Diazotization–Cyanation of Aromatic Amines with Crosslinked Poly(4-vinylpyridine)-Supported Cyanide Ions

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ABSTRACT: A simple, mild, and efficient method for the cyanation of stable arenediazonium salts was developed with polymer-supported cyanide. Arenediazonium hydrogen sulfate ($Ar-N_2^+HSO_4^-$) was obtained by the reaction between a primary aryl amine and sodium nitrite in the presence of concentrated sulfuric acid (H_2SO_4) at low temperature (0–5°C). By an ion-exchange reaction between $Ar-N_2^+HSO_4^-$ and $NaBF_4$, the stable arenediazonium tetrafluoroborate, $Ar-N_2^+BF_4^-$, was prepared. $Ar-N_2^+BF_4^-$ was then converted to aryl nitrile with crosslinked poly(4-vinylpyridine) supported cyanide ion in acetonitrile at room temperature. The spent polymeric reagent was regenerated and reused several times without any loss in its activity. This procedure offered advantages, including a higher isolated yield, shorter reaction time, and simple reaction workup. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2163–2169, 2012

Key words: functionalization of polymers; macroporous polymers; modification; networks; supports

INTRODUCTION

Aromatic diazonium salts are important building blocks, not only in classical organic synthesis but also in the preparation of modern organic nanocompounds and the grafting of organic molecules onto metallic or nonmetallic surfaces.[1–6] Aromatic diazonium salts have gained attention in synthetic chemistry because of their powerful synthetic and industrial importance.[7–9] Despite wide applicability in the synthesis of compounds with a diazonium motif, diazonium salts have serious drawbacks: their intrinsic instability and explosive nature. Because of this instability, subsequent reactions with diazonium salts must be carried out in the same medium in which they were produced. This restricts many chemists from approaching potentially important transformations of these salts.[1] In a continuance of our studies on Sandmeyer-type reactions with polymeric reagents, aryl nitriles were chosen as the target compound in this work with a polymer-supported cyanide ion.

Substituted benzonitriles are an integral part of dyes, natural products, herbicides, agrochemicals, and pharmaceuticals.[10] In organic synthesis, nitriles play a crucial role as they can be easily converted into a variety of functional groups,[11] such as acids, esters, and amides. In medicinal chemistry, nitriles are very useful, as they can be transformed into a variety of biologically important structures, such as tetrazoles, triazoles, oxazoles, thiazoles, and oxazolidinones, to name just a few. For example, tetrazoles are very often used as the metabolically stable bioisosteres of carboxylic groups.[12–14]

In general, aryl nitriles are synthesized from aryl halides and stoichiometric amounts of copper(I) cyanide (Rosemmund–von Braun reaction)[15,16] on an industrial scale via the amoxidation of the corresponding toluene and its derivatives[17] or from aniline[18] via diazotization and a subsequent Sandmeyer reaction. Nickel-[19–21] and palladium-catalyzed[22–27] methods have been developed as milder alternatives to the classical Rosemmund–von Braun nitrile synthesis, but these transition-metal-catalyzed reactions take several hours. Recently, microwave heating has been proven to be very effective in accelerating the cyanation reactions.[28–33] The major problems associated with the broad application of currently known transition-metal-catalyzed cyanation reactions in high-throughput synthesis is the removal of the homogeneous palladium catalyst and dissociated ligand byproducts that add purification steps to the synthesis.

The problems associated with classical multistep synthesis in solution were overcome by a modified technique that was introduced by Merrifield in 1963.[34] This technique has been used in the production of large amount of products. However, recently,

the chemistry of functional polymers has received great attention and has become a practical method for the efficient preparation of novel chemical libraries.[35–40] Functional polymers can be used for the chemical modifications of substrates. These polymeric reagents are generally used in single-step reactions; their main advantage over nonpolymeric reagents is their insolubility in the reaction medium and, consequently, their easier workup by simple filtration. The reactions often can be driven to completion with excess amounts of reagents without fear of separation of the excess reagents from the products. The spent polymeric reagents usually can be removed quantitatively and regenerated. These reagents usually can be prepared from commercial anion-exchange resins or polymers such as crosslinked poly(4-vinylpyridine) as supports.

