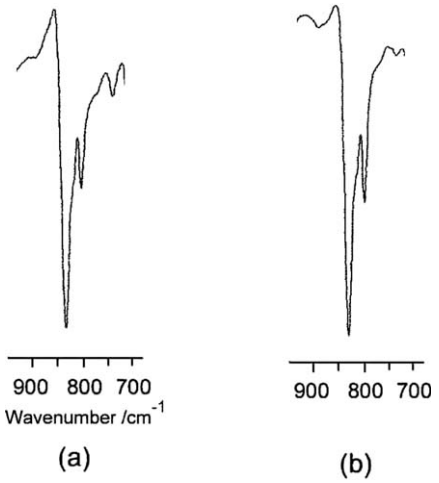

Figure 9. IR spectra of PPR prepared by the reactions (a) at 40°C for 30 min and (b) at 40°C for 24 h.

for PPR produced by the reaction of pyrene with $FeCl_3$ in hexane–nitromethane.[46] The new absorptions at 682 and 1637 cm^{-1} could be ascribed to the newly formed carbon–carbon bond between pyrene units.[46] We could not measure the UV/Vis absorption spectra because of the insolubility of PPR to any examined solvents. The ^1H NMR spectrum of the soluble part of PPR in DMSO-d_6 obtained by the reactions at 40°C for 30 min is shown in Figure 10. No peak was observed in the aliphatic region. The obtained spectrum (400 MHz) was similar to that of the reported one and the chemical shifts of the signals were in accordance with those of the literature, indicating that these signals could be attributed to the protons of PPR which coupled between (2- or 1-) and (2′- or 1′-) positions on the pyrene ring (Figure 11).[46] From the results for elemental analyses and IR spectroscopy, the polymer obtained in our study would be further condensed polymer between the pyrene ring.

PPR polymerized at 40°C for 24 h was converted into S-PPR as the black powder by the treatment with concentrated sulfuric acid at 25°C for 24 h under nitrogen (Table X, entry 4). It was insoluble to boiling water and hot MeOH but slightly soluble to hot DMSO. PPR was sulfonated with chlorosulfonic acid in dichloromethane at 25°C for 24 h under nitrogen to give S-PPR (entry 5). It was insoluble to boiling water and many hot organic solvents such as benzene, THF, chloroform, acetone, EtOAc, CH_3CN methanol, DMF, and DMSO. Although the rate constant ($k = 4.44 \times 10^{-4}$) was smaller than that of S-PPR sulfonated by sulfuric acid ($k = 6.98 \times 10^{-4}$), we employed S-PPR sulfonated by chlorosulfonic acid for further evaluation because of insolubility to many organic solvents involving hot DMSO (entries 4 and 5). It possessed the composition of $(C_{16}H_{8.03}Cl_{0.30}O_{3.70}S_{0.62})_n$. The IR spectrum showed characteristic absorptions at 1603, 1490, 834, and 816 cm^{-1} owing to the benzene ring and 1198 and 1042 cm^{-1} owing to the SO_3H group.

Table IX. The Results for Elemental Analyses of PPR

Entry	Temp. (°C)	Time (h)	Chemical composition
1	40	0.5	$(C_{16}H_{7.50}Cl_{0.03})_n$
2	40	24	$(C_{16}H_{6.98}Cl_{0.14})_n$

