

# Synthesis of Azo Chromophores by Using a Polymer-Supported Sodium Nitrite

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**ABSTRACT:** Polymer supported reagents especially anion exchange resins have been widely applied in organic synthesis. The recent developments in polymer-supported reactions have led to the propagation of combinatorial chemistry as a method for the rapid and efficient preparation of novel functionalized molecules. An interesting and fast growing branch of this area is polymer-supported reagents. In this study, diazonium salts are generated and are coupled with

a coupling component by using a polymer supported nitrite and a polymeric acid. In this procedure, the azo chromophores are formed in a clean and efficient manner, the work-up is easy and yields are high to excellent. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 538–543, 2011

**Key words:** diazotization; azo compounds; amines; polymer supported reagents; polymeric reagents; dyes

## INTRODUCTION

Azo compounds are very important in the field of dyes,<sup>1</sup> azoic dye is the most important group of all synthetic dyes. Azo chromophores have a wide range of applications in the textile, leather, paper and food, pharmaceutical, and cosmetic industries. On the other hand, azo compounds have more recently found potential applications in various fields such as biomedicine<sup>2,3</sup> and organic synthesis.<sup>4,5</sup> They also have excellent optical and photoelectric properties.<sup>6–8</sup>

There are many methods available for the synthesis of azo compounds.<sup>9–15</sup> Direct synthesis of azo derivatives in good yields can be accomplished by the reduction of nitro aromatics with metal hydrides,<sup>16,17</sup> zinc in strongly alkaline media,<sup>18</sup> lead and triethylammonium formate,<sup>19</sup> active-iron base reducing system,<sup>20</sup> dicobalt octacarbonyl,<sup>21</sup> etc.<sup>22</sup> These methods all suffer from either low yields, complex work-up procedures, or undesired side reactions. In addition, they may also require harsh conditions or can generate dangerous pollutants for the environment.<sup>22</sup> Consequently, new methodologies with milder reaction conditions and simple work-up are welcomed.

Polymer-supported reagents especially anion exchange resins have been widely applied in organic synthesis.<sup>23–42</sup>

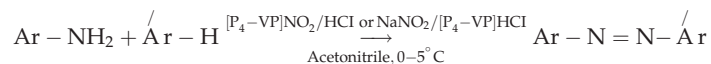
A literature search shows few reports covering the preparation of azo compounds based on polymeric acid or polymer-supported reagents under heterogeneous conditions.<sup>40–42</sup> One of them is reported by Ley et al. for the synthesis of azo chromophores using Amberlyst A-26 NO<sub>2</sub><sup>-</sup> form.<sup>40</sup> In this procedure, the reactions are carried out with excess aniline and then, after filtration, the solution must be subjected to a catch-and-release work-up, which involved shaking the colored solution with Dowex (OH), to remove unreacted aniline. Another polymeric reagent that may be used for preparation of azo compounds is polymer-supported diazonium salts. This polymeric reagent is reported by Bradly et al.<sup>41</sup> In this communication, diazonium salts are prepared by using Amberlyst A-26 NO<sub>2</sub><sup>-</sup> form and then, diazonium salts are supported on sulfonic acid-based cation-exchange resin to synthesize azo chromophores. However, in these methods, the work-up to obtain products required several steps<sup>40</sup> or the preparation of polymeric reagent needs an additional step.

Recently, we prepared and used crosslinked poly(4-vinylpyridine) supported sodium nitrite, [P<sub>4</sub>-VP]NO<sub>2</sub>, for the synthesis of nitroalkanes,<sup>31</sup> and [P<sub>4</sub>-VP]NO<sub>2</sub>/HCl or [P<sub>4</sub>-VP]HCl/NaNO<sub>2</sub> used for N-nitrosation of secondary amines, as a heterogeneous system,<sup>32</sup> or solvent-free N-nitrosation of secondary amines.<sup>33</sup>