Although polymer-supported reagents, especially anion-exchange resins, have been widely applied in organic synthesis,[34–52] to the best of our knowledge, there has been no report on the synthesis of aryl nitriles via a dediazoniation–cyanation reaction based on polymer-supported cyanide ions. Very recently Harrison and Hodge[52] reported the synthesis of alkyl nitriles from alkyl halides with the Amberlyst A 26 CN^- form. Also, Srivastava and Collibee[53] reported polymer-supported triphenyl phosphine in a palladium-catalyzed cyanation reaction under microwave conditions. However, this polymer was used as a heterogeneous catalyst for the synthesis of aryl nitriles, and polymer-supported triphenyl phosphine acted as a ligand.

Recently, we prepared crosslinked poly(4-vinylpyridine)-supported nitrite ions and examined their application in organic transformation, such as in the synthesis of nitro alkanes from alkyl halides,[43] azo chromophores,[46,47] N-nitrosation of secondary amines,[44,45] nitration of aromatic compounds,[48,49] diazotization–iodination of aromatic amines (Sandmeyer type reaction),[50] and diazotization–azidation of aromatic amines.[51] In some of these studies, arenediazonium salts were generated in situ. In this work, we prepared arenediazonium salts, stabilized them by treatment with an aqueous solution of $NaBF_4$, and used them for the synthesis of aryl nitriles with crosslinked poly(4-vinylpyridine)-supported cyanide ion ([P₄-VP]CN; Sandmeyer-type reaction).

EXPERIMENTAL

Materials and instruments

The chemicals were either prepared in our laboratory or were purchased from Fluka (Buchs, Switzerland), Aldrich (Milwaukee, WI), or and Merck (Germany) chemical companies. Poly(4-vinylpyridine) crosslinked with 2% divinyl benzene {[P₄-VP] 2% divinyl benzene (DVB); white powder, 100–200 mesh} was purchased from Fluka. Crosslinked poly(N-methyl-4-vinylpyridinium) iodide ([P₄-VP]I) was synthesized according to our reported procedures[43–45] (Scheme 1). The progress of the reaction was monitored by thin-layer chromatography (TLC) with silica gel PolyGram SIL G/UV 254 plates. All products were characterized by comparison of their melting points, Germany, Fourier transform infrared (FTIR) spectroscopy, and ¹H-NMR spectral data with those of known samples, and all yields refer to the isolated pure products. The melting points were determined with a Buchi melting point B-540 B. V. CHI apparatus. The FTIR spectra were obtained with a Bruker Equinox (model 55), Germany, and the NMR spectra were recorded on a Bruker AC 400 Avance DPX spectrophotometer, Germany at 400 MHz in $CDCl_3$ solution.

Preparation of [P₄-VP]I and [P₄-VP]CN

Poly(4-vinylpyridine) crosslinked with 2% DVB (1.00 g) was added to a solution of methyl iodide (20 mmol, 3.24 g) in acetonitrile (10 mL), and the mixture was slowly stirred for 24 h at room temperature. The yellow quaternized polymer ([P₄-VP]I) was filtered and washed with acetone (3 × 5 mL). It was then dried in vacuo in the presence of P_2O_5 at 40°C overnight (Scheme 1, step 1).

The obtained [P₄-VP]I was added to an excess amount of an aqueous solution of CuCN/NaCN (1/2 molar ratio) and was slowly stirred for 24 h. The prepared resin, [P₄-VP]CN, was filtered off and washed with distilled water until the filtrate gave a negative test for CN^{-1} (with aqueous $AgNO_3$). It was then washed with diethyl ether (5 mL) and dried in vacuo in the presence of P_2O_5 at 40°C overnight. The capacity of CN^{-1} ion on the polymer was determined by potentiometric titration of the filtrates with a 0.1M aqueous solution of silver nitrate, and it was found to be 3.6 mmol/g of the polymer.

