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# Synthesis of the sulfonated condensed polynuclear aromatic (S-COPNA) resins as strong protonic acids

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#### ABSTRACT

The mixture (PXG/PR=1.00) of pyrene (PR) and *p*-xylylene glycol (1,4-benzenedimethanol) (PXG) in the presence of 5 wt % of *p*-toluenesulfonic acid (TsOH) was heated at 140 °C for 45 min under nitrogen to give the highly viscous condensed polynuclear aromatic (COPNA) resin. It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained material was treated with fuming sulfuric acid at 80 °C for 15 h under nitrogen to give the sulfonated COPNA resin. The similar acidic resin was prepared by the reaction of phenanthrene or naphthalene with PXG in the presence of TsOH followed by sulfonation. The performance of the sulfonated polymers as the strong protonic acids was evaluated.

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#### 1. Introduction

Sulfonated polymers have attracted considerable attention for a wide range of potential usefulness as solid acid catalysts, conductive polymers, and materials for making fuel cell membranes.<sup>1</sup> Cation exchange resins, such as Amberlyte are superior acid catalysts easy to synthesize, however, these polymers cannot be employed at high temperature. Nafion-H is typically used as the polymeric superacid, however, it is difficult to synthesize and its acid activity is low. Recently, the sugar catalyst, which was a new class of sulfonated carbons derived from incomplete carbonization and sulfonation of simple sugars, has been devised.<sup>2,3</sup> Sulfonated poly(1,4-diphenoxyphenylene)<sup>4</sup> and sulfonated carbon material derived from polynuclear aromatic compounds, such as naphthalene,<sup>5</sup> have been prepared. The advantage utilizing polynuclear aromatic compounds as the starting material is that sulfonated polymers with various substituents can be designed.

Otani et al. have reported the synthesis of the condensed polynuclear aromatic (COPNA) resins with extremely high thermostability through the dehydration reaction between fused aromatic hydrocarbons (Aro) and *p*-xylylene glycol (1,4-benzenedimethanol) (PXG) catalyzed by *p*-toluenesulfonic acid (TsOH).<sup>6–10</sup>

These results prompted us to study the synthesis of the sulfonated COPNA (S-COPNA) resins. The obtained materials were

quite insoluble to boiling water and many hot organic solvents. Furthermore, these can be employed at high temperature and showed high acid activities. In this paper, we wish to report the synthesis and evaluation of the S-COPNA resins.

#### 2. Results and discussions

#### 2.1. Synthesis of the S-COPNA resins

First, synthesis of the S-COPNA(PR) resin (PXG/PR=1.25 in the molar ratio) (PR=pyrene) was investigated as the model case. By Otani's method,<sup>6</sup> the mixture of pyrene, PXG, and *p*-TsOH (5 wt % of [PXG+PR]) was heated at 140 °C for 45 min under nitrogen to give a highly viscous yellow melt (called as a B-stage resin). The melt was converted into an infusible and insoluble black solid by subsequent post-curing at 300 °C for 1 h under nitrogen.

The post-cured COPNA(PR) resin was sulfonated by fuming sulfuric acid (15 wt % SO<sub>3</sub>) at 80 °C for 15 h under nitrogen to give the S-COPNA(PR) resin as the black powder (Table 1, entry 2). The plausible structural model of the S-COPNA(PR) resin was shown in Fig. 1. Acid density was determined by acid titration. The rate constant (k) for the esterification of acetic acid with EtOH was determined by acid titration of remaining acetic acid included in the reaction mixture. Although sulfonation at 150 °C afforded the material with the highest acid density, k was smaller than that of 80 °C (entries 1 and 2). We considered that the approach of substrates might be difficult with the decrease of hydrophobic nature of the catalyst by the



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<sup>0040-4020/\$ —</sup> see front matter @ 2010 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2010.11.077

 Table 1

 Sulfonation of the post-cured COPNA(PR) resin by fuming sulfuric acid<sup>a</sup>

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	Entry	Temp (°C)	Time (h)	Acid density (mmol g <sup>-1</sup> ) <sup>b</sup>	$k^{c} \times 10^{-4}$	Solubility <sup>d</sup>
	1	150	15	6.01	4.63	+
	2	80	15	5.12	6.59	_
	3	25	24	4.44	5.43	_
	4 <sup>e</sup>	150	15	5.70	3.66	_
	5 <sup>e</sup>	80	15	4.44	3.44	_
	6 <sup>e</sup>	25	24	0.30	0.63	_

 $^a$  Reagents and conditions: the post-cured COPNA(PR) resin (PXG/PR=1.25 in the molar ratio, post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO<sub>3</sub>) 20 mL, N<sub>2</sub>.