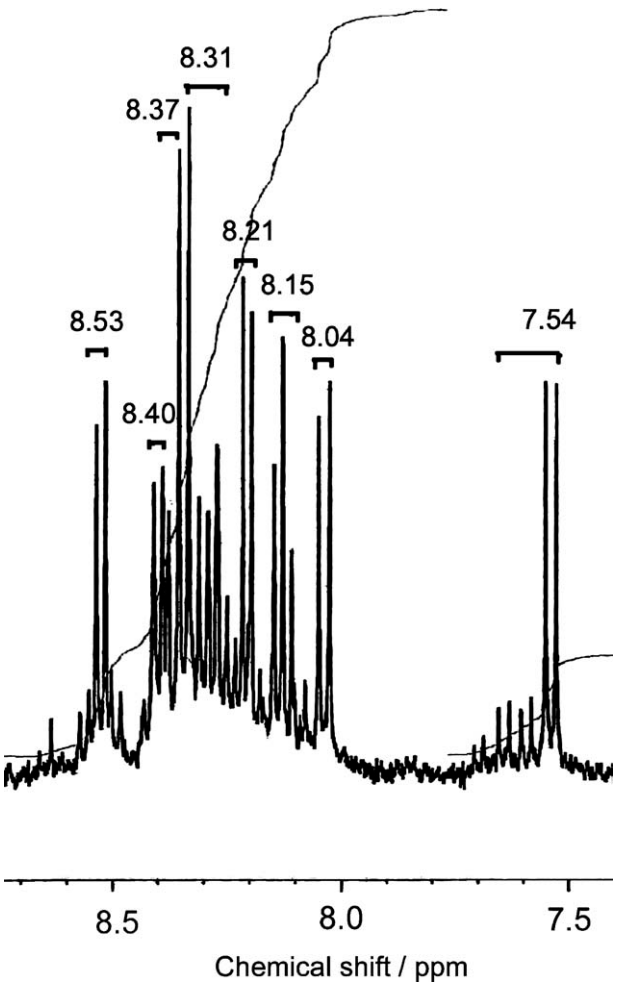

Figure 10. The ^1H NMR spectrum (400 MHz) of PPR in DMSO-d_6.

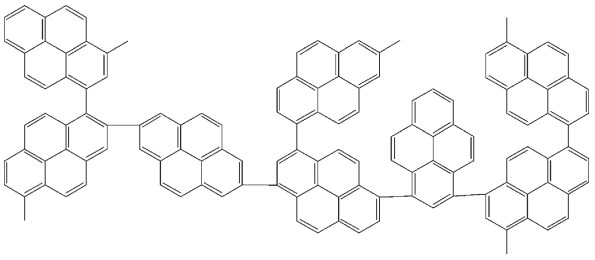

Figure 11. Plausible structure of PPR.

Figure 12 shows the XRD patterns of (a) PPR and (b) S-PPR. The broad diffraction peaks (2θ = 5–15 and 15–35°) can be attributed to the amorphous structure. Existence of the broad diffraction peak (2θ = 5–15°) suggests that PPR indeed consists of the pyrene repetitive units.[46,51] The weak broad diffraction peak (2θ = 35–50°) is owing to the *a* axis of the graphite structure.[11,17,18,49] The larger broad diffraction peak (2θ = 5–15°) compared with those of PAT and PNP indicates that larger content of the pyrene repetitive units was involved. It was also supported by the elemental analyses of PAR, PNP, and PPR (entry 3 in Table II, entry 3 in Table VI, and entry 2 in Table IX). There was a large difference in the XRD patterns between PPR and S-PPR, suggesting that the sulfonation process led to

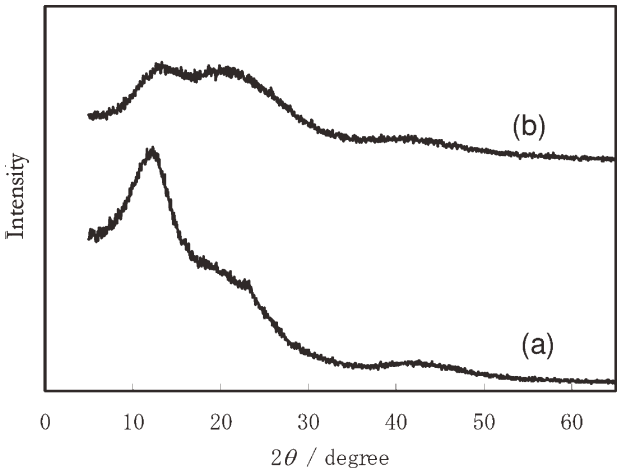

Figure 12. XRD patterns of (a) PPR and (b) S-PPR.