General procedure for preparation of stable arenediazonium salts

An aryl amine (1 mmol) was added to the mixture of concentrated sulfuric acid (H_2SO_4; 2 mmol) in water (5 mL), and the mixture was slowly stirred magnetically at 60°C for an appropriate time until the ammonium salt was formed and the aromatic amine disappeared. Then, the cooled aqueous solution of $NaNO_2$ s(2 mmol) was added stepwise, and stirring was continued until the diazonium salt was formed and the aromatic amine disappeared. The progress of the reaction was monitored by TLC [eluent: n-hexane/ethyl acetate (80/20)]. After completion of the diazotization, the cooled aqueous solution

of NaBF$_4$ (1.5 mmol) was added stepwise,; the mixture was slowly stirred at 10–15°C for 10–20 min, and the stable arenediazonium tetrafluoroborate was precipitated. The mixture was filtered and washed with about 30 mL of ice–water, 15 mL of methanol, and 30 mL of diethyl ether. The yellow solid was allowed to dry overnight. The dried stable arenediazonium tetrafluoroborate was dissolved in acetonitrile (5 mL), and 0.75 g of [P$_4$-VP]CN (3 mmol of CN^{-1}) was added (the salient of nitrogen gas was observed), and the mixture was slowly stirred magnetically at room temperature for an appropriate time, as indicated in Table II (shown later, 12–30 min). After completion of the reaction (TLC), the spent polymer was filtered and washed with acetonitrile (3 × 5 mL). The substituted benzonitrile products were obtained by filtration and evaporation of the solvent.

When further purification was needed, crystallization in ethanol or column chromatography on silica gel [eluent: acetone–petroleum ether (1 : 9)] was applied, and a highly pure product was obtained. When the product was liquid, the reaction mixture was extracted with diethyl ether (3 × 8 mL) and after the organic layer (with MgSO$_4$) was dried and the solvent was evaporated, a highly pure product was obtained (Table II, shown later, entries 1, 11, and 14).
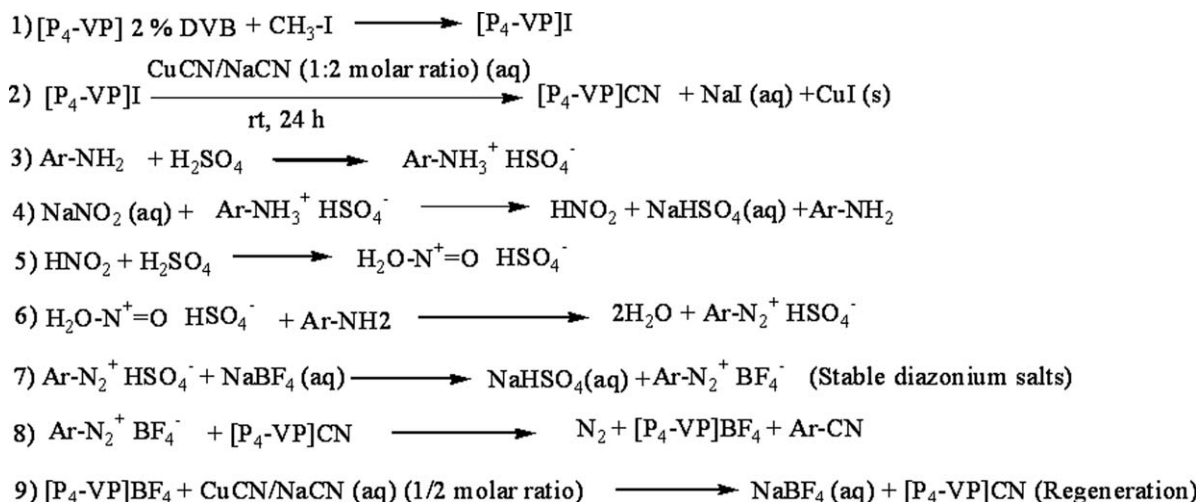
Regeneration of [P$_4$-VP]CN

The spent cream-colored polymer, [P$_4$-VP]BF$_4$ (1.00 g) was treated with an excess aqueous solution of CuCN/NaCN (molar ratio = 1/2) and stirred for 24 h at room temperature. The mixture was filtered and washed several times with distilled water and dried *in vacuo* in the presence of P$_2$O$_5$ at 40°C overnight

(Scheme 1, step 7). The capacity of CN^{-1} on the polymer was found to be 3.6 mmol/g of polymer (the same capacity as the original form). The regenerated polymer could be reused several times without any loss in its activity. The uses of the [P$_4$-VP]CN that was recycled for the third time are given in Table II (shown later, entries 3–5).

