

# Synthesis and Properties of PVC-Bound *N,N*-Dialkylaminopyridine

RONGBAO WEI, YA LIANG, SUZHAN CHEN, CHENXI JIA, FAN LI, TAO ZHANG

Department of Chemical Engineering, Tianjin Institute of Technology, Tianjin 300191, People's Republic of China

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**ABSTRACT:** A linear poly(vinyl chloride) (PVC)-supported dialkylaminopyridine was prepared through PVC treated with *N*-methylaminopyridine and NaH in tetrahydrofuran. The properties of this PVC-bound catalyst were examined by acetylation of linalool and 5-FU. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1067–1069, 2002; DOI 10.1002/app.10391

**Key words:** poly(vinyl chloride) (PVC); catalyst; resins; esterification

## INTRODUCTION

In previous articles, dimethylaminopyridine moieties bound to insoluble polymer supports were reported.<sup>1–3</sup> Insoluble polymer-bound dimethylaminopyridine (DMAP) catalysts can be easily separated from a reaction mixture by simple filtration, and the catalysts are reusable. However, the catalytic activity of the DMAP unit bound to polymers is somewhat lower than is DMAP in a homogeneous system.<sup>4</sup>

In this work, poly(vinyl chloride) (PVC)-supported dialkylaminopyridine was prepared through PVC treated with *N*-methylaminopyridine and NaH in tetrahydrofuran (THF). The properties of the PVC-bound catalyst were examined by acetylation of linalool and 5-FU. The PVC-bound catalyst dissolved in the reaction mixture; therefore, the reaction is homogeneous. After the reaction was finished, water was added to the reaction mixture and the PVC-bound catalyst could be removed by filtration. The catalyst is reusable by treating it with an organic base.

## EXPERIMENTAL

4-Aminopyridine was prepared by the method described in the literature. *N,N*-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were refluxed with sodium and distilled over CaH<sub>2</sub>; hexane and THF were refluxed and distilled over sodium wire and biphenyl ketone. The PVC was from the Tianjin Chemical Plant (Tianjin, China).

### Preparation of PVC-supported Dialkylaminopyridine

#### Example 1

A 250-mL four-necked flask with a sealed mechanical stirrer, a double-surface reflux condenser, and a gas inlet tube extending to a point just above the bottom of the stirrer was used. NaH, 2 mmol (55% in mineral oil), was washed with hexane (3 × 30 mL) to remove the mineral oil and added to the flask. Then, 50 mL THF was added to the flask and a 100-mL solution of 4-aminopyridine (1 mmol) in THF was added to the stirred mixture at room temperature under a nitrogen atmosphere. After the evolution of hydrogen was completed, 1.4 mmol tetrabutylammonium bromide and 19.9 g of PVC in THF were added to the mixture. The mixture was

**Table I** Data for Alcohol Acetylation Using PVC-bound Catalyst

Linalool (mol)	Acetic Anhydride (mol)	PVC-bound Catalyst (g)	Reaction Time (h)	Reaction Temperature (°C)	Conversion (%)
0.1	0.1	1	10	50	95.6
0.1 <sup>a</sup>	0.1	1	25	50	95.4
0.1	0.1	(DMAP) 1%	2	50	99.8

<sup>a</sup>Catalyst: polystyrene-bound DMAP.

stirred at room temperature for 2 h and at 60°C for an additional 24 h under a nitrogen atmosphere. After cooling, the reaction mixture was poured into water and the PVC-bound *N,N*-dialkylaminopyridine was isolated from the solution by using a fritted glass funnel, washed with water, and dried at 30°C in a vacuum for 48 h.

### Example 2

A 500-mL four-necked flask with a sealed mechanical stirrer, a double-surface reflux condenser, and a gas inlet tube extending to a point just above the bottom of the stirrer was used. NaH, 1 mmol (70% in mineral oil), was washed with hexane (3 × 30 mL) to remove the mineral oil and added to the flask. Then, 50 mL THF was added, followed by a 200-mL solution of 4-*N*-methylaminopyridine (1 mmol) in THF added to the stirred mixture at room temperature under a nitrogen atmosphere. After the evolution of hydrogen was completed, 1.4 mmol tetrabutylammonium chloride and 19.9 g of PVC in THF were added to the mixture. The mixture was stirred at room temperature for 5 h and at 70–90°C for 48 h under a nitrogen atmosphere. The reaction mixture was poured into water and the PVC-bound *N*-methyl-*N*-alkylaminopyridine was isolated from the solution, washed with water, and dried at 30°C in a vacuum for 48 h.

