Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Active immobilized palladium catalyst based on multiporous amphiphilic graft copolymer

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ARTICLE INFO

Article history: Received 19 May 2011 Received in revised form 12 July 2011 Accepted 14 July 2011 Available online 21 July 2011

Keywords: Graft copolymer Porosimetry Multiporous material Pd-nano particle Suzuki coupling

ABSTRACT

Poly(vinylidene fluoride)-g-poly(dimethylaminoethyl methacrylate) (PVDF-g-PDMAEMA)/camphor system produces thermoreversible gel and leaching of camphor with cyclohexane yields amphiphilic multiporous material characterized from scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and nitrogen adsorption porosimetry. Pd nanoparticles (Pd NPs, dia. 2.5–4.5 nm) are grown on this porous material by adsorption of $Pd(OAc)_2$ followed by reduction with hydrazine. MIP and nitrogen porosimetry show that the xerogels are multiporous in nature and the pore size decreases in the Pd NPs captured sample. The BET surface area of the Pd NPs captured dried gel (24.3 m² g⁻¹) is lower than that of pure gel (32.5 m² g⁻¹) due to the blocking of some pores by Pd NPs. The Pd NPs captured amphiphilic porous PVDF-g-PDMAEMA act as an effective catalyst for aerobic ligand free Suzuki coupling of aryl halides (X = I, Br and CI) in aqueous medium.

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1. Introduction

Porous materials have attracted widespread attention because of their increased potential application in heterogeneous catalysis [1-6], super adsorbents [7,8], optoelectronic devices [9,10], ultra low dielectric materials [11,12], sensors [13-15], sorption processes [16-18], size selective separation [19-21], hosts for synthesis of nano-objects [22], tissue engineering [23,24], photonics [25], drug delivery [26–28], medical diagnosis [29], etc. For specific uses porous materials of particular pore diameters and chemical characteristics are required