RESULTS AND DISCUSSION

In this article, we report the first procedure for the direct diazotization–cyanation of aryl amines with crosslinked [P$_4$-VP]CN, which we prepared as described in the Experimental section via the reaction of [P$_4$-VP]I with CuCN/NaCN (1/2 molar ratio). In this study, we used [P$_4$-VP]CN for the synthesis of aryl nitriles from stable arenediazonium tetrafluoroborates. Arenediazonium hydrogen sulfate (Ar—N$_2$$^+HSO_4$$^-$) was prepared by the reaction of a primary aromatic amine with sodium nitrite in the presence of concentrated H$_2$SO$_4$. By an exchange reaction between Ar—N$_2$$^+HSO_4$$^-$ and NaBF$_4$, stable arenediazonium tetrafluoroborates were obtained, and consequently, dediazoniation–cyanation occurred with [P$_4$-VP]CN. It is important to note that this polymeric reagent was stable and could be stored for a long time (months) without losing its activity; it could be readily used for the diazotization–cyanation of anilines. [P$_4$-VP]I was recently prepared and used for the preparation of other functionalized polymers, including polymer-supported thiocyanate, polymer-supported carboxylate, polymer-supported potassium ferrate, polymer-supported azide ion,[51] and polymer-supported nitrite ion.[46–50] Although [P$_4$-VP]I is well known, [P$_4$-VP]CN was used the first procedure for the direct diazotization–cyanation of aryl amines, and on the basis of our knowledge,

1) [P$_4$-VP] 2 % DVB + CH$_3$-I $\longrightarrow$ [P$_4$-VP]I

2) [P$_4$-VP]I $\xrightarrow[\text{rt, 24 h}]{\text{CuCN/NaCN (1:2 molar ratio) (aq)}}$ [P$_4$-VP]CN + NaI (aq) + CuI (s)

3) Ar-NH$_2$ + H$_2$SO$_4$ $\longrightarrow$ Ar-NH$_3$$^+$ HSO$_4$$^-$

4) NaNO$_2$ (aq) + Ar-NH$_3$$^+$ HSO$_4$$^-$ $\longrightarrow$ HNO$_2$ + NaHSO$_4$(aq) + Ar-NH$_2$

5) HNO$_2$ + H$_2$SO$_4$ $\longrightarrow$ H$_2$O-N$^+$=O HSO$_4$$^-$

6) H$_2$O-N$^+$=O HSO$_4$$^-$ + Ar-NH2 $\longrightarrow$ 2H$_2$O + Ar-N$_2$$^+$ HSO$_4$$^-$

7) Ar-N$_2$$^+HSO_4$$^-$ + NaBF$_4$ (aq) $\longrightarrow$ NaHSO$_4$(aq) + Ar-N$_2$$^+$ BF$_4$$^-$ (Stable diazonium salts)

8) Ar-N$_2$$^+$ BF$_4$$^-$ + [P$_4$-VP]CN $\longrightarrow$ N$_2$ + [P$_4$-VP]BF$_4$ + Ar-CN

9) [P$_4$-VP]BF$_4$ + CuCN/NaCN (aq) (1/2 molar ratio) $\longrightarrow$ NaBF$_4$ (aq) + [P$_4$-VP]CN (Regeneration)

Scheme 1 Preparation of the [P$_4$-VP]CN reaction pathway of the diazotization–cyanation of the aromatic amines and regeneration of the polymer.
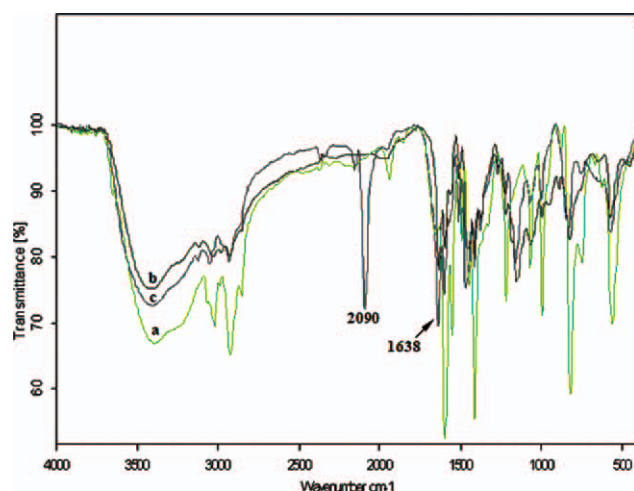
Figure 1 FTIR spectra of (a) [P$_4$-VP] 2% DVB, (b) [P$_4$-VP]I, and (c) [P$_4$-VP]CN. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE I
Optimization of the Reaction Conditions for the Dediazoniation–Cyanation of *p*-Nitrobenzene Diazonium Tetrafluoroborate (Obtained from 2 mmol of *p*-Nitroaniline) with [P$_4$-VP]CN[a]