<sup>b</sup> Determined by titration.

- <sup>c</sup> Rate constant for the esterification of acetic acid with EtOH.
- <sup>d</sup> Solubility to boiling water: -(insoluble)<+<++(partially soluble).

e Sulfuric acid (20 mL) was used.



Fig. 1. Schematic model of the S-COPNA(PR) resin.

introduction of the hydrophilic SO<sub>3</sub>H group. In addition, it was partially soluble to boiling water. When sulfonation was carried out by concentrated sulfuric acid, rate constants were smaller than those by fuming sulfuric acid (entries 4–6). It is interesting to note that the rate constant (k=5.43×10<sup>-4</sup>) of the material sulfonated by fuming sulfuric acid at 25 °C was larger than that by concentrated sulfuric acid at 80 °C (k=3.44×10<sup>-4</sup>) in spite of the same acid density (4.44 mmol g<sup>-1</sup>)(entries 3 and 5). The S-COPNA(PR) resin obtained by the reaction at 80 °C in fuming sulfuric acid was the most active material (entry 2).

Table 2 summarizes the results for sulfonation of the post-cured COPNA(PR) resins with various molar ratios PXG/PR. We chose the post-cured COPNA(PR) resins with PXG/PR=1.00, 1.25, and 1.50, which were suitable for the formation of the B-stage resin.<sup>6</sup> The best result was obtained by the sulfonation of the post-cured COPNA resin with PXG/PR=1.00 (entry 1).

The influence of post-curing temperature on the activity of the S-COPNA resin was explored (Table 3, entries 1–4). When the COPNA(PR) resin without post-curing was treated with fuming

#### Table 2

Sulfonation of the post-cured COPNA(PR) resins with various molar ratios by fuming sulfuric acida  $\,$ 

Entry	PXG/PR	Acid density (mmol g <sup>-1</sup> ) <sup>b</sup>	$k^{c} \times 10^{-4}$	Solubility <sup>d</sup>
1	1.00	5.18	7.08	_
2	1.25	5.12	6.59	_
3	1.50	4.67	5.08	_

 $^a\,$  Reagents and conditions: the post-cured COPNA(PR) resin (post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO<sub>3</sub>) 20 mL, 80 °C, 15 h, N<sub>2</sub>.

<sup>b</sup> Determined by titration.

<sup>c</sup> Rate constant for the esterification of acetic acid with EtOH.

 $^{\rm d}\,$  Solubility to boiling water: –(insoluble) <+<++(partially soluble).

#### Table 3

Sulfonation of the COPNA(PR) resins treated at various curing temperature by fuming sulfuric acid<sup>a</sup>

Entry	Curing temp (°C)	Temp (°C)	Acid density (mmol g <sup>-1</sup> ) <sup>b</sup>	$k^{c} \times 10^{-4}$	Solubility <sup>d</sup>
1	400	80	4.96	6.98	-
2	300	80	5.18	7.08	_
3	200	80	5.51	7.84	_
4	none	80	5.33	8.56	_
5 <sup>e</sup>	400	25	4.93	7.98	+
6 <sup>e</sup>	300	25	5.04	8.59	_
7 <sup>e</sup>	none	25	5.23	9.35	++

<sup>a</sup> Reagents and conditions: the COPNA(PR) resin (PXG/PR=1.00 in the molar ratio) 2.5 g, fuming sulfuric acid (15 wt % SO<sub>3</sub>) 20 mL, 15 h, N<sub>2</sub>.

<sup>b</sup> Determined by titration.

<sup>c</sup> Rate constant for the esterification of acetic acid with EtOH.

