



## Sulfonated polypyrene (S-PPR) as efficient catalyst for esterification of carboxylic acids with equimolar amounts of alcohols without removing water

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### ABSTRACT

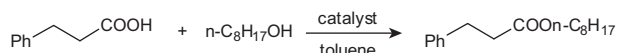
Sulfonated polypyrene (S-PPR) efficiently catalyzed the reactions between carboxylic acids and equimolar amounts of alcohols with and without heptane to give the corresponding esters in good to excellent yields. Esterification was carried out at 110 °C without removing water. Transesterification of carboxylic esters with a slight excess of alcohols smoothly proceeded without heptane to give the corresponding esters in good yields. For these reactions, S-PPR was recycled without significant loss of activities.

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Esterification of carboxylic acids with alcohols is one of the most important reactions in synthetic organic chemistry.<sup>1–9</sup> In 2000, Tanabe and co-workers<sup>10,11</sup> reported that diphenylammonium triflate ( $[\text{Ph}_2\text{NH}_2]^+[\text{OTf}]^-$ )<sup>12</sup> efficiently catalyzed the esterification of carboxylic acids with equimolar amounts of alcohols under mild conditions without removing water. In 2005, Ishihara et al.<sup>13–15</sup> reported dimesitylammonium pentafluorobenzenesulfonate as a mild and extremely active dehydrative ester condensation catalyst. A large problem using soluble catalysts was caused by the compli-

**Table 1**

Esterification between 3-phenylpropionic acid and 1-octanol catalyzed by various catalysts<sup>a</sup>



Entry	Catalyst (mg)	SO <sub>3</sub> H/mmole·g <sup>-1</sup>	Yield <sup>b</sup> (%)
1	S-PPR (100)	2.25 <sup>24</sup>	98
2	S-COPNA(PR,TPA) (148)	1.52 <sup>23</sup>	86
3	S-COPNA(PR,PXG) (56)	4.02 <sup>22</sup>	21
4	Amberlyst 15 (47)	4.8 <sup>28</sup>	89
5	Nafion NR50 (250)	0.9 <sup>28</sup>	65

<sup>a</sup> Reagents and conditions: 3-phenylpropionic acid 2.0 mmol, 1-octanol 2.0 mmol, toluene 4 mL, catalyst 0.225 mmol SO<sub>3</sub>H, temp. 120 °C, Time 2 h.

<sup>b</sup> Isolated yield.

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cated procedure on the recovery of the catalyst from the reaction mixture. Although many methods using solid acids have been reported for esterification,<sup>16–21</sup> only one example by Ishihara et al. which did not require the dehydrating system such as a Dean-Stark apparatus has been known as far as we know.<sup>13,14</sup>

During the course of our investigations, we devised the sulfonated condensed polynuclear aromatic (S-COPNA(PR)) resin<sup>22,23</sup> (PR = pyrene) and sulfonated polypyrene (S-PPR),<sup>24</sup> which were much more active than conventional solid acids such as Amberlyst 15 and Nafion NR50. Although S-PPR was less active than the S-COPNA(PR) resin, S-PPR possessed more hydrophobic surface than the S-COPNA(PR) resin.<sup>24</sup> We found that S-PPR was the quite efficient catalyst for esterification of carboxylic acids with equimolar amounts of alcohols in heptane without the dehydration system. In this Letter, we wish to report the results for esterification and transesterification catalyzed by S-PPR.

**Table 2**

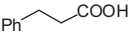
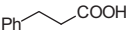
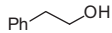
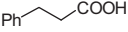
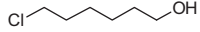
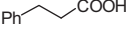

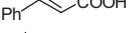

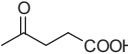







Esterification between 3-phenylpropionic acid and 1-octanol in various solvents<sup>a</sup>

Entry	Solvent	Temp (°C)	Time (h)	Yield <sup>b</sup> (%)
1	Heptane	110	1	95
2	Toluene	120	2	98
3	1,2-Dichloroethane	90	2	85
4	1,4-Dioxane	110	2	49
5	CH <sub>3</sub> CN	90	2	45
6	DMF	110	2	0

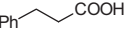
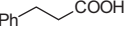
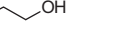
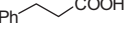
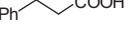

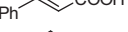
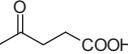

<sup>a</sup> Reagents and conditions: 3-phenylpropionic acid 2.0 mmol, 1-octanol 2.0 mmol, solvent 4 mL, S-PPR 100 mg.