In continuing our studies on the development of the application of [P<sub>4</sub>-VP]NO<sub>2</sub> and [P<sub>4</sub>-VP]HCl in organic synthesis, we decided to apply a completely heterogeneous system. In this regard, a number of different reaction conditions based on the generation of HNO<sub>2</sub> by relatively strong organic acidic resins and polymer-supported nitrite or sodium nitrite for synthesis of azo chromophores was investigated. But the study of the

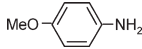
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**TABLE I**  
**Synthesis of Azo Chromophores by Using [P<sub>4</sub>-VP]HCl/NaNO<sub>2</sub> or HCl/[P<sub>4</sub>-VP]NO<sub>2</sub> and Ar-NH<sub>2</sub> in the Presence of a Coupling Component in Acetonitrile at 0–5°C**



Entry	Ar-NH <sub>2</sub>	Ar'-H (Coupling component)	Product <sup>a</sup>	Procedure A <sup>b</sup>		Procedure B <sup>c</sup>	
				Time (min)	Yield <sup>d</sup> (%)	Time (min)	Yield <sup>d</sup> (%)
1	Ph-NH <sub>2</sub>	Ph-OH		45	97	40	98
2	Ph-NH <sub>2</sub>		No reaction	240	0	240	0
3	Ph-NH <sub>2</sub>	2-Naphthol		55	92	45	95
4	Ph-NH <sub>2</sub>	Ph-N(Me) <sub>2</sub>		100	96	80	97
5	Ph-NH <sub>2</sub>	Ph-OMe	No reaction	240	0	240	0
6		Ph-OH		120	89	100	92
7			No reaction	240	0	240	0
8		2-Naphthol		150	82	125	87
9		Ph-N(Me) <sub>2</sub>		135	82	115	85
10		Ph-OMe	No reaction	240	0	240	0
11		Ph-OH		35	94	32	91
12			No reaction	240	0	240	0
13		2-Naphthol		40	91	35	89
14		Ph-N(Me) <sub>2</sub>		85	97	75	95

TABLE I. Continued

Entry	Ar-NH <sub>2</sub>	Ar'-H (Coupling component)	Product <sup>a</sup>	Procedure A <sup>b</sup>		Procedure B <sup>c</sup>	
				Time (min)	Yield <sup>d</sup> (%)	Time (min)	Yield <sup>d</sup> (%)
15		Ph-OMe	No reaction	240	0	240	0

<sup>a</sup> The structures were confirmed by comparison of the melting point, FTIR and <sup>1</sup>H-NMR spectra with those of pure compounds.

<sup>b</sup> Molar ratio of [P<sub>4</sub>-VP]HCl NaNO<sub>2</sub>: amine equal to 3 : 2 : 1.

<sup>c</sup> Molar ratio of HCl: [P<sub>4</sub>-VP]NO<sub>2</sub>: amine equal to 3 : 2 : 1.

<sup>d</sup> Isolated yields.

diazotization of primary aromatic amines in the presence of [P<sub>4</sub>-VP]NO<sub>2</sub>/HCl, or NaNO<sub>2</sub>/[P<sub>4</sub>-VP]HCl is only reported.

On the other hand, any reduction in the amount of strong inorganic acids needed and any simplification in handling procedures are required for risk reduction, economic advantage, and economic protection.<sup>43</sup> In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.<sup>44</sup>

## EXPERIMENTAL

### General

Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Poly(4-vinylpyridine) crosslinked with 2% DVB, (III), and crosslinked with 25% DVB, (I), were commercially available (Fluka). Crosslinked poly(4-vinylpyridine)-supported hydrochloric acid, [P<sub>4</sub>-VP]HCl, (II), and crosslinked poly(4-vinylpyridine)-supported sodium nitrite, [P<sub>4</sub>-VP]NO<sub>2</sub>, (V), were synthesized according to our procedure,<sup>31–33</sup> that is, summarized in Scheme 1. Progress of the reaction was followed by TLC using silica gel Poly Gram SIL G/UV 254 plates. Products were characterized by comparison of their FT-IR and <sup>1</sup>H- and <sup>13</sup>C-NMR spectra and physical data with those of pure compounds.