Table X. The Sulfonation of PPR by H_2SO_4[a]

Entry	Temp. (°C)	Time (h)	Acid density (mmol·g^{-1})[b]	$k^c \times 10^{-4}$	Solubility to boiling water[d]	Solubility to hot MeOH[d]	Solubility to hot DMSO[d]
1[e]	25	24	3.89	6.49	-	-	+
2	150	15	4.40	1.90	-	-	+
3	80	24	4.05	6.76	+	+	+
4	25	24	3.73	6.98	-	-	+
5[f]	25	24	2.57	4.44	-	-	-

[a]Reagents and conditions: PPR 2.5 g, H_2SO_4 20 mL, N_2, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ < ++++ (partially soluble), [e]Fuming sulfuric acid (SO_3, 15 wt %) (20 mL) was used, [f]Sulfonated by $ClSO_3H$ in dichloromethane.

Table XI. Analytical Data and Catalytic Activities of S-PPR

Entry	Sulfonating agents	Chemical composition	SO_3H (mmol·g^{-1})[a]	Acid density (mmol·g^{-1})[b]	$k^c \times 10^{-4}$	SO_3H/acid density	Solubility to hot DMSO[d]
1	SO_3-H_2SO_4	$(C_{16}H_{8.08}Cl_{0.14}O_{4.46}S_{0.86})_n$	2.84	3.89	6.49	0.73	+
2	H_2SO_4	$(C_{16}H_{9.25}Cl_{0.21}O_{4.05}S_{0.83})_n$	1.92	3.73	6.98	0.51	+
3	$ClSO_3H$	$(C_{16}H_{8.03}Cl_{0.30}O_{2.88}S_{0.62})_n$	2.25	2.57	4.44	0.88	-

[a]Calculated from chemical composition, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Solubility: - (insoluble) < + < ++ < +++ < ++++ (partially soluble).

Table XII. Analytical Data and Catalytic Activities of S-PPR, S-PAT, and S-PNP Sulfonated by Chlorosulfonic Acid

Entry	Substrate	Chemical composition	SO_3H (mmol·g^{-1})[a]	Acid density (mmol·g^{-1})[b]	$k^c \times 10^{-4}$	SO_3H/acid density
1	S-PPR[d]	$(C_{16}H_{8.03}Cl_{0.30}O_{2.88}S_{0.62})_n$	2.25	2.57	4.44	0.88
2	S-PAT[d]	$(C_{14}H_{6.61}Cl_{0.45}O_{2.56}S_{0.55})_n$	2.19	2.33	3.26	0.94
3	S-PNP[d]	$(C_{10}H_{4.92}Cl_{0.30}O_{1.78}S_{0.36})_n$	2.05	2.11	2.65	0.97

[a]Calculated from chemical composition, [b]Determined by titration, [c]Rate constant for the esterification of acetic acid with EtOH, [d]Sulfonated by $ClSO_3H$ in dichloromethane.

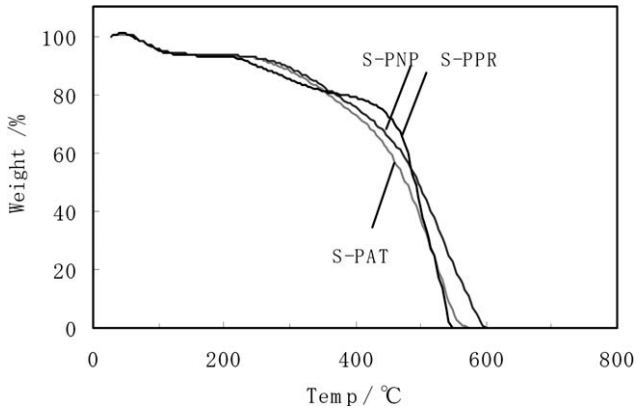

Figure 13. TGA curves in air of the sulfonated polymers.

the change of the microstructure of PPR which was caused by further crosslinking between the pyrene ring.

