



Aniline–terephthalaldehyde resin *p*-toluenesulfonic acid (ATRT) salt as efficient mild polymeric solid acid catalyst



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ABSTRACT

Aniline–terephthalaldehyde resin *p*-toluenesulfonic acid (ATRT) salt was easily prepared by the reaction of aniline with 1.25 equiv of terephthalaldehyde in the presence of 1.0 equiv of *p*-toluenesulfonic acid at 75 °C for 24 h in EtOH. ATRT efficiently catalyzed the tetrahydropyranylation of alcohols and deprotection of tetrahydropyranyl (THP), triethylsilyl (TES), and *tert*-butyldimethylsilyl (TBDMS) ethers. Deprotection of dodecyl THP ether and dodecyl TBDMS ether catalyzed by ATRT proceeded faster than those by pyridinium *p*-toluenesulfonate (PPTS). ATRT was reused without significant loss of activities.

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Use of solid acid catalysts in organic syntheses and industrial purposes provides some merits such as simple work-up procedure, repeated use of the catalyst, and less corrosion of the reaction vessel. A number of strongly acidic resin catalysts such as Amberlyst 15,¹ Dowex 50 series,² Nafion NR50,³ and Nafion SAC-13⁴ have been developed.^{5,6} These solid acids have limitations when applied to compounds involving acid-sensitive groups. On the other hand, a survey of literature revealed that commercially available weakly acidic resin catalysts seem to be limited to a few examples such as poly(4-vinylpyridinium *p*-toluenesulfonate) (polyPPTS)⁷ and Poly(4-vinylpyridinium chloride) (polyPCL).⁸ In addition, these catalysts are expensive and their frequency of use has been limited.

Aniline–aldehyde resins are one of the important synthetic polymers.⁹ Formaldehyde (FA), furfural, and benzaldehyde have been employed as aldehyde components. For example, aniline–formaldehyde resins have been prepared by the treatment of aniline (AN) with formalin in the presence of hydrochloric acid followed by neutralization with NaOH.¹⁰ They are superior to elasticity, impact resistance, and electric insulation, and have been employed for electrical insulators.⁹

We found that aniline–terephthalaldehyde resin *p*-toluenesulfonic acid (ATRT) salt acted as a mild polymeric solid acid catalyst. The resin can be synthesized from the condensation of AN with terephthalaldehyde (TPA) in the presence of *p*-toluenesulfonic acid (TsOH) by *only one step*. In this Letter, we wish to report the results for the synthesis of ATRT. In addition, tetrahydropyranylation of

alcohols and deprotection of tetrahydropyranyl (THP) and silyl ethers catalyzed by ATRT are described.

First, we prepared aniline–formaldehyde resin *p*-toluenesulfonic acid (AFRT) salt. AN was treated with various amounts of formalin in the presence of 1.0 equiv of TsOH at room temperature in water. Since the produced solids were soluble to hot DMSO and DMF, the resins were post-cured at 160 °C for 6 h. The results are summarized in Table 1. Acid density of AFRT was determined by acid titration. When the ratio of AN:FA is 1.0:1.5, tetrahydropyranylation of 1-dodecanol at room temperature for 8 h in CH₃CN gave dodecyl THP ether (**1b**) in 91% yield. However, AFRT was partially soluble in hot DMSO and DMF (entry 1).¹¹ When the ratio of AN:FA is 1.0:3.0, the yield of THP ether **1b** decreased (10%) although it was insoluble in hot DMSO and DMF (entry 4).

We examined the formation of aniline–benzaldehyde resin *p*-toluenesulfonic acid (ABRT) salt. However, the reaction of AN with 1.5 equiv of benzaldehyde in the presence of 1.0 equiv of TsOH at 75 °C for 24 h in EtOH did not give the solid.