FT-IR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectra were run on a Bruker, Equinox (Model 55), and Bruker AC 500, Aavance DPX spectrophotometer, respectively (using SiMe<sub>4</sub> as internal reference). Melting points were determined with a Buchi melting point B-540 B.V. CHI apparatus.

General procedure for synthesis of azo chromophores

To a mixture of primary aromatic amine (1 mmol) in a round-bottomed flask (50 mL), [P<sub>4</sub>-VP]HCl (0.4 g, 2 mmol), or HCl (2 mmol) and acetonitrile (5 mL), 158 mg NaNO<sub>2</sub> (2 mmol), or 0.9 g of [P<sub>4</sub>-VP]NO<sub>2</sub> (2 mmol) was added, and while keeping the suspension at 0–5°C, it was stirred for 30 min.

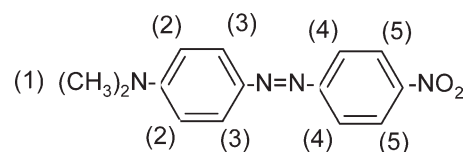
A solution of 1 mmol of a coupling component in 5 mL of acetonitrile was added slowly with a dropper to the arenediazonium salt solution while the mixture was stirred well during addition. When the

addition was completed, stirring was continued for the time specified in Table I until a yellow-orange-red color appeared and coupling component disappeared. Reaction monitoring was accomplished by TLC with ethyl acetate/*n*-hexane (30/70) as eluent. After completion of the reaction, the suspension was filtered, and the solvent was evaporated. In general, the crystalline yellow-orange-red solid products were obtained in high to excellent yields (Table I).

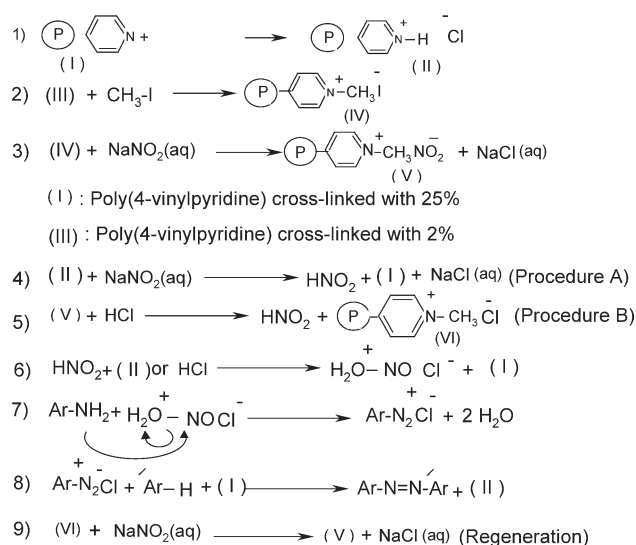
If further purification was needed, chromatography on silica gel [eluent: ethyl acetate/*n*-hexane (30/70)] was used, which provides highly pure products.

### Synthesis of 4-dimethylamino-4'-nitroazobenzene

To a mixture of 4-nitroaniline (138 mg, 1 mmol), HCl (2 mmol) or [P<sub>4</sub>-VP]HCl (0.4 g, 2 mmol), and acetonitrile (5 mL) in a round-bottomed flask (50 mL) 0.9 g of [P<sub>4</sub>-VP]NO<sub>2</sub> (2 mmol), or 158 mg NaNO<sub>2</sub> (2 mmol) was added, and while keeping the suspension at 0–5°C, was stirred for 30 min. The slightly turbid pale grey solution as a *p*-nitrobenzenediazonium salt solution was obtained. Then, the solution of 121 mg of *N,N*-dimethylaniline (1 mmol) in 5 mL acetonitrile was added slowly with a dropper to the *p*-nitrobenzenediazonium salt solution while the mixture was stirred well during addition. When the addition was completed, stirring was continued for 135 min in the presence of [P<sub>4</sub>-VP]NO<sub>2</sub>/HCl (Procedure A), and 115 min in the presence of [P<sub>4</sub>-VP]HCl/NaNO<sub>2</sub> (Procedure B), until an orange-red color appeared. Reaction monitoring was accomplished by TLC with ethyl acetate/*n*-hexane (30/70) as eluent. After completion of the reaction, the suspension was filtered, and the solvent was evaporated. The crystalline orange-red solid product was obtained in 82% yield (in Procedure A), and in 85% (in Procedure B).