<sup>d</sup> Solubility to boiling water: –(insoluble) <+<++(partially soluble).

<sup>e</sup> Sulfonated by chlorosulfonic acid in dichloromethane.

sulfuric acid, a color change from yellow to black was observed, suggesting that aromatization of the carbon skeleton may occur during sulfonation. Although the obtained resin possessed the highest activity, it required long time to filter the precipitate and the sedimentation in water was slow (entry 4). Post-curing, especially at 300 °C, was effective for quick filtration and fast sedimentation (entry 2). Sulfonation of the COPNA(PR) resin with and without post-curing by CISO<sub>3</sub>H in dichloromethane gave the S-COPNA(PR) resins with high activities (entries 5–7). The color change of the precipitate from brown to black during work-up, especially heating at 150 °C, was observed. However, it was difficult to exclude adsorbed chlorosulfonic acid. Therefore, complex experimental procedures were required.

Table 4 shows the analytical data and catalytic activities of the S-COPNA(PR) resins synthesized by the different sulfonating agents. Rate constants were correlated with the degree of sulfonation calculated from chemical composition. Acid densities of the sulfonated resins determined by titration were larger than the degree of sulfonation. Especially, there was a large difference in the sulfonated resin prepared by the reaction with sulfuric acid (entry 2). It will be because of containing weakly acidic functional groups, such as phenolic hydroxyl groups. However, it was difficult to discuss the detailed structure of the sulfonated resins, since IR spectra of the S-COPNA(PR) resin prepared by the sulfonation with sulfuric acid was almost the same as the others except for the appearance of the new absorption at 1560 cm<sup>-1</sup> due to the benzene ring.

Next, we prepared the post-cured COPNA resins consisting of the other condensed polynuclear aromatic structure. The results are shown in Table 5. The post-cured COPNA(PH) (PH=phenanthrene) and the COPNA(NP) (NP=naphthalene) resins were prepared in good yields by the similar procedure with the post-cured COPNA(PR) resin (curing temp 300 °C) (entries 2 and 5). Attempts to prepare the COPNA(AT)(AT=anthracene) resin failed because the mixture of PXG, anthracene, and 5 wt % of TsOH did not make the uniform melt even at 260 °C because of the high melting point of anthracene (218 °C)<sup>11</sup> (entries 3 and 4). Table 6 shows the results for the sulfonation of the various post-cured COPNA resins by fuming sulfuric acid. Although sulfonation of the post-cured COPNA(PH) resin at 150 °C gave the solid with higher acid density, the activity was lower than that of the solid sulfonated at 80 °C (entries 2 and 3). In addition, it was partially soluble to boiling water. Sulfonation at 80 °C led to the most active material (entry 3). The rate constant  $(k=6.22\times10^{-4})$  of the S-COPNA(PH) resin was smaller than that of the S-COPNA(PR) resin ( $k=7.08 \times 10^{-4}$ ) (entries 1 and 3). Similarly, the S-COPNA(NP) resin was obtained by the sulfonation of the postcured COPNA(NP) resin at 150 °C (entry 5). The rate constant  $(k=4.87\times10^{-4})$  of the S-COPNA(NP) resin was smaller than those of the S-COPNA(PR) and the S-COPNA(PH) resins. The obtained S-COPNA resins were insoluble to boiling water and many hot

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#### Table 4

Analytical data and catalytic activities of the S-COPNA(PR) resins

Entry	Sulfonating agent	Chemical composition	$SO_3H (mmol \cdot g^{-1})^d$	Acid density (mmol g <sup>-1</sup> ) <sup>e</sup>	$k^{\rm f} \times 10^{-4}$	Solubility <sup>g</sup>
1	Fuming sulfuric acid <sup>a</sup>	CH <sub>0.725</sub> O <sub>0.396</sub> S <sub>0.088</sub>	4.02	5.18	7.08	_
2	Sulfuric acid <sup>b</sup>	CH <sub>0.438</sub> O <sub>0.265</sub> S <sub>0.030</sub>	1.70	4.88	3.50	-
3	Chlorosulfonic acid <sup>c</sup>	CH <sub>0.671</sub> O <sub>0.312</sub> S <sub>0.086</sub>	4.21	5.04	8.59	_

<sup>a</sup> Reagents and conditions: the post-cured COPNA resin (PXG/Aro=1.00 in the molar ratio, post-cured at 300 °C for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO<sub>3</sub>) 20 mL, 80 °C, 15 h, N<sub>2</sub>.