Next, we conducted the synthesis of ATRT. AN was treated with various amounts of TPA in the presence of 1.0 equiv of TsOH at 75 °C for 24 h in EtOH. The results are shown in Table 2. Soft material was obtained from the case of AN:TPA = 1.0:0.75. When the ratio of AN:TPA is 1.0:1.0, THP ether **1b** was obtained in 97% yield after 2.5 h, but the obtained resin was somewhat wet (entry 1). When the ratio of AN:TPA is 1.0:1.25, THP ether **1b** was obtained in 98% yield after 2.5 h in CH₃CN (entry 2).¹² We employed ATRT (AN:TPA = 1.0:1.25) for the reactions described below. ATRT was quite insoluble to hot water and hot organic solvents such as hexane, benzene, CH₂Cl₂, CHCl₃, THF, acetone, CH₃CN, MeOH, DMSO,

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Table 1
Solubility and activity of AFRT

Entry	AN:FA	Solubility ^a		Acid density (mmol g ⁻¹)	THP ether 1b ^b	
		DMSO	DMF		Time (h)	Yield ^c (%)
1	1.0:1.5	++	++	0.70	8	91
2	1.0:2.0	+	+	0.59	8	15
3	1.0:2.5	+	+	0.43	8	11
4	1.0:3.0	–	–	0.30	8	10

^a Solubility to hot solvents:–(insoluble) < + < ++ (partially soluble).^b Reagents and conditions: 1-dodecanol (1.0 mmol), DHP (1.5 mmol), AFRT (200 mg), CH₃CN (5 mL), room temp.^c Isolated yields.**Table 2**
Solubility and activity of ATRT

Entry	AN:TPA	Solubility ^a		Acid density (mmol g ⁻¹)	THP ether 1b ^b	
		DMSO	DMF		Time (h)	Yield ^c (%)
1	1.0:1.0	–	–	1.70	2.5	97
2	1.0:1.25	–	–	1.35	2.5	98
3	1.0:1.5	–	–	1.05	3	94
4	1.0:2.0	–	–	0.65	3	100
5	1.0:2.5	–	–	0.24	2.5	95

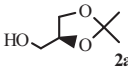
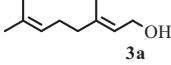
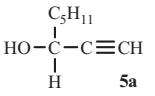
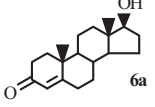
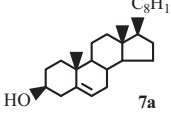
^a Solubility to hot solvents:–(insoluble) < + < ++ (partially soluble).^b Reagents and conditions: 1-dodecanol (1.0 mmol), DHP (1.5 mmol), ATRT (200 mg), CH₃CN (5 mL), room temp.^c Isolated yields.

and DMF. ATRT possessed the composition of C_{1.000}H_{0.875}N_{0.053}-O_{0.161}S_{0.017}, indicating that the amount of salt formation was 32% per aniline unit.

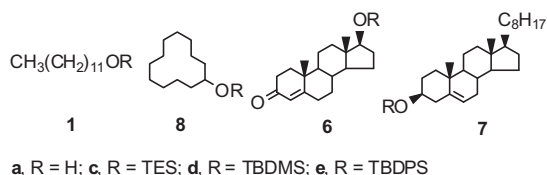
In order to increase the acid density, further treatment of ATRT with TsOH at 90 °C for 24 h in water was carried out. The acid density increased from 1.35 to 1.92 mmol g⁻¹, but the activity of ATRT for tetrahydropyranylation of 1-dodecanol decreased (6 h, 97%). The reason is not clear at the present moment.

The results of tetrahydropyranylation of alcohols and deprotection of THP ethers catalyzed by ATRT are shown in Table 3. Various alcohols involving acetals, allylic hydroxy, triple bonds, and conjugated ketones were treated with 3,4-dihydro-2H-pyran (DHP) in CH₃CN to give the corresponding THP ethers in good to excellent yields. Similarly, various THP ethers were transformed to their corresponding alcohols in MeOH in good to excellent yields.