M.P.: 217–222°C (lit. 45: 215–225°C), FT-IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3060 (C–H, aromatic), 2924 (C–H,



**Scheme 1** Mechanism of the reaction.

aliphatic), 1617 (N=N), 1600 (C=C), 1530 and 1351 (N=O), 1235 (C-N), 1054, 850 (C-H, bending).  $^1H$ -NMR (500 MHz,  $CDCl_3/DMSO-d_6$ )  $\delta$ : 8.6 [2H (5), d,  $J = 8.9$  Hz], 8.2 [2H (4), d,  $J = 8.9$  Hz], 8.1 [2H (3), d,  $J = 9.5$  Hz], 6.94 [2H (2), d,  $J = 9.5$  Hz], 3.25 [6H (1), s].

## RESULTS AND DISCUSSION

Crosslinked poly(4-vinylpyridinyl)-supported hydrochloric acid,  $[P_4-VP]HCl$ , (Step 1 in Scheme 1) and crosslinked poly(4-vinylpyridinyl)-supported sodium nitrite,  $[P_4-VP]NO_2$ , (Steps 2 and 3 in Scheme 1) are easily prepared according to our procedure,<sup>31-33</sup> and used as an efficient reagent combination for synthesis of azo chromophores (Scheme 1). We have investigated a number of different reaction conditions based on the generation of  $HNO_2$  by relatively strong organic acidic resins and polymer-supported nitrite or sodium nitrite for synthesis of azo chromophores.

We observed that primary aromatic amine in the presence of  $[P_4-VP]HCl/NaNO_2$  or  $HCl/[P_4-VP]NO_2$  is converted to corresponding diazonium salts (Steps 4-7 in Scheme 1). Aniline-based diazo chromophore was prepared by coupling of diazonium salt with a coupling component (Step 8 in Scheme 1). The process involves a simple mixing of primary aromatic amine,  $[P_4-VP]HCl/NaNO_2$  or  $HCl/[P_4-VP]NO_2$  (Step 4, Procedure A, or Step 5, Procedure B, in Scheme 1) in acetonitrile and stirring them for 30 min at 0-5°C. Then, a coupling component was added and stirring was continued until the reaction was completed and the coupling component was disappeared.

Regeneration of the polymeric reagents can be carried out by the treatment with an aqueous solution of sodium nitrite (Step 9 in Scheme 1).

Capacity of  $[P_4-VP]NO_2$  was determined by potentiometric titration with a 0.1N solution of silver nitrate that was obtained 2.2 mmol  $g^{-1}$  of the polymer, and the capacity of  $[P_4-VP]HCl$  was determined by titration with a 0.1N solution of NaOH, and was obtained 5 mmol  $g^{-1}$  of the polymer.

Optimization of the reaction conditions showed that, for most of the reactions, among other solvents, acetonitrile (as shown in Table II, for reaction 1 of Table I) and  $[P_4-VP]HCl/NaNO_2$ /amine (Procedure A) or  $HCl/[P_4-VP]NO_2$ /amine (Procedure B) ratio of 3 : 2 : 1 were the best (Table III).

In these methods, purification of product is very easy (only filtration and evaporation of the solvent is required), and excess of reagent and by-products remain bounded to the resin. The reaction is believed to follow the typical pathway shown in Scheme 1.