<sup>b</sup> Isolated yield.

**Table 3**  
Esterification between various carboxylic acids and alcohols catalyzed S-PPR<sup>a</sup>

Entry	Carboxylic acid	Alcohol	Time (h)	Yield <sup>b</sup> (%)
1		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	2	98
2 <sup>c</sup>			15	98
3	<i>n</i> -C <sub>11</sub> H <sub>23</sub> COOH	<i>n</i> -C <sub>12</sub> H <sub>25</sub> OH	3	96
4			1	96
5			1	98
6			1	93
7		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	20	92
8		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	16	91
9	Ph-C≡C-COOH	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	2	83
10	MeO-CH <sub>2</sub> -COOH	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	1	95
11		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	1	99
12 <sup>d</sup>		PhCH <sub>2</sub> OH	2	65 <sup>f</sup>
13 <sup>e</sup>	PhCOOH	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	10	91
14		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	25	89
15 <sup>d,e</sup>			24	45 <sup>g</sup>
16 <sup>d,e</sup>		<i>n</i> -C <sub>9</sub> H <sub>11</sub> -OH <i>n</i> -C <sub>9</sub> H <sub>11</sub> -OH	24	37 <sup>h</sup>
17 <sup>e</sup>		PhOH	41	81
18 <sup>e</sup>	MeO-CH <sub>2</sub> -COOH		24	80

<sup>a</sup> Reagents and conditions: carboxylic acid 2.0 mmol, alcohol 2.0 mmol, heptane 4 mL, S-PPR 50 mg, temp. 110 °C.<sup>b</sup> Isolated yield.<sup>c</sup> S-PNP (50 mg) was added instead of S-PPR.<sup>d</sup> The reaction was conducted at 80 °C.<sup>e</sup> S-PPR 100 mg.<sup>f</sup> Dibenzyl ether was obtained in 23% yield.<sup>g</sup> Cyclododecene was obtained in 35% yield.<sup>h</sup> 5-Undecene was obtained in 43% yield.**Table 4**  
Esterification between various carboxylic acids and alcohols catalyzed S-PPR without solvent<sup>a</sup>

Entry	Carboxylic acid	Alcohol	Time (h)	Yield <sup>b</sup> (%)
1		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	2	90
2	<i>n</i> -C <sub>11</sub> H <sub>23</sub> COOH	<i>n</i> -C <sub>12</sub> H <sub>25</sub> OH	3	95
3			1	92
4		Cl-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -OH	1	90
5			1	90
6		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	20	90
7	MeO-CH <sub>2</sub> -COOH	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	1	93
8		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	1	92
9 <sup>c</sup>	PhCOOH	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	10	90
10		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	25	81

<sup>a</sup> Reagents and conditions: carboxylic acid 2.0 mmol, alcohol 2.0 mmol, S-PPR 50 mg, temp. 110 °C.<sup>b</sup> Isolated yield.<sup>c</sup> S-PPR 100 mg.

First, we examined the reactions between 3-phenylpropionic acid and equimolar amounts of 1-octanol in the presence of various

sulfonated polymers at 120 °C for 2 h in toluene. The results are summarized in Table 1. The reaction catalyzed by S-PPR gave octyl 3-phenylpropionate in 98% yield (entry 1). In the cases of S-PPR and the S-COPNA resins, the yields of the octyl ester increased as the catalyst became more hydrophobic<sup>24</sup> [S-PPR > S-COPNA(PR,TPA) > S-COPNA(PR,PXG)] (entries 1–3). Amberlyst 15-catalyzed reaction afforded the octyl ester in 89% yield together with the recovery of the starting materials (entry 4). It required 8 h to yield the product in 97% yield. Esterification catalyzed by Nafion NR50 proceeded more slowly than that of Amberlyst 15 to give the octyl ester in 65% yield (entry 5). From these observations, S-PPR was the most effective catalyst (entry 1).