Table 3
Tetrahydropyranylation of alcohols and deprotection of THP ethers catalyzed by ATRT

Entry	Alcohol	Protection ^a		Deprotection ^b	
		Time (h)	Yield (%)	Time (h)	Yield (%)
1	CH ₃ (CH ₂) ₁₁ OH 1a	2.5	98	3.5	100
2	 2a	7	91	8	– ^c
3	 3a	8	100	7	90
4	PhCH ₂ OH 4a	2	94	3	87
5	 5a	24	88	3	81
6	 6a	24	100 ^d	8	92
7	 7a	15	90 ^e	7	97 ^f

^a Reagents and conditions: alcohol (1.0 mmol), DHP (1.5 mmol), ATRT (200 mg), CH₃CN (5 mL), room temp.^b Reagents and conditions: THP ether (1.0 mmol), ATRT (200 mg), MeOH (5 mL), room temp.^c Glycerol was obtained in 91% yield.^d DHP (2.0 mmol), ATRT (400 mg), CH₃CN (10 mL) were used.^e CH₂Cl₂ (5 mL) was used.^f MeOH (5 mL)–CH₂Cl₂ (5 mL) was used.

Table 4
Deprotection of silyl ethers catalyzed by ATRT^a

Entry	Substrate	Time	Yield ^b (%)
1	1c	10 min	99
2	1d	1 h	100
3	1e	1 h	0
4	8c	10 min	97
5	8d	3 h	98
6	8e	3 h	0
7 ^c	6c	15 min	98
8 ^c	6d	32 h	100
9 ^c	6e	32 h	0
10 ^d	7c	10 min	99
11 ^d	7d	32 h	99
12 ^d	7e	32 h	0

^a Reagents and conditions: silyl ether (1.0 mmol), ATRT (25 mg), MeOH (10 mL), room temp.

^b Isolated yields.

^c ATRT (50 mg) was used.

^d ATRT (50 mg), MeOH (5 mL)–THF (5 mL) were used.

Table 4 shows the results of deprotection of various silyl ethers. Triethylsilyl (TES) and *tert*-butyldimethylsilyl (TBDMS) ethers converted into the corresponding alcohols in excellent yields. TES ethers were more easily cleaved than TBDMS ethers. *tert*-butyldiphenylsilyl (TBDPS) ethers were inert under the employed conditions. **Table 5** shows the results of tetrahydropyranlation of 1-dodecanol promoted by various catalysts using the amount which corresponds to 0.10 mmol acidic units or 75 mg. THP ether **1b** was isolated in excellent yields from the reactions catalyzed by ATRT, polyPPTS, polyPCL, and PPTS. The yields decreased in the cases of Montmorillonite K10 and mordenite due to the production of troublesome pyran oligomers (entries 4 and 5). The order of activities of polymeric solid acids was polyPPTS > ATRT > polyPCL (entries 1–3).

As shown in **Table 6**, deprotection of THP ether **1b** catalyzed by ATRT proceeded more quickly than those of polyPPTS and polyPCL when the amount corresponding to 0.17 mmol acidic units of the catalysts was used. ATRT-catalyzed deprotection of **1b** proceeded more slowly than those of polyPPTS and polyPCL when 50 mg of the catalysts was employed.

Table 7 shows the results of deprotection of TBDMS ether **1d** catalyzed by various catalysts. The reactions were completed within 1.5–2 h for polymeric solid acids (entries 1–3). It is noteworthy

Table 5
Tetrahydropyranlation of 1-dodecanol catalyzed by various catalysts^a

Entry	Catalyst	Acid density (mmol g ⁻¹)	Time (h)/yield ^b (%)	Time (h)/yield ^c (%)
1	ATRT	1.35	5/97	5/97
2	PolyPPTS	3.5	4/100	2.5/98
3	PolyPCL	6.5	24/92	8/91
4	Montmorillonite K10	0.65	1.5/81 ^d	2/88 ^d
5	Mordenite	0.512	1.5/75 ^d	3/83 ^d
6	PPTS	—	3/100	2/95

^a Reagents and conditions: 1-dodecanol (1.0 mmol), DHP (1.5 mmol), CH₃CN (5 mL), room temp.