Entry	Solvent	[P$_4$-VP]CN (mmol of CN$^-$)	Isolated yield (%)
1	H$_2$O	1	0.0[b]
2	Ethanol	1	0.0[b]
3	Acetone	1	45
4	Acetonitrile	1	65
5	Acetonitrile	1.5	76
6	Acetonitrile	2	85
7	Acetonitrile	3	95
8	Acetonitrile	3.5	95

[a] The reactions were performed at room temperature for 30 min.
[b] Probably, the decomposition of diazonium salt took place, byproducts were observed before the [P$_4$-VP]CN was added, and no nitrile compound was detected.

there has been no report in the literature on the synthesis of aryl nitriles based on polymer-supported cyanide ion. Hence, in this work, the preparation of aryl nitriles from primary aromatic amines is described. To ensure the presence of CN^{-1} ions on the polymer, the concentration of the iodide ions in the filtrates was determined by potentiometric titration of the filtrates with a 0.1M aqueous solution of silver nitrate. Then, the capacity of CN^{-1} ions on the polymer was determined on the basis of the concentration of the iodide ion, and it was found to be 3.6 mmol of CN^{-1} ion/g of polymer.

On the other hand, the FTIR spectra of [P$_4$-VP] 2% DVB, [P$_4$-VP]I, and [P$_4$-VP]CN are shown in Figure 1. As shown in Figure 1(c), the appearance of a peak at 2090 cm^{-1} indicated that the CN^{-1} was supported on the polymer.
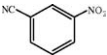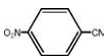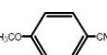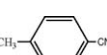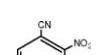
To increase the yields of nitrile compounds, the optimization of the reaction conditions was accomplished. 4-Nitroaniline (2 mmol) was chosen as a model substrate and was converted to 4-nitrophenyl diazonium tetrafluoroborate according to a previously reported method in the literature[54] with NaNO$_2$ (2 mmol)/H$_2$SO$_4$ (2 mmol)/NaBF$_4$ (1.5

TABLE II
Diazotization–Cyanation of the Aromatic Amines by NaNO$_2$/H$_2$SO$_4$/NaBF$_4$ in Water at 0–5°C and then with [P$_4$-VP]CN in Acetonitrile at Room Temperature

Entry	Ar—NH$_2$	Ar—CN	Diazotization/cyanation time (min)	Isolated yield (%)	mp/Literature mp (°C)[57]
1	Ph-NH$_2$	Ph-CN	20/15	65	Oil/Oil
2	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	10/15	95	145/144–147
3	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	10/15[a]	95	145/144–147
4	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	10/15[a]	92	145/144–147
5	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	10/15[a]	90	145/144–147
6	3-NO$_2$C$_6$H$_4$NH$_2$	3-NO$_2$C$_6$H$_4$CN	15/20	89	113/114–116
7	2-NO$_2$C$_6$H$_4$NH$_2$	2-NO$_2$C$_6$H$_4$CN	20/25	87	107/107–109
8	4-NCC$_6$H$_4$NH$_2$	4-NCC$_6$H$_4$CN	10/12	96	125/124–128
9	4-IC$_6$H$_4$NH$_2$	4-IC$_6$H$_4$CN	10/15	93	224/221–225
10	2-IC$_6$H$_4$NH$_2$	2-IC$_6$H$_4$CN	20/20	85	Oil/Oil
11	4-BrC$_6$H$_4$NH$_2$	4-BrC$_6$H$_4$CN	15/15	94	111/110–115
12	4-ClC$_6$H$_4$NH$_2$	4-ClC$_6$H$_4$CN	15/25	78	92/90–93
13	4-MeC$_6$H$_4$NH$_2$	4-MeC$_6$H$_4$CN	15/30	81	Oil/Oil
14	2-BrC$_6$H$_4$NH$_2$	2-BrC$_6$H$_4$CN	20/20	75	55/53–57
15	4-PhOC$_6$H$_4$NH$_2$	4-PhOCC$_6$H$_4$CN	20/15	91	45/42–46
16	4-MeOC$_6$H$_4$NH$_2$	4-MeOC$_6$H$_4$CN	10/18	90	58/57–59
17	4-MeCOC$_6$H$_4$NH$_2$	4-MeCOC$_6$H$_4$CN	10/15	93	58/56–59
18	3-NH$_2$C$_6$H$_4$CN	3-CNC$_6$H$_4$CN	15/15	92	160/163–165
19	2-NH$_2$C$_6$H$_4$CO$_2$H	2-CNC$_6$H$_4$CO$_2$H	15/25	92	213/212

