



Synthesis of a nitrite functionalized star-like poly ionic compound as a highly efficient nitrosonium source and catalyst for the diazotization of anilines and subsequent facile synthesis of azo dyes under solvent-free conditions



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ABSTRACT

Nitrite functionalized star-like poly ionic (NFSPi) compound was synthesized and used as a highly efficient nitrosonium source and catalyst for the conversion of aniline derivatives to diazonium salts. Azo dyes were prepared via in situ azo-coupling reaction of these diazoniums with active aromatic compounds under solvent-free conditions in very short reaction time in excellent yields. NFSPi plays dual role as a three-dimensional nitrosonium source and catalyst because of its poly ionic characteristic. The isolated products were confirmed with FT-IR spectrum, ¹H-NMR, ¹³C-NMR spectroscopy and CHNSO analysis. The structure of heterogeneous reagent and catalyst was confirmed by FT-IR spectrum, SEM images, EDX and CHNSO analysis. Yields and reaction times for the synthesis of a variety of products via this procedure were compared with reported values in literature.

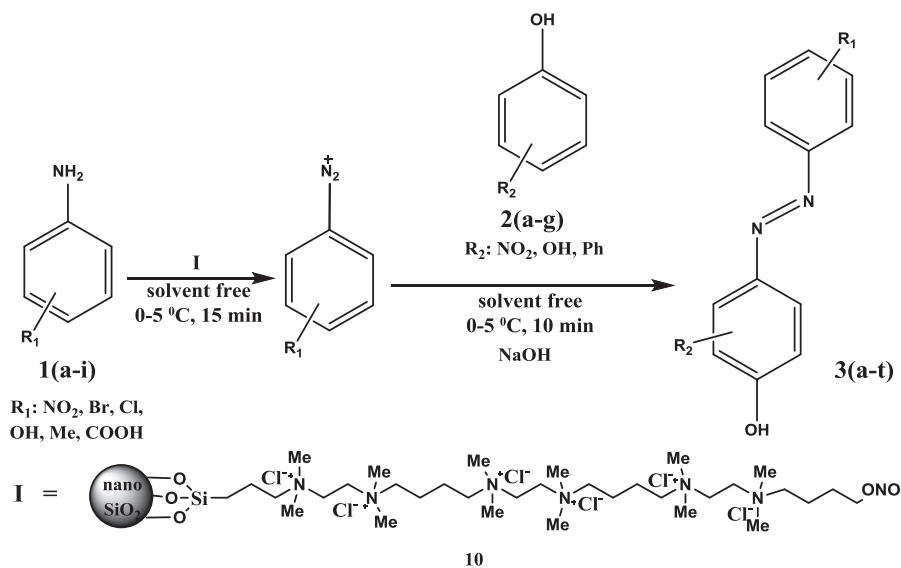
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1. Introduction

Aromatic azo compounds are very important chemical materials because of their widely applications in industry as dyes and pigments [1], therapeutic agents [2] and drug deliveries [3]. Diazonium salts have been frequently used for the preparation of synthetic azo dyes [4]. Many reports have been published for diazotization and also for azo-coupling reactions in literature [5–7]. However, many of these reported methods suffer from one or more practical drawbacks associated with hazardous reagents, long reaction times, less effective catalysts, formation of side products and difficult and time consumed work-up procedure. To eliminate of some of these explained limitations, in the present research we utilize a poly ionic heterogonous nitrosonium source which plays the dual role as reagent and catalyst. The easy work-up procedure, very short reaction times and also high yields of the products were achieved by using of this reagent.

Having the unique behavior of organic-inorganic composites, there are a lot of interests in developing of the synthesis and applications of new structures of these compounds [8]. Recently, a lot of attentions have been paid to the construction of three-dimensional molecules such as star-like polymers due to their importance in drug-delivery [9], catalysis [10], etc. Liu et al. have been reported the preparation of a three-dimensional star-like polymer that was prepared via connection of linear polymers to a central reactive core [11]. The most of reported star-like polymers are on the base of organic materials which are unstable, toxic, and non-ionic compounds [12]. According to the some interesting characteristics of ionic liquids, synthesis of three-dimensional star-like compounds based on ionic liquids could play an important role in synthetic organic chemistry. In continuation of our work on the using of nitrite ionic liquid immobilized on silica for the diazotization of aniline derivatives [13], herein we introduced a new rapid and efficient method for this reaction and subsequent synthesis of azo dyes. In this study, NFSPi compound was used as a new nitrosonium source and catalyst for the efficient diazotization of aniline derivatives and synthesis of azo dyes under solvent free conditions (Scheme 1).

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Scheme 1. Diazotization of anilines using NFSPI and subsequent synthesis of azo dyes.