ANAL. Cl, 40.51%; N, 2.67%.

IR (cm<sup>-1</sup>): 3020, 3010 (=CH pyridine ring), 2950, 2846 (CH<sub>2</sub> or CH), 1640–1530 (pyridine ring), 1201 (C–N). <sup>1</sup>H-NMR (δ): 7.8–8.5 (m, =CH pyridine), 3.1 (m, CH–Cl), 2.8 (m, CH–N), 2.4 (s, CH<sub>3</sub>), 1.1–1.2 (m, CH<sub>2</sub>).

### Acetylation of Alcohols and Amines

The reactions were carried out as described in the references cited in Table I. An illustrative procedure is given here for the acetylating of alcohols and amine.

### Example 3

Linalool (0.1 mol), acetic anhydride (0.1 mol), the polymer catalyst (1 g), triethylamine (10 mL), and THF (100 mL) were stirred magnetically for 0.5 h at room temperature, then kept for 10 h at 50°C and cooled to room temperature. Fifty milliliters of water was added to the reaction mixture and the polymer–catalyst was removed by gravity filtration. The organic layer was washed to neutrality by 10% NaHCO<sub>3</sub>/H<sub>2</sub>O and dried by anhydrous MgSO<sub>4</sub>. The THF was removed by a rotary evaporator, giving a yellow liquid, which was distilled in a vacuum. See Table I.

IR (cm<sup>-1</sup>): 3011, 2962, 2851, 1724. <sup>1</sup>H-NMR (δ): 1.42 (3H, s), 1.60 (2 H, t), 1.72 (6H, s), 1.95 (2H, m), 2.00 (3H, s), 5.01–3.2 (3H, m), 5.80–6.20 (1H, m).

### Example 4

5-FU (0.15 mol), acetic anhydride (0.15 mol), the polymer catalyst (1 g), triethylamine (10 mL), and THF (100 mL) were stirred magnetically for 0.5 h at room temperature and kept for 4–6 h at 50°C until the reaction was finished and then cooled to room temperature with a thin layer chromatograph (TLC, CHCl<sub>3</sub>:CH<sub>3</sub>COCH<sub>3</sub> = 1:1). Fifty milliliters of water was added to the reaction mixture, and the polymer catalyst was removed by gravity filtration. The organic layer was washed to neutrality with 10% NaHCO<sub>3</sub>/H<sub>2</sub>O and dried by anhydrous MgSO<sub>4</sub>. The THF was removed by a rotary evaporator, giving a pale solid, and then recrystallized using ethanol. See Table II. Mp: 110–111°C.

IR(KBr) cm<sup>-1</sup>: 3320, 3230, 2920, 1720–1740, 1680, 1660, 1510, 1445, 1340, 1272, 1200, 1090, 1042, 802, 770, 750. <sup>1</sup>H-NMR (δ): 0.93 (3H, t), 1.67–1.73 (8H, m), 3.78 (2H, t), 5.45 (1H, s), 8.45 (1H, s), 9.05 (1H, s).

ANAL. C, 51.30%; H, 6.17%; N, 16.38%.

**Table II** Data for 5-FU Acetylation Using PVC-bound Catalyst

5-FU (mol)	Acetic Anhydride (mol)	PVC-bound Catalyst (g)	Reaction Time (h)	Reaction Temperature (°C)	Conversion (%)
0.15	0.15	1	5	50	96.6
0.1 <sup>a</sup>	0.1	1	25	50	96.4
0.1	0.1	(DMAP) 1%	2	50	99.6

<sup>a</sup>Catalyst: polystyrene-bound DMAP.

## CONCLUSIONS

PVC-supported dialkylaminopyridine was prepared through PVC treated with *N*-methylaminopyridine and NaH in THF. The PVC-bound catalyst could be dissolved in the acetylating mixture; therefore, the reaction is homogeneous. After the reaction was finished, water was added to the reaction mixture. The PVC-bound catalyst could be removed by filtration.

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