Evaluation of S-PNP, S-PAT, and S-PPR

Table XI summarizes the analytical data and catalytic activities of S-PPR synthesized by the different sulfonating agents. Acid densities of S-PPR determined by titration were larger than the degree of sulfonation. Especially, there was a large difference in S-PPR prepared by the reaction with sulfuric acid (SO_3H/acid density = 0.51) (entry 2). It will be because of containing weakly acidic functional groups such as phenolic hydroxyl groups. S-PPR sulfonated by chlorosulfonic acid was the most hydrophobic catalyst (SO_3H/acid density = 0.84) (entry 3). The order of SO_3H/acid density on the sulfonating methods was the same as that of the S-COPNA(PR) resins.[19] Interestingly, S-PPR sulfonated with more drastic fuming sulfuric acid was more hydrophobic than that with sulfuric acid (entries 1 and 2). Oxidation of phenolic hydroxyl groups to nonacidic groups such as quinone skeletons may be caused. However, it was difficult to discuss the detailed structure of S-PPR, as IR spectra of these catalysts in Table XI were almost the same.

Table XII summarizes the analytical data and catalytic activities of S-PPR, S-PAT, and S-PNP sulfonated by chlorosulfonic acid. S-PPR was the most active catalyst ($k = 4.44 \times 10^{-4}$) in spite of the similar degrees of sulfonation (entry 1). S-PPR possesses the most hydrophobic surface because of the largest polynuclear aromatic skeleton and the approach of the substrates to the catalyst may be easy.[15,16]

Thermal stability of the sulfonated polymers was examined by TGA in air atmosphere (Figure 13). After an initial weight loss owing to evaporation of absorbed water, the two-step decomposition process was observed for all sulfonated polymers. For S-PNP, S-PAT, and S-PPR, the decomposition reaction started at 240, 230, and 205°C, respectively. Heating these polymers above around 430–460°C resulted in a rapid decrease in weight.

Rate constants for the esterification of carboxylic acids and the hydrolysis of esters by S-PPR, S-PAT, and S-PNP are summarized in Table XIII together with the results of the S-COPNA(PR) resin (PR = pyrene) sulfonated by chlorosulfonic acid.[20] Figure 14(a, b) shows the rate constants for the formation of ethyl acetate (80°C) and ethyl benzoate (80°C). These catalysts exhibited higher activities than conventional solid acids such as mordenite, Montmorillonite K10, Nafion NR50, Nafion SAC-13, and Amberlyst 15, but activities were lower than that of the S-COPNA(PR) resin. For the hydrolysis of cyclohexyl acetate (90°C) and oleyl acetate (100°C) in water, activities of S-PPR, S-PAT, and S-PNP were considerably higher than that of sulfuric acid as well as those of conventional solid acids [Figure 14(c, d)]. It is noteworthy that rate constants of S-PPR were 2.8 and 11.7 times larger than those of the S-COPNA(PR) resin for the hydrolysis of cyclohexyl acetate and oleyl acetate, respectively (Table XIII). It is probably owing to the less poisoning of SO_3H groups of S-PPR with water molecules caused by the more hydrophobic surface. Interestingly, S-PPR, S-PAT, and S-PNP as well as Nafion NR50 were enough hydrophobic to be suspended in the ester phase rather than the aqueous phase during the reactions in spite of involving polar SO_3H groups, whereas the S-COPNA resins, mordenite,

Table XIII. Rate Constants for Various Reactions

Catalyst	$CH_3COOH + EtOH$ ($\times 10^{-4}$ mol·dm^3·min^{-1})[a]	$PhCOOH + EtOH$ ($\times 10^{-5}$ mol·dm^3·min^{-1})[b]	$CyOAc + H_2O$ ($\times 10^{-4}$ mol·dm^3·min^{-1})[c]	$OleOAc + H_2O$ ($\times 10^{-5}$ mol·dm^3·min^{-1})[d]
S-COPNA(PR)	8.59	3.68	6.00	1.20
S-PPR	4.44	0.73	16.90	14.00
S-PAT	3.26	0.62	2.68	4.35
S-PNP	2.65	0.35	1.12	2.27
Mordenite	0.11	0.00	0.04	0.15
Montmorillonite K10	1.63	0.00	0.03	0.00
Nafion NR50	0.56	0.00	0.25	0.00
Nafion SAC-13	0.79	0.00	0.15	0.00
Amberlyst 15	2.33	0.00	0.26	0.08
Sulfuric acid	46.00	15.50	0.80	1.00