2. Experimental

2.1. Materials and instrumentation

All reagents purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr and determined on a Perkin Elmer FT-IR spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance AC-400 MHz using $\text{DMSO}-d_6$ or CDCl_3 as the deuterated solvent and TMS as internal standard. All melting point measured in open glass-capillaries using a Stuart melting point apparatus. The morphology of the catalyst was studied by field emission scanning electron microscopy using FESEM; Hitachi, model S-4160. Structure of catalyst was confirmed by energy-dispersive X-ray analysis using EDX; Tescan; model MIRA3FEG-SEM and elemental analysis was determined by CHNSO; Euro EA; model EA3000.

2.2. Synthesis of silica nanoparticles

Ammonia solution 25% (750 μL , 10 mmol) and water (1.98 mL) were poured in a 250 mL round bottom flask containing absolute methanol (100 mL). While stirring of the solution, tetraethoxysilane, TEOS (11 ml, 50 mmol) was added slowly. The solution was stirred for 3 day at ambient temperature. The silica nano particles was isolated and confirmed by scanning electron microscopy image. FT-IR (KBr, cm^{-1}): 3456 (Si–OH), 1639 (O–H), 1097 and 803 (Si–O).

2.3. Synthesis of star-like poly ionic compound **8**

N,N,N',N' -Tetramethylethylenediamine (11 mmol) was added to a round bottom flask containing acetonitrile (10 mL). While stirring, (3-chloropropyl)trimethoxysilane (10 mmol) was poured into the solution dropwise. Then, the solution was stirred for 3 day at 80 °C to produce ionic liquid **6**. The unreacted materials were washed by acetonitrile. The resulted ionic liquid **6** and silica nanoparticles were refluxed in acetonitrile for 3 day at 60 °C. The acetonitrile was removed under reduced pressure at 40 °C to produce crude product **7**. Isolated yield was 90%. FT-IR (KBr, cm^{-1}): 3451 (Si–OH), 2956 (C–H), 1637, 1486 (C–H), 1090 (SiO–H), 800 (Si–O). EDX: Calcd. (%w):

N/C = 0.259; Found (%): C, 16.93; N, 4.37; H, 3.92; %w N/C = 0.258. CHNSO: Calcd. (%w): N/C = 0.259; Found (%): C, 16.93; N, 4.37; H, 3.92; N/C = 0.258. Then, 1,4-dichlorobutane (10 mmol) and product **7** were added to acetonitrile (15 mL) and mixed thoroughly. The mixture was refluxed at 80 °C for three days. Then the mixture was poured in acetonitrile and stirred thoroughly and unreacted reagents were removed by centrifuging. After this, the product was reacted with diamine and then with 1,4-dichlorobutane under the above described conditions to produce the product **8**. The morphology and structure of the product was confirmed and identified by scanning electron microscopy FE-SEM, FT-IR spectroscopy, EDX, and CHNSO analysis. FT-IR (KBr, cm^{-1}): 3442 (Si–OH), 2958 (C–H), 1638, 1486 (C–H), 1093 (SiO–H), 800 (Si–O). EDX: Calcd. (%w): N/C = 0.246. CHNSO: Calcd. N/C (%w) = 0.241; Found (%): C, 17.76; N, 4.37; H, 4.24, N/C = 0.246.

2.4. Synthesis of hydroxyl functionalized star-like poly ionic compound **9**

4-Chlorobutanol (10 mmol) was added into a solution of compound **8** in acetonitrile while stirring and the mixture was refluxed for 3 day at 80 °C. Hydroxyl functionalized star-like poly ionic product **9** was isolated as the same work-up procedure which described for the compound **8**. The structure of product was confirmed by comparison of FT-IR spectroscopy of compounds **8** and **9** (Fig. 2B). FT-IR (KBr, cm^{-1}): 3420 (O–H), 2958 (C–H), 1636 (O–H), 1482 (C–H), 1402 (bending O–H), 1087 (Si–O), 951 (Si–OH), 801 (Si–O).

2.5. Synthesis of NFSPI compound **10**

Freshly prepared compound **9** (10 g) was added to an aqueous solution of sodium nitrite (15 ml). HCl (37%, 3 mL) was added slowly to the mixture while stirring at 0–5 °C. The mixture was filtered off and washed with cold water (20 mL) and the crude product **10** was dried under vacuum at room temperature. Functional group conversion was confirmed by comparison of the FT-IR spectra of compounds **9** and **10** (Fig. 2B). FT-IR (KBr, cm^{-1}): 3440 (SiO–H), 2958 (C–H), 1637 (O–H), 1483 (C–H), 1384 (N=O), 1090 (Si–O), 952 (Si–OH), 801 (Si–O).

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