^b Catalyst (0.10 mmol acidic units) was used.

^c Catalyst (75 mg) was used.

^d Pyran oligomers were produced.

Table 6
Deprotection of dodecyl THP ether catalyzed by various catalysts^a

Entry	Catalyst	Acid density (mmol g ⁻¹)	Time (h)/yield ^b (%)	Time (h)/yield ^c (%)
1	ATRT	1.35	4/99	5/93
2	PolyPPTS	3.5	8/98	3.5/96
3	PolyPCL	6.5	8/98	3.5/97
4	Montmorillonite K10	0.65	15/95	60/92
5	Mordenite	0.512	8/98	32/93
6	PPTS	—	31/99	24/97

^a Reagents and conditions: dodecyl THP ether (1.0 mmol), MeOH (5 mL), room temp.

^b Catalyst (0.17 mmol acidic units) was used.

^c Catalyst (50 mg) was used.

Table 7
Deprotection of dodecyl TBDMS ether catalyzed by various catalysts^a

Entry	Catalyst	Acid density (mmol g ⁻¹)	Time (h)/yield ^b (%)	Time (h)/yield ^c (%)
1	ATRT	1.35	1.5/99	2/99
2	PolyPPTS	3.5	2/100	2/97
3	PolyPCL	6.5	2/99	2/99
4	Montmorillonite K10	0.65	15/98	24/94
5	Mordenite	0.512	15/0	24/0
6	PPTS	—	10/97	10/100

^a Reagents and conditions: dodecyl TBDMS ether (1.0 mmol), MeOH (10 mL), room temp.

^b Catalyst (0.017 mmol acidic units) was used.

^c Catalyst (5 mg) was used.

that polymeric solid acids involving ATRT were more active than PPTS for the deprotection of THP ether **1b** and TBDMS ether **1d** (entries 1–3 in **Table 6** and entries 1–3 in **Table 7**). This may be due to the hydrophobic effect of polymers.¹³

In order to check the reusability of ATRT, the catalyst was removed by filtration and employed for the next experiment. ATRT was recycled without significant loss of activities (**Table 8**).

IR spectrum of ATRT showed characteristic absorptions at 3422 cm⁻¹ owing to the small amount of the hydroxy group, 1699 cm⁻¹ owing to the aromatic CHO group, 2972, 2926, 2869, 2733, 2612, 1577 cm⁻¹ owing to the NH₃⁺ group, and 3054, 3024, 1607, 1509, 836 (sh), 814, 781 (sh) cm⁻¹ owing to the benzene ring. The hydroxy group might be generated by the reaction between the formyl group and the benzene ring of aniline.^{5b} The absorptions at 836 (sh), 814, and 781 (sh) were assigned to out-of-plane carbon–hydrogen vibration for one, two, and three adjacent hydrogen atoms of the benzene ring, respectively. **Figure 1** shows the XRD pattern of ATRT. The broad diffraction peaks

Table 8
Recycle experiments using ATRT

Entry	Yields ^a (%)				
	1st	2nd	3rd	4th	5th
1 ^b	98	97	92	97	97
2 ^c	100	95	93	95	94
3 ^d	99	96	92	99	95

^a Isolated yields.

^b Reagents and conditions: 1-dodecanol (1.0 mmol), DHP (1.5 mmol), ATRT (200 mg), CH₃CN (5 mL), room temp, 2.5 h.

^c Reagents and conditions: dodecyl THP ether (1.0 mmol), ATRT (200 mg), MeOH (5 mL), room temp, 4 h.

^d Reagents and conditions: dodecyl TBDMS ether (1.0 mmol), ATRT (25 mg), MeOH (10 mL), room temp, 1.5 h.