[a]Reagents and conditions: EtOH (1.0 mol), CH_3COOH (0.1 mol), catalyst (200 mg), 80°C, [b]Reagents and conditions: EtOH (1.0 mol), PhCOOH (0.1 mol), catalyst (200 mg), 80°C, [c]Reagents and conditions: CyOAc (4.4 mmol), H_2O (3.3 mol), catalyst (200 mg), 90°C, [d]Reagents and conditions: OleOAc (4.4 mmol), H_2O (3.3 mol), catalyst (200 mg), 100°C.

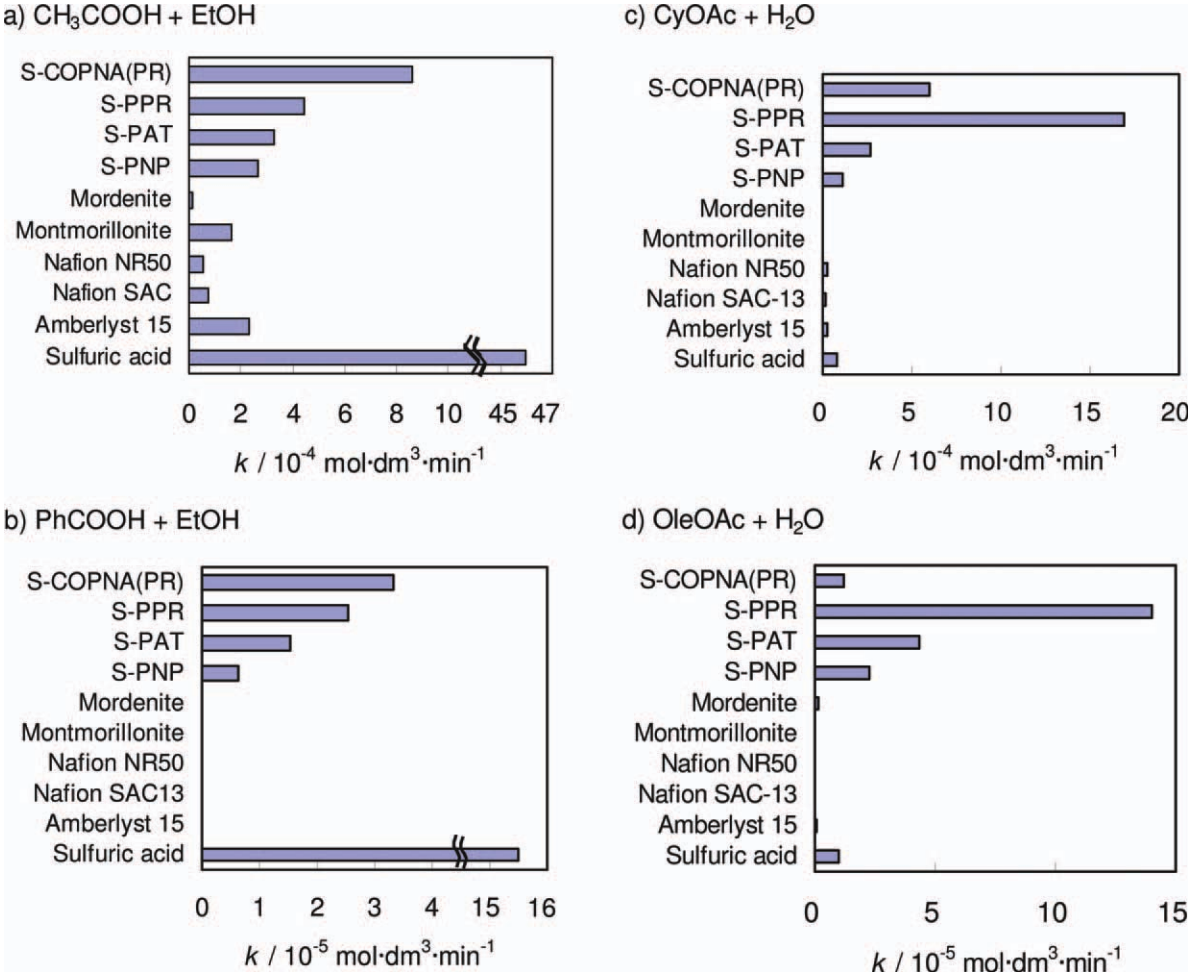

Figure 14. Acid-catalyzed liquid-phase reactions. (a) Rate constants for the formation of ethyl acetate (80°C); (b) rate constants for the formation of ethyl benzoate (80°C); (c) rate constants for the hydrolysis of cyclohexyl acetate (90°C); (d) rate constants for the hydrolysis of oleyl acetate (100°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

montmorillonite K10, and Amberlyst 15 were suspended in the aqueous phase. In the case of S-PPR, the approach of the ester molecule to the catalyst would be easier compared with the S-COPNA(PR) resin.

To check the reusability of S-PPR, S-PAT, and S-PNP for the formation of ethyl acetate, the catalysts were removed by filtration and used for the next experiment. These catalysts were reused without significant loss of activities as summarized in Table XIV. Tables XV and XVI summarize the results for the hydrolysis of cyclohexyl acetate and oleyl acetate in water, respectively. S-PPR, S-PAT, and S-PNP were reused without significant loss of activities.

CONCLUSIONS

S-PNP, S-PAT, and S-PPR were synthesized by oxidative coupling polymerization of naphthalene, anthracene, and pyrene