Table 2 shows the results for esterification in a variety of solvents. In less polar solvents, reaction rates increased. In particular, the reaction proceeded most rapidly in heptane (entry 1). Although most of carboxylic acids hardly dissolve in heptane, the mixtures of the carboxylic acid and the alcohol could be dissolved in heptane on heating.

Table 3 shows the esterification of various substrates in heptane.<sup>25,26</sup> The long reaction time (15 h) was required in the presence of sulfonated polynaphthalene (S-PNP) (entry 2). It would be due to the less hydrophobic nature of S-PNP than S-PPR.<sup>24</sup> In spite of the strongly acidic SO<sub>3</sub>H groups of S-PPR, several functionalities such as a halogen, a double bond, a triple bond, a methoxy group, and a ketone were tolerated (entries 5–11). Esterification with acid-sensitive alcohols gave the products in low yields. The

reaction of 4-phenylbutyric acid with benzyl alcohol gave benzyl 4-phenylbutyrate (65%) and dibenzyl ether (23%) (entry 12). The reactions with secondary alcohols afforded the undesired alkenes as well as the corresponding esters (entries 15 and 16). Relatively sterically crowded benzoic acid, pivalic acid, phenol, and 1-adamantanol were also converted into the corresponding esters in good yields (entries 13, 14, 17, and 18).

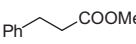
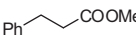
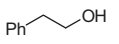
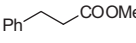
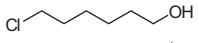
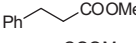
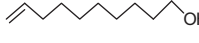
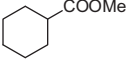
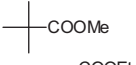
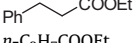
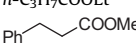
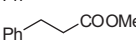
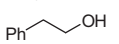
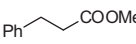
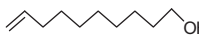
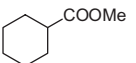
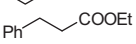
For these reactions, the hydrolysis of the produced esters was restricted. The irreversibility of esterification was confirmed by the following experiment. A mixture of octyl 3-phenylpropionate (2 mmol), water (20 mmol), and S-PPR (50 mg) in heptane (4 mL) was heated at 110 °C. After 2 h, the starting material was recovered in 90%. A large amount of the recovery of the octyl ester is a consequence of the structure of S-PPR. The hydrophobic surface of pyrene units of S-PPR prevents the approach of water molecules to catalytically important SO<sub>3</sub>H groups.

Esterification was also carried out without heptane to give the corresponding esters in good to excellent yields as shown in Table 4.

Next, we examined transesterification of carboxylic esters with alcohols in the presence of S-PPR. The results are summarized in Table 5. The reaction of methyl 3-phenylpropionate with 1.5 equiv. of 1-octanol gave octyl 3-phenylpropionate in 97% yield (entry 1). When 1.0 equiv. of 1-octanol was employed, the yield was reduced (8 h, 84%) (entry 2). The reactions of various carboxylic esters with alcohols afforded the corresponding esters in good yields (entries 3–9).<sup>25</sup> Transesterification without the solvent gave the corresponding esters in good yields (entries 10–15).<sup>27</sup>

In order to check the reusability of the catalyst, S-PPR was removed by filtration and used for the next experiment. S-PPR

**Table 5**  
Transesterification between various esters and alcohols catalyzed S-PPR with and without heptane<sup>a</sup>

Entry	Ester	Alcohol	Times (h)	yield <sup>b</sup> (%)
1		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	4	97
2 <sup>c</sup>			8	84
3			8	88
4 <sup>d</sup>			24	77
5 <sup>d</sup>			16	91
6		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	12	91
7 <sup>e</sup>		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	24	84
8		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	6	97
9	<i>n</i> -C <sub>3</sub> H <sub>7</sub> COOEt	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	14	87
10 <sup>f</sup>		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	4	88
11 <sup>f</sup>			8	84
12 <sup>d,f</sup>			16	82
13 <sup>f</sup>		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	12	93
14 <sup>f</sup>		<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	6	92
15 <sup>f</sup>	<i>n</i> -C <sub>3</sub> H <sub>7</sub> COOEt	<i>n</i> -C <sub>8</sub> H <sub>17</sub> OH	14	87

<sup>a</sup> Reagents and conditions: ester 2.0 mmol, alcohol 3.0 mmol, heptane 4 mL, S-PPR 100 mg, temp. 110 °C.