A number of primary amines such as aniline and substituted anilines, such as *p*-nitroaniline and *p*-methoxyaniline were used for synthesis of the corresponding diazonium salts by using these procedures. Also, a number of different coupling components

**TABLE II**  
 Synthesis of Azo Chromophores by Using  $[P_4-VP]HCl/NaNO_2$  or  $HCl/[P_4-VP]NO_2$  and Aniline in the Presence of Phenol (1 mmol) as a Coupling Component in Different Available Solvents at 0-5°C

Entry	Solvent	Procedure A <sup>a</sup>		Procedure B <sup>b</sup>	
		Time (min)	Yield <sup>c</sup> (%)	Time (min)	Yield (%)
1	<i>n</i> -hexane	60	12	60	15
2	Ethanol	60	63	60	65
3	Acetone	60	45	60	49
4	Chloroform	60	41	60	44
5	Dichloromethane	60	27	60	30
6	Toluene	60	15	60	18
7	Acetonitrile	45	97	40	98

<sup>a</sup> Molar ratio of  $[P_4-VP]HCl : NaNO_2 : \text{amine}$  equal to 3 : 2 : 1.

<sup>b</sup> Molar ratio of  $HCl : [P_4-VP]NO_2 : \text{amine}$  equal to 3 : 2 : 1.

<sup>c</sup> Isolated yields.



TABLE III  
Synthesis of Azo Chromophores by Using Different Molar Ratio of [P<sub>4</sub>-VP]HCl/NaNO<sub>2</sub> or HCl/[P<sub>4</sub>-VP]NO<sub>2</sub> with Aniline (1 mmol) in the Presence of Phenol (1 mmol) in Acetonitrile at 0–5°C

Entry	Molar ratio of [P <sub>4</sub> -VP]HCl/NaNO <sub>2</sub> or HCl/[P <sub>4</sub> -VP]NO <sub>2</sub>	Procedure A		Procedure B	
		Time (min)	Yield <sup>a</sup> (%)	Time (min)	Yield (%)
1	2-Jan	60	22	60	25
2	1-Jan	60	14	60	20
3	2-Mar	45	97	40	98
4	3-Feb	60	41	60	44
5	2/1.5	60	90	60	92

<sup>a</sup> Isolated yields.

such as phenol, *p*-nitrophenol, 2-naphthol, anisole, and *N,N*-dimethylaniline were examined for coupling with diazonium salts to obtain corresponding azo chromophores. Although the diazonium salt derived from arylamines was coupled with *N,N*-dimethylaniline, but an attempt to couple it with anisole and with *p*-nitrophenol after 4 h, no azo chromophore product is observed (entries 2, 5, 7, 10, 12, and 15 in Table I). Our results are in accord with the previously reported results by Ley et al.,<sup>40</sup> and Bradly et al.<sup>41</sup>

As seen in Table I, the reaction time in Procedure B is shorter than in Procedure A and slightly has the best results than Procedure A. These differences probably are arising from differential crosslinking of polymers. In Procedure A, [P<sub>4</sub>-VP]HCl (crosslinked with 25% DVB) was used, that the swelling of the NaNO<sub>2</sub> solution do not occurred as well as swelling the HCl solution in [P<sub>4</sub>-VP]NO<sub>2</sub> (crosslinked with 2% DVB) that used in Procedure B.

In summary, the use of crosslinked poly(4-vinylpyridinium)-supported hydrochloric acid, [P<sub>4</sub>-VP]HCl, as a solid acid and poly(4-vinylpyridine)-supported sodium nitrite, [P<sub>4</sub>-VP]NO<sub>2</sub>, as an efficient polymeric reagent for the suspended solution phase synthesis of azo chromophores has been demonstrated. Azo chromophores were obtained in high to excellent yields and high purity by simple filtration and evaporation of the solvent.

## CONCLUSION

In conclusion, we have developed an efficient and green method for synthesis of azo chromophores. With the ever increasing environmental restrictions and control on the release of effluent, the capability of this process, which provides a clean and efficient synthesis of the azo-compound, is demonstrated.

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