Table XIV. Recycle Experiments for the Formation of Ethyl Acetate Catalyzed by S-PPR, S-PAT, and S-PNP[a]

Cycle	1st	2nd	3rd	4th	5th
S-PPR, 4 h Conv. (%)[b]	64	61	59	57	59
S-PAT, 4 h Conv. (%)[b]	58	56	55	55	53
S-PNP, 4 h Conv. (%)[b]	54	52	50	48	50

[a]Reagents and conditions: EtOH (1.0 mol), CH_3COOH (0.1 mol), catalyst (200 mg), 80°C, 4 h, [b]Determined by titration.

Table XV. Recycle Experiments for the Hydrolysis of Cyclohexyl Acetate Catalyzed by S-PPR, S-PAT, and S-PNP[a]

Cycle	1st	2nd	3rd	4th	5th
S-PPR, 1 h Conv. (%)[b]	99	98	98	99	99
S-PAT, 1 h Conv. (%)[b]	61	60	59	57	60
S-PNP, 1 h Conv. (%)[b]	35	37	35	35	34

[a]Reagents and conditions: H_2O (3.3 mol), CyOAc (4.4 mmol), catalyst (200 mg), 90°C, 1 h, [b]Determined by titration.

Table XVI. Recycle Experiments for the Hydrolysis of Oleyl Acetate Catalyzed by S-PPR, S-PAT, and S-PNP[a]

Cycle	1st	2nd	3rd	4th	5th
S-PPR, 7 h Conv. (%)[b]	71	76	73	71	73
S-PAT, 7 h Conv. (%)[b]	39	40	44	44	40
S-PNP, 7 h Conv. (%)[b]	28	28	28	29	28

[a]Reagents and conditions: H_2O (3.3 mol), OleOAc (4.4 mmol), catalyst (200 mg), 100°C, 7h, [b]Determined by titration.

followed by sulfonation with chlorosulfonic acid. Oxidative coupling polymerization using $FeCl_3$ in nitrobenzene was useful for the synthesis S-PNP, S-PAT, and S-PPR. Especially, S-PPR was insoluble to boiling water and hot organic solvents. S-PPR was quite effective for the hydrolysis of esters in water.