[a] Entries 3–5 refer to the use of [P$_4$-VP]CN that was recycled a first, second, and third time, respectively, under identical conditions.

TABLE III
Characteristic Spectral Data of Some Aryl Nitrile Products

Entry	Product	ν_{max} (cm^{-1})	^{1}H-NMR δ (ppm)
1	Cl—C$_6$H$_4$—CN	3078 (C—H, ArH); 2218 (CN); 1592 (C=C); 1473 (C=C); 1318, 1089, 1015, 825, 779, 663	7.473 (d, 2H, J = 8.4 Hz), 7.609 (d, 2H, J = 8.4 Hz)
2	Br—C$_6$H$_4$—CN	3094 (C—H, ArH); 2225 (CN); 1593 (C=C); 1484 (C=C); 1399, 1087, 1017, 827, 780, 663	7.534 (d, 2H, J = 8.4 Hz), 7.643 (d, 2H, J = 8.4 Hz)
3	NC—C$_6$H$_4$—NO$_2$	3081 (C—H, ArH); 2237 (CN); 1618 (C=C); 1551 (NO$_2$); 1351 (NO$_2$); 1475, 1305, 1202, 1102, 1081, 922, 904, 817, 787, 734, 669, 617	7.759 (t, 1H, J = 8 Hz), 8.011 (d, 1H, J = 7.6 Hz), 8.490 (d, 1H, J = 7.6 Hz), 8.540 (s, 1H)
4	O$_2$N—C$_6$H$_4$—CN	3108 (C—H, ArH); 2234 (CN); 1600 (C=C); 1522 (NO$_2$); 1406 (C=C); 1345 (NO$_2$); 1316, 1294, 1107, 1016, 858, 747, 735, 682, 641	7.905 (d, 2H, J = 8.4 Hz), 8.370 (d, 2H, J = 8.4 Hz)
5	H$_3$CO—C$_6$H$_4$—CN	3045 (C—H, ArH); 2216 (CN); 1603 (C=C); 1507 (C=C); 1303, 1255 (C—O); 1173 (C—O); 1021, 828, 682	3.872 (s, 3H, OCH$_3$), 6.952 (d, 2H, J = 8.4 Hz), 7.589 (d, 2H, J = 8.4 Hz)
6	CH$_3$—C$_6$H$_4$—CN	3090 (C—H, ArH); 2984 (C—H, aliphatic); 2228 (CN); 1608, 1537, 1509 (C=C); 1354, 1178, 815, 735, 669	2.381 (s, 3H, CH$_3$), 7.230 (d, 2H, J = 8 Hz), 7.48 (d, 1H, J = 8 Hz)
7	C$_6$H$_4$(CN)(NO$_2$)	3080 (C—H, ArH), 2235 (CN), 1617 (C=C), 1530 (NO$_2$), 1353 (NO$_2$), 1011, 922, 817, 788, 734, 668	7.846–7.862 (m, 2H), 7.947 (d, 1H), 8.358 (t, 1H)

J is the coupling constant in NMR and is known for chemists.

mmol) in water at 0–5°C. For optimization of the reaction conditions, the dediazoniation–cyanation of 4-nitrophenyl diazonium tetrafluoroborate was performed with different molar ratios of 4-NO$_2$—C$_6$H$_4$—N$_2^+$BF$_4^-$/[P$_4$-VP]CN and in different solvents, and the results are summarized in Table I. It was observed that a molar ratio of 2/3 and an aprotic solvent (acetonitrile) at room temperature were the optimal reaction conditions and gave the highest yield of the product (Table I).