<sup>b</sup> Reagents and conditions: the post-cured COPNA resin (PXG/Aro=1.00 in the molar ratio, post-cured at 300 °C for 1 h) 2.5 g, sulfuric acid 20 mL, 150 °C, 15 h, N<sub>2</sub>.

<sup>c</sup> Reagents and conditions: the post-cured COPNA resin (PXG/Aro=1.00 in the molar ratio, post-cured at 300 °C for 1 h) 2.5 g, chlorosulfonic acid 3.9 mL, dichloromethane 22.5 mL, 25 °C, 24 h, N<sub>2</sub>.

<sup>d</sup> Calculated from chemical composition.

<sup>e</sup> Determined by titration.

<sup>f</sup> Rate constant for the esterification of acetic acid with EtOH.

<sup>g</sup> Solubility to boiling water: -(insoluble) <+<++(partially soluble).

#### Table 5

Synthesis of the various post-cured COPNA(Aro) resins<sup>a</sup>

Entry	Aro	Temp (°C)	Time (h)	Yield (%)
1	PR	140	0.75	91
2	PH	130	2	89
3	AT	260	2	0
4		180	2	0
5	NP	120	3.5	81

 $^a$  Reagents and conditions: Aro (100 mmol), PXG (100 mmol), TsOH (5 wt % of [PXG+Aro]), post-cured at 300  $^\circ C$  for 1 h,  $N_2.$ 

### Table 6 Sulfonation of the various post-cured COPNA(Aro) resins by fuming sulfuric acid<sup>a</sup>

Entr	y Aro	Temp (°C)	Time (h)	$\begin{array}{l} SO_{3}H\\ (mmol \cdot g^{-1})^{b}\end{array}$	Acid density (mmol g <sup>-1</sup> ) <sup>c</sup>	$k^{\rm d} \times 10^{-4}$	Solubility <sup>e</sup>
1	PR	80	15	4.02	5.18	7.08	-
2	PH	150	15		5.20	6.10	+
3		80	15	2.42	3.62	6.22	_
4		25	24		0.58	1.35	_
5	NP	150	15	3.42	4.92	4.87	_
6		80	15		2.53	3.44	_
7		25	24		0.53	1.33	-

 $^a$  Reagents and conditions: the post-cured COPNA resin (PXG/Aro=1.00 in the molar ratio, post-cured at 300  $^\circ C$  for 1 h) 2.5 g, fuming sulfuric acid (15 wt % SO<sub>3</sub>) 20 mL, N<sub>2</sub>.

<sup>b</sup> Calculated from chemical composition.

<sup>c</sup> Determined by titration.

<sup>d</sup> Rate constant for the esterification of acetic acid with EtOH.

<sup>e</sup> Solubility to boiling water: -(insoluble) <+<++(partially soluble).

organic solvents, such as benzene, THF, chloroform, ethanol, acetone, EtOAc, CH<sub>3</sub>CN, DMF, and DMSO.

The thermal stability of the S-COPNA resins was examined by thermogravimetric analysis (TGA) in air atmosphere (Fig. 2). The thermal stability increased in the order: the S-COPNA(NP) resin>the S-COPNA(PH) resin>the S-COPNA(PR) resin. After an initial weight loss due to evaporation of absorbed water, the two-step



Fig. 2. TGA curves in air of the S-COPNA resins.

decomposition process was observed for all polymers. For the S-COPNA(PR) resin, the decomposition reaction started at around 190 °C, while for the S-COPNA(PH) and the S-COPNA(NP) resins, the reactions started at 240–250 °C. In the case of the S-COPNA(NP) resin, the weight decreased largely at 510–530 °C. Heating these polymers above 480–530 °C resulted in a rapid decrease in weight.