ACKNOWLEDGMENTS

The authors thank the Division of Chemical Analysis, Systems Engineering for elemental analyses. The authors thank the Division of Chemical Analysis, the Institute of Physical, and Chemical Research (RIKEN) for elemental analyses. The authors thank Hitachi Chemical Techno Service Co., Ltd., for ^1H NMR measurements (400 MHz). The authors thank AGNE Gijutsu Center Inc., for XRD measurements. The authors thank the Research Promotion Grant (NDUF-11-09) from Nippon Dental University.

REFERENCES

1. Miyatake, K.; Shimura, T.; Mikami, T.; Watanabe, M. Chem. Commun. **2009,** *42*, 6403.
2. Miyatake, K.; Iyotani, H.; Yamamoto, K.; Tsuchida, E. *Macromolecules* **1996,** *29*, 6969.
3. Kobayashi, T.; Rikukawa, M.; Sanui, K.; Ogata, N. *Solid State Ionics* **1998,** *106*, 219.
4. Tago, T.; Kuwashiro, N.; Nishide, H. *Bull. Chem. Soc. Jpn.* **2007,** *80*, 1429.
5. Fujimoto, C. H.; Hickner, M. A.; Cornelius, C. J.; Loy, D. A. *Macromolecules* **2005,** *38*, 5010.
6. Granados-Focil, S.; Litt, M. H. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* **2004,** *49*, 528.
7. Schuster, M.; de Araujo, C. C.; Atanasov, V.; Andersen, H. T.; Kreuer, K.-D.; Maier, J. *Macromolecules* **2009,** *42*, 3129.
8. Wang, L.; Xiang, S.; Zhu, G. *Chem. Lett.* **2009,** *38*, 1004.
9. Son, W.-K.; Kim, S. H.; Park, S.-G. *Bull. Korean Chem. Soc.* **2001,** *22*, 53.
10. Pang, J.; Wang, A.; Zheng, M.; Zhang, T. *Chem. Commun.* **2010,** *46*, 6935.
11. Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Nature* **2005,** *438*, 178.
12. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Mohammadpoor-Baltork, I.; Mahdavi, M. *Monatsh. Chem.* **2009,** *140*, 1489.
13. Mo, X.; Lotero, E.; Lu, C.; Liu, Y.; Goodwin, J. G. *Catal. Lett.* **2008,** *123*, 1.
14. Liu, X.-Y.; Huang, M.; Ma, H.-L.; Zhang, Z.-Q.; Gao, J.-M.; Zhu, Y.-L.; Han, X.-J.; Guo, X.-Y. *Molecules* **2010,** *15*, 7188.
15. Okuhara, T. *Chem. Rev.* **2002,** *102*, 3641.
16. Kamiya, Y.; Okuhara, T.; Misono, M.; Miyaji, A.; Ysuji, K.; Nakajo, T. *Catal. Surv. Asia* **2008,** *12*, 101.
17. Hara, M.; Yoshida, T.; Takagaki, A.; Takata, T.; Kondo, J. N.; Hayashi, S.; Domen, K. *Angew. Chem. Int. Edn.* **2004,** *43*, 2955.
18. Takagaki, A.; Toda, M.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Catal. Today* **2006,** *116*, 157.
19. Tanemura, K.; Suzuki, T.; Nishida, Y.; Horaguchi, T. *Tetrahedron* **2011,** *67*, 1314.
20. Tanemura, K.; Suzuki, T.; Nishida, Y.; Horaguchi, T. *Polym. Bull.* **2012,** *68*, 705; DOI: 10.1007/s00289-011-0574-0.
21. Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987,** *87*, 357.
22. Kovacic, P.; Kyriakis, A. *J. Am. Chem. Soc.* **1963,** *85*, 454.
23. Kovacic, P.; Oziomer, J. *J. Org. Chem.* **1964,** *29*, 100.
24. Yamamoto, K.; Asada, T.; Nishide, H.; Tsuchida, E. *Bull. Chem. Soc. Jpn.* **1988,** *61*, 1731.
25. King, B. T.; Kroulik, J.; Robertson, C. R.; Rempala, R.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007,** *72*, 2279.
26. Lu, Y.; Moore, H. S. *Tetrahedron Lett.* **2009,** *50*, 4071.
27. Matsumoto, K.; Ando, S.; Ueda, M. *Polym. J.* **2007,** *39*, 882.
28. Kovacic, P.; Koch, F. W. *J. Org. Chem.* **1965,** *30*, 3176.
29. Hara, S.; Toshima, N. *Chem. Lett.* **1990,** 269.
30. Minato, H.; Higosaki, N.; Isobe, C. *Bull. Chem. Soc. Jpn.* **1969,** *42*, 779.
31. Ota, E.; Otani, S. *Chem. Lett.* **1975,** *4*, 241.
32. Ohsawa, T.; Nishihara, H.; Aramaki, K.; Takeda, S.; Yoshino, K. *Polym. Commun.* **1987,** *28*, 140.
33. Satoh, M.; Uesugi, F., Tabata, M.; Kaneto, K.; Yoshino, K. J. *Chem. Soc. Chem. Commun.* **1986,** *1986*, 979.
34. Drachev, A. I.; Gil'man, A. B.; Kuznetsov, A. A. *High Energy Chem. (Engl. Transl.)* **2005,** *39*, 418.
35. Berlin, A. A.; Grigorovskaya, V. A.; Parini, V. P.; Belova, G. V.; Chernikova, N. S. *Vysokomol Sordin Ser. B* **1967,** *9*, 423; Chem. Abstr. 1967, 67, 82422.
36. Buchanan, A. C., III, Dworkin, A. S.; Smith, G. P. *J. Am. Chem. Soc.* **1980,** *102*, 5262.
37. Dworkin, A. S.; Poustma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith. G. P. *J. Am. Chem. Soc.* **1979,** *101*, 5299.
38. Paustma, M. L.; Dworkin, A. S.; Brynestad, J.; Brown, L. L.; Benjamin, B. M.; Smith. G. P. *Tetrahedron Lett.* **1978,** *19*, 873.
39. Sato, H.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1973,** *46*, 631.
40. Dworkin, A. S.; Brown, L. L.; Buchanan, A. C., III; Smith, G. P. *Tetrahedron Lett.* **1985,** *23*, 2727.