After realization of the successful cyanation of 4-nitrophenyl diazonium tetrafluoroborate, the diazotization–cyanation reactions were investigated under mild and completely heterogeneous conditions at room temperature, and the results are summarized in Table II. This new, simple method can be successfully applied to the synthesis of a wide range of aryl nitriles, starting from the corresponding aryl amines. Various primary aromatic amines, with electron-withdrawing groups and electron-donating groups, were transformed into aromatic nitriles in good to

excellent yields and in very short reaction times (Table II). Although in our previously study of the diazotization–iodination of aniline, even after 100 min, no iodo product was separated, in this study, benzonitrile was obtained at good yield (65%) after 15 min, probably because of the higher nucleophilicity of CN^{-1} compared to I$^-$. On the other hand, the higher nucleophilicity of CN^{-1} rendered both shorter reaction times and a decreasing amount of polymer that was needed for these transformations. In the conversion of aryl amines to the corresponding aryl nitriles, a 3/2 molar ratio of [P$_4$-VP]CN to amine was needed, although in the conversion of aryl amines to the corresponding aryl iodide, a 3/1 molar ratio of [P$_4$-VP]I to amine was needed (Table II).[50]

All the prepared aryl nitriles were known compounds, and the products' structures were confirmed by comparison of the TLC, melting points (Table II, column 6), and FTIR spectra, and in some cases, comparison of the ^{1}H-NMR spectra with those

TABLE IV
Comparison of the Reaction Times and Isolated Yields of Some Obtained Products from Our Method with Those of a Reported Classical Method[55]

Entry	Ar—NH$_2$	Ar—CN	Total reaction time of diazotization and cyanation (min)	Isolated yield (%)
1	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	120	93
2	4-NO$_2$C$_6$H$_4$NH$_2$	4-NO$_2$C$_6$H$_4$CN	25	95
3	4-MeCOC$_6$H$_4$NH$_2$	4-MeCOC$_6$H$_4$CN	120	88
4	4-MeCOC$_6$H$_4$NH$_2$	4-MeCOC$_6$H$_4$CN	25	93
5	4-MeC$_6$H$_4$NH$_2$	4-MeC$_6$H$_4$CN	120	66
6	4-MeC$_6$H$_4$NH$_2$	4-MeC$_6$H$_4$CN	45	81
7	4-MeOC$_6$H$_4$NH$_2$	4-MeOC$_6$H$_4$CN	120	52
8	4-MeOC$_6$H$_4$NH$_2$	4-MeOC$_6$H$_4$CN	28	90

of an authentic specimen. The appearance of a characteristic peak at 2216–2235 cm^{-1} (CN stretching) in the FTIR spectra indicated the formation of the corresponding nitrile products. The FTIR and ^{1}H-NMR spectral data of some prepared nitriles are given in Table III.

We also successfully applied this new method on a nearly large scale. For example, up to 15 mmol of *p*-nitroaniline (Table II, entry 2) could be converted into 4-nitrobenzonitrile without any loss of efficiency. In this method, the reaction time was almost shorter than that of the previously reported classical method for the diazotization–cyanation of aromatic amines.[55] This was probably due to the high local concentration of cyanide ion species inside the pores.

The preparation of [P$_4$-VP]CN, the reaction pathway of the diazotization–cyanation of the aromatic amines, and the regeneration of the polymer are shown in Scheme 1.

In Table IV, the reaction times and isolated yields of some obtained products from this method are compared with those of the reported classical method.[55] As shown in Table IV, in this procedure (entries 2, 4, 6, and 8), the isolated yields of the products were higher and the corresponding reaction times were shorter than in the classical method. This was probably due to the high local concentration of cyanide ion species inside the pores.

The advantages of this method over the conventional classical method for the conversion of arenediazonium tetrafluoroborates include mild reaction conditions, safe handling, and mildness of the polymeric cyanating reagent, high isolated yield, shorter reaction time, and very simple workup. In addition, there is current research and general interest in heterogeneous systems because these systems are important in industry and developing technologies.[56]

CONCLUSIONS

This research demonstrates the synthesis of aromatic nitriles from various aniline derivatives via a polymer-supported cyanide ion and the stable arenediazonium tetrafluoroborates. This method has the advantages of operational simplicity, mild reaction conditions, ready availability, fast reaction rates, and simple reaction workup.

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