#### 2.2. Evaluation of the S-COPNA resins

Rate constants for esterification of carboxylic acids and hydrolysis of esters were summarized in Table 7. Fig. 3a shows the rate constants for the formation of ethyl acetate (80 °C) on the most active S-COPNA(PR) and the easily accessible S-COPNA(NP) resins (200 mg). These catalysts exhibited higher activities than conventional solid acids, such as mordenite, Montmorillonite K10, Nafion NR50, Nafion SAC-13, and Amberlyst 15. The rate constant ( $k=7.08 \times 10^{-4}$ ) of the S-COPNA(PR) resin was 1.8 times larger than that of the sugar catalyst ( $k=4.04 \times 10^{-4}$ ). The S-COPNA(PR) and the S-COPNA(NP) resins showed high activities for the formation of ethyl benzoate (80 °C), while conventional solid acids were inert for the reaction (Fig. 3b). For the hydrolysis of cyclohexyl acetate and oleyl acetate, activities of the S-COPNA(PR) resin were considerably higher than those of the other acidic catalysts including sulfuric acid (Fig. 3c and d).

In order to check the reusability of the catalysts, the catalysts were removed by decantation and used for the next experiment. The catalysts were reused without significant loss of activities (Table 8).

#### 3. Conclusions

We synthesized the S-COPNA resins by the reactions of polynuclear aromatic compounds and PXG in the presence of TsOH followed by sulfonation. It is noteworthy that *synthetic procedures are quite simple* because preparations of the COPNA resins are conducted by only mixing and heating of the substrates. The S-COPNA resins exhibited the higher performance than conventional solid acids. The activities of the S-COPNA(PR) resin were higher than those of the S-COPNA(NP) resin. The S-COPNA(NP) resin will be also useful because of the lower price of naphthalene. The S-COPNA resins can be easily removed by simple decantation from the reaction mixture.

#### 4. Experimental

#### 4.1. General methods

IR spectra were recorded on a JEOL FT/IR-620 spectrophotometer. UV spectra were recorded on a Shimadzu UV–vis spectrophotometer UV-2550. Thermogravimetric analysis (TGA) in air atmosphere was carried out on a Rigaku Thermo Plus 2 station

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Rate constants	for	various	reactions

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Catalyst	$\begin{array}{l} CH_{3}COOH+EtOH \\ (\times 10^{-4} \ mol \ dm^{3} \ min^{-1})^{a} \end{array}$	PhCOOH+EtOH (×10 <sup>-5</sup> mol dm <sup>3</sup> min <sup>-1</sup> ) <sup>b</sup>	$CyOAc+H_2O$ (×10 <sup>-4</sup> mol dm <sup>3</sup> min <sup>-1</sup> ) <sup>c</sup>	$\begin{array}{l} OleOAc{+}H_2O \\ (\times 10^{-5} \mbox{ mol } dm^3 \mbox{ min}^{-1})^d \end{array}$
S-COPNA(PR)	7.08	3.33	10.30	3.41
S-COPNA(NP)	4.87	1.15	3.47	1.23
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

<sup>a</sup> Reagents and conditions: EtOH (1.0 mol), CH<sub>3</sub>COOH (0.1 mol), catalyst (200 mg), 80 °C.

<sup>b</sup> Reagents and conditions: EtOH (1.0 mol), PhCOOH (0.1 mol), catalyst (200 mg), 80 °C.

<sup>c</sup> Reagents and conditions: CyOAc (4.4 mmol), H<sub>2</sub>O (3.3 mol), catalyst (200 mg), 90 °C.

<sup>d</sup> Reagents and conditions: OleOAc (4.4 mmol), H<sub>2</sub>O (3.3 mol), catalyst (200 mg), 100 °C.

TG-DTA TG 8120 at a heating rate of 10 °C/min. All samples were evacuated at 150 °C for 1 h under reduced pressure prior to the measurement of TGA. The grinding was conducted by Wonder Blender WB-1 (Osaka Chemical Co., purchased from AS ONE Co.).

#### 4.2. Preparation of the post-cured COPNA(PR) resin

The mixture of pyrene (20.2 g, 100 mmol), PXG (13.8 g, 100 mmol), and TsOH (1.70 g, 5 wt % of [PXG+pyrene]) was heated at

140 °C for 45 min in a stream of nitrogen to produce a highly viscous material. The yield was 31.6 g (93%); IR (KBr)  $\nu_{max}$  3437 (OH), 3036 (ArH), 2903, 2850 (CH<sub>2</sub>), 1602, 1508, 841, 817, 748 cm<sup>-1</sup> (ArH).