<sup>b</sup> Isolated yield.

<sup>c</sup> 2.0 mmol, 1-octanol was used.

<sup>d</sup> The reaction was conducted at 80 °C.

<sup>e</sup> S-PPR 200 mg.

<sup>f</sup> Without heptane.

**Table 6**

Recycle experiments for esterification of 3-phenylpropionic acid and transesterification of methyl 3-phenylpropionate

Entry	Yields <sup>a</sup> (%)				
	1st	2nd	3rd	4th	5th
1 <sup>b</sup>	98	99	99	99	98
2 <sup>c</sup>	90	94	93	91	90
3 <sup>d</sup>	97	81	59	40	23
4 <sup>e</sup>	88	92	90	89	89

<sup>a</sup> Isolated yields.

<sup>b</sup> Reagents and conditions: 3-phenylpropionic acid 2.0 mmol, 1-octanol 2.0 mmol, heptane 4 mL, S-PPR 50 mg, temp. 110 °C, 2 h.

<sup>c</sup> Reagents and conditions: 3-phenylpropionic acid 2.0 mmol, 1-octanol 2.0 mmol, S-PPR 50 mg, temp. 110 °C, 2 h.

<sup>d</sup> Reagents and conditions: methyl 3-phenylpropionate 2.0 mmol, 1-octanol 3.0 mmol, heptane 4 mL, S-PPR 100 mg, temp. 110 °C, 4 h.

<sup>e</sup> Reagents and conditions: methyl 3-phenylpropionate 2.0 mmol, 1-octanol 3.0 mmol, S-PPR 100 mg, temp. 110 °C, 4 h.

was recycled without significant loss of activities with and without heptane for esterification of carboxylic acids with alcohols (Table 6, entries 1 and 2). On the other hand, activities of S-PPR gradually decreased on recycling for transesterification in heptane (entry 3). The IR spectrum showed that SO<sub>3</sub>H groups of S-PPR were esterified by the produced MeOH. The intensity of the characteristic absorption at 3421 cm<sup>-1</sup> assigned to OH vibration of the SO<sub>3</sub>H groups decreased and the new absorptions at 2920, 2850, 1457, and 1362 cm<sup>-1</sup> due to the methyl groups appeared. For transesterification without heptane, S-PPR was recycled without significant loss of activities (entry 4).

In conclusion, we devised the efficient procedure for esterification of carboxylic acids with equimolar amounts of alcohols with and without heptane. In addition, transesterification of carboxylic esters with alcohols was carried out under neat conditions. For these reactions, S-PPR can be easily recovered by filtration and reused. The dehydrating system such as a Dean-Stark apparatus is not necessary. Activities of S-PPR were higher than those of conventional sulfonated polymers such as Amberlyst 15 and Nafion NR50. From these features, this method will become an environmentally benign procedure.

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25. The obtained esters were completely identified by comparison of their spectroscopic behaviors with those of authentic samples.<sup>4,10,14</sup>
26. *A typical procedure for esterification:* The mixture of 3-phenylpropionic acid (300 mg, 2.0 mmol), 1-octanol (260 mg, 2.0 mmol), and S-PPR (50 mg) in heptane (4 mL) was stirred at 110 °C for 2 h in a 10 mL pear-shaped round-bottom flask (Shibata, SPC-15 joint) equipped with a Liebig condenser. S-PPR was removed by filtration. The filtrate was evaporated (40 °C) under reduced pressure. The residue was purified by column chromatography (hexane/ethyl acetate = 20:1) to give octyl 3-phenylpropionate (515 mg, 98%) (Table 3, entry 1).
27. *A typical procedure for transesterification:* The mixture of methyl 3-phenylpropionate (328 mg, 2.0 mmol), 1-octanol (390 mg, 3.0 mmol), and S-PPR (100 mg) was stirred at 110 °C for 4 h. The obtained mixture was treated in a manner similar to the esterification of carboxylic acids to give octyl 3-phenylpropionate (462 mg, 88%) (Table 5, entry 10).
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