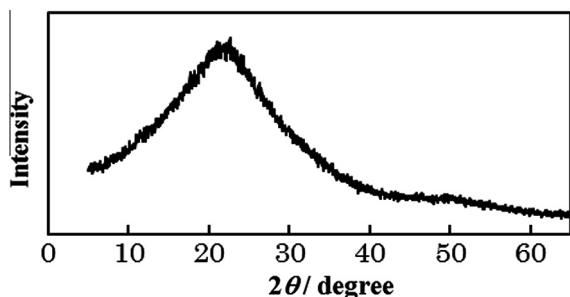


Figure 1. The XRD pattern of ATRT.

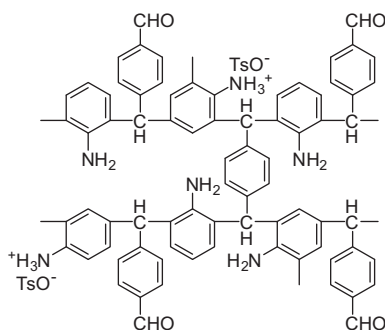


Figure 2. Plausible structure of ATRT.

($2\theta = 5\text{--}40$ and $40\text{--}60^\circ$) can be attributed to the amorphous structure. There are numerous investigations on the structure of aniline–formaldehyde resins⁹ and aniline–furfural resins.^{14b–d} It was difficult to determine the structure because ATRT was quite insoluble to water and organic solvents. The plausible structure of ATRT is shown in Figure 2.¹⁴

In conclusion, we synthesized ATRT from the condensation between AN and TPA in the presence of TsOH, and applied it to the mild polymeric solid acid catalyst. ATRT efficiently catalyzed the tetrahydropyranylation of alcohols and deprotection of THP, TES, and TBDMS ethers. It is worth pointing out that (1) preparation of the catalyst is quite easy, (2) the catalyst can be recycled, and (3) the work-up procedure is remarkably simple. Continuing studies on other derivatives of ATRT are now in progress.

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Supplementary data

Supplementary data associated (general experimental procedures, copies of IR spectra of AFRT and ATRT) with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.tetlet.2013.09.137>.