The obtained material was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h under nitrogen. The obtained solid was ground to a powder by the mill. The yield was 30.7 g (91%); IR (KBr)  $\nu_{\rm max}$  3448 (OH), 3040 (ArH), 2925 (CH<sub>2</sub>), 1637, 1508, 839 cm<sup>-1</sup> (ArH). The nominal sample composition was determined by elemental analysis to be CH<sub>0.675</sub>O<sub>0.010</sub>.



Fig. 3. 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).

b) PhCOOH + EtOH

#### Table 8

Recycle experiments of the formation of ethyl acetate catalyzed by the S-COPNA(PR) or the S-COPNA(NP) resin  $^{\rm a}$ 

Cycle	First	Second	Third	Fourth	Fifth
S-COPNA(PR), 4 h Conv. (%) <sup>b</sup>	90	88	90	90	88
$3-\text{COPINA(INP)}, 4 \text{ II COIIV}. (\%)^2$	10	15	15	75	/4

 $^a\,$  Reagents and conditions: EtOH (1.0 mol), CH\_3COOH (0.1 mol), catalyst (200 mg), 80  $^\circ C,$  4h.

<sup>b</sup> Determined by titration.

#### 4.3. Preparation of the post-cured COPNA(PH) resin

The mixture of phenanthrene (17.8 g, 100 mmol), PXG (13.8 g, 100 mmol) and TsOH (1.58 g, 5 wt %) was heated at 130°C for 2 h under nitrogen to produce a highly viscous material. It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained solid was ground to a powder. The yield was 28.0 g (89%); IR (KBr)  $\nu_{\rm max}$  3436 (OH), 3017 (ArH), 2915 (CH<sub>2</sub>), 1618, 1508, 885, 803, 742, 721 cm<sup>-1</sup> (ArH). The nominal sample composition was determined by elemental analysis to be CH<sub>0.734</sub>O<sub>0.012</sub>.

#### 4.4. Preparation of the post-cured COPNA(NP) resin

The mixture of naphthalene (15.4 g, 120 mmol), PXG (16.6 g, 120 mmol), and TsOH (1.60 g, 5 wt %) was heated at 120 °C for 3.5 h under nitrogen to produce a highly viscous material. It was converted into an infusible and insoluble solid by further heating at 300 °C for 1 h. The obtained solid was ground to a powder. The yield was 25.5 g (81%); IR (KBr)  $\nu_{\rm max}$  3432 (OH), 3043, 3005 (ArH), 2901 (CH<sub>2</sub>), 1596, 1508, 780 cm<sup>-1</sup> (ArH). The nominal sample composition was determined by elemental analysis to be CH<sub>0.789</sub>O<sub>0.010</sub>.

#### 4.5. Preparation of the S-COPNA(PR) resin

Post-cured COPNA(PR) (7.5 g) was added to fuming sulfuric acid (15 wt % SO<sub>3</sub>) (60 mL). The mixture was stirred at 80 °C for 15 h under nitrogen. The mixture was poured into distilled water (400 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. The S-COPNA(PR) resin (10.5 g) was obtained as the hygroscopic black powder; IR (KBr)  $\nu_{max}$  2925 (CH<sub>2</sub>), 1636 (ArH), 1165, 1023 cm<sup>-1</sup> (SO<sub>3</sub>H). The nominal sample composition was determined by elemental analysis to be CH<sub>0.725</sub>O<sub>0.396</sub>S<sub>0.088</sub>.

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.

#### 4.6. Preparation of the S-COPNA(PH) resin

Post-cured COPNA(PH) (2.5 g) was added to fuming sulfuric acid (15 wt % SO<sub>3</sub>) (20 mL). The mixture was stirred at 80 °C for 15 h under nitrogen. The mixture was poured into distilled water (133 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. The S-COPNA(PH) resin (3.0 g) was obtained as the hygroscopic black powder; IR (KBr)  $\nu_{max}$  2925 (CH<sub>2</sub>), 1637 (ArH), 1170, 1033 cm<sup>-1</sup> (SO<sub>3</sub>H). The nominal sample composition was determined by elemental analysis to be CH<sub>0.914</sub>O<sub>0.262</sub>S<sub>0.045</sub>.

#### 4.7. Preparation of the S-COPNA(NP) resin

Post-cured COPNA(NP) (7.5 g) was added to fuming sulfuric acid (15 wt % SO<sub>3</sub>) (60 mL). The mixture was stirred at 150 °C for 15 h under nitrogen. The mixture was poured into distilled water (400 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. The S-COPNA(NP) resin (10.5 g) was obtained as the hygroscopic black powder; IR (KBr)  $\nu_{max}$  2921 (CH<sub>2</sub>), 1619 (ArH), 1168, 1029 cm<sup>-1</sup> (SO<sub>3</sub>H). The nominal sample composition was determined by elemental analysis to be CH<sub>0.918</sub>O<sub>0.576</sub>S<sub>0.085</sub>.

# 4.8. Sulfonation of the post-cured COPNA(PR) resin by sulfuric acid

Post-cured COPNA(PR) (2.5 g) was added to sulfuric acid (20 mL). The mixture was stirred at 150 °C for 15 h under nitrogen. The mixture was poured into distilled water (133 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. The S-COPNA(PR) resin (2.9 g) was obtained as the hygroscopic black powder; IR (KBr)  $\nu_{max}$  2923 (CH<sub>2</sub>), 1637, 1560 (ArH), 1170, 1026 cm<sup>-1</sup> (SO<sub>3</sub>H). The nominal sample composition was determined by elemental analysis to be CH<sub>0.438</sub>O<sub>0.265</sub>S<sub>0.030</sub>.

### 4.9. Sulfonation of the post-cured COPNA(PR) resin by chlorosulfonic acid

A solution of chlorosulfonic acid (3.9 mL, 60 mmol) in dichloromethane (7.5 mL) was slowly added to the mixture of postcured COPNA(PR) (2.5 g) in dichloromethane (15 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 distilled water (100 mL). The mixture was filtered and the precipitate was washed with hot distilled water (>80 °C) until the wash water reached a pH of 7. Procedures of heating at 150 °C for 30 min, dispersion in distilled water (100 mL), and filtration were repeated until hydrogen chloride does not evolve. The precipitate was dried at 150 °C for 3 h under reduced pressure to give the sulfonated polymer. The yield was 3.0 g; IR (KBr)  $v_{max}$  2925 (CH<sub>2</sub>), 1637 (ArH), 1166, 1020 cm<sup>-1</sup> (SO<sub>3</sub>H). The nominal sample composition was determined by elemental analysis to be CH<sub>0.671</sub>O<sub>0.312</sub>S<sub>0.086</sub>.

# 4.10. Determination of the rate constant (*k*) for the esterification of carboxylic acids and 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* versus [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). The S-COPNA resins 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  $^{\circ}$ C. The reaction mixture at 10, 20, 40, 60, 100, 140,

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180, 220, 260, 300, 340, and 380 min was analyzed by titration with 0.1 M aqueous NaOH solution.

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  $^{\circ}$ C. The reaction mixture at 10, 20, 30, 40, 50, 60, 80, 100, 120, and 140 min was analyzed by titration with 0.05 M aqueous NaOH solution.

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 0.05 M aqueous NaOH solution.

#### 4.11. Preparation of the sugar catalyst<sup>3,12</sup>

D-Glucose (20 g, 111 mmol) was heated at 400 °C for 2 h under nitrogen to produce a brown-black solid. The solid was ground to a powder and heated in 35 mL of fuming sulfuric acid (15 wt % SO<sub>3</sub>) at 150 °C under nitrogen. After heating for 15 h, the mixture was poured into distilled water (230 mL) to form black precipitate. 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. The rate constant for esterification of acetic acid with ethanol was determined by the method described above.

### **4.12.** Recycle experiments of the formation of ethyl acetate catalyzed by the S-COPNA resins

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

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#### **References and notes**

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