41. Buchanan, A. C., III; Dworkin, A. S.; Brown, L. L.; Smith, G. P. *Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem.* **1981,** *26*, 112.
42. Fatiadi, A. J. *J. Org. Chem.* **1967,** *32*, 2903.
43. Clar, E.; Kühn, O. *Justus Liebigs Ann. Chem.* **1956,** *601*, 181.
44. Guenther, H.; Kovacic, P. *Synth. Commun.* **1984,** *14*, 413.
45. Packham, D. I. *Chem. Commun.* **1965,** *1965*, 207.
46. Li, X. G.; Liu, Y. W.; Huang, M. R.; Peng, S.; Gong, L. Z.; Moloney, M. G. *Chem. Eur. J.* **2010,** *16*, 4803.
47. Qu, L.; Shi, G. *Chem. Commun.* **2004,** *2004*, 2800.
48. Gharge, M. N.; Bhattar, S. L.; Kolekar, G. B.; Patil, S. R. *Ind. J. Chem.* **2008,** *47A*, 1642.
49. Sinha, N.; Gupta, M. K.; Goel, N.; Kumar, B. *Phys. B* **2011,** *406*, 3206.
50. Zong, M. H.; Duan, Z. Q.; Lou, W. Y.; Smith, T. J.; Wu, H. *Green Chem.* **2007,** *9*, 434.
51. Oguchi, T.; Limmatvapirat, S.; Takahashi, C.; Sungthongjeen, S.; Choi, W. S.; Yonemochi, E.; Yamamoto, K. *Bull. Chem. Soc. Jpn.* **1998,** *71*, 1573.