References and notes

- (a) Meshram, H. M.; Reddy, P. N.; Sadashiv, K.; Yadav, J. S. *Tetrahedron Lett.* **2005**, *46*, 623–626; (b) Shelkar, R.; Singh, A.; Nagarkar, J. *Tetrahedron Lett.* **2013**, *54*, 106–109; (c) Chavan, S. P.; Harale, K. R. *Tetrahedron Lett.* **2012**, *53*, 4683–4686; Murthy, P. V. N. S.; Rambabu, D.; Krishna, G. R.; Reddy, C. M.; Prasad, K. R. S.; Rao, M. V. B.; Pal, M. *Tetrahedron Lett.* **2012**, *53*, 863–867; (e) Talukder, M. M. R.; Wu, J. C.; Lau, S. K.; Cui, L. C.; Shimin, G.; Lim, A. *Energy Fuels* **2009**, *23*, 1–4.
- (a) Chopra, P.; Thomson, R. J.; Grice, D.; Itzstein, M. *Tetrahedron Lett.* **2012**, *53*, 6254–6256; (b) Guilera, J.; Bringue, R.; Ramirez, E.; Iborra, M.; Tejero, J. *Appl. Catal. A* **2012**, *413–414*, 21–29; (c) Wang, H.-M.; Hou, R.-S.; Du, H.-D.; Chen, L.-C.; Kang, I.-J. *Heterocycles* **2011**, *83*, 331–338; (d) Leveneur, S.; Murzin, D. Y.; Salmi, T.; Mikkola, J.-P.; Kumar, N.; Eraenen, K.; Leveneur, S.; Estel, L. *Chem. Eng. J.* **2009**, *147*, 323–329.
- (a) Olah, G. A.; Mehrota, A. K. *Synthesis* **1982**, 962–963; (b) Polshettiwar, V.; Varma, R. S. *Tetrahedron Lett.* **2008**, *49*, 2661–2664; (c) Polshettiwar, V.; Varma, R. S. *Tetrahedron Lett.* **2008**, *49*, 879–883; (d) Schager, F.; Bonrath, W. *J. Catal.* **1999**, *182*, 282–284.
- (a) Prakash, G. K. S.; Vaghoo, H.; Panja, C.; Molnár, A.; Mathew, T.; Olah, G. A. *Synthesis* **2008**, 897–902; (b) Liu, Y.; Lotero, E.; Goodwin, J. G., Jr. *J. Catal.* **2006**, *242*, 278–286.
- (a) Tanemura, K.; Suzuki, T.; Nishida, Y.; Horaguchi, T. *Tetrahedron* **2011**, *67*, 1314–1319; (b) Tanemura, K.; Suzuki, T.; Nishida, Y.; Horaguchi, T. *Polym. Bull.* **2012**, *68*, 705–719; (c) Tanemura, K.; Suzuki, T.; Horaguchi, T. *J. Appl. Polym. Sci.* **2013**, *127*, 4524–4536; (d) Tanemura, K.; Suzuki, T. *Tetrahedron Lett.* **2013**, *54*, 1972–1975.
- (a) Gelbard, G. *Ind. Eng. Chem. Res.* **2005**, *44*, 8468–8498; (b) Shanmugam, S.; Viswanathan, B.; Varadarajan, T. K. *J. Mol. Catal. A: Chem.* **2004**, *223*, 143–147; (c) Toda, M.; Takagaki, A.; Okamura, M.; Kondo, J. N.; Hayashi, S.; Domen, K.; Hara, M. *Nature* **2005**, *438*, 178.
- (a) Menger, F. M.; Chu, C. H. *J. Org. Chem.* **1981**, *46*, 5044–5045; (b) Ganesan, A. *Synth. Commun.* **1998**, *28*, 3209–3212.
- Johnston, R. D.; Marston, C. R.; Krieger, P. E.; Goe, G. L. *Synthesis* **1988**, 393–394.
- Hanyu, T. *Kobunshi* **1958**, *7*, 78–81.
- (a) Frey, K. *Helv. Chim. Acta* **1935**, *18*, 491–513; (b) Noda, M.; Imoto, M. *Kogyo Kagaku Zasshi* **1952**, *55*, 485–487; (c) Noda, M. *Kogyo Kagaku Zasshi* **1952**, *55*, 538–539; Ho, K.-S.; Hsieh, T.-H.; Kuo, C.-W.; Lee, S.-W.; Lin, J.-J.; Huang, Y.-J. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 3116–3125.
- AFRT post-cured at 160 °C for 24 h was partially soluble to hot DMSO and DMF.
- Yields of THP ether **1b** in the other solvents: CH₂Cl₂ (48%), C₆H₆ (2%), THF (0%), dioxane (0%), and CH₃CN (98%).
- (a) Cheng, S.; Yan, H.; Zhao, C. *Chromatogr. A* **2006**, *1108*, 43–49; (b) Guo, X.; Wang, X.; Zhou, X.; Kong, X.; Tao, S.; Xing, B. *Environ. Sci. Technol.* **2012**, *46*, 7252–7259; (c) Iimura, S.; Manabe, K.; Kobayashi, S. *Org. Biomol. Chem.* **2003**, *1*, 2416–2418; (d) Sanquer, -B. M.; Delaire, J. A. *J. New Chem.* **1992**, *16*, 801–808.
- (a) Tanaka, M.; Sekiguchi, T. *Nippon Kagaku Kaishi* **1983**, 1499–1504; (b) Imoto, M.; Asao, C. *Kogyo Kagaku Zasshi* **1947**, *50*, 11–12; (c) Imoto, M. *Kogyo Kagaku Zasshi* **1947**, *50*, 12–13; (d) Imoto, M.; Asao, C. *Kogyo Kagaku Zasshi* **1947**, *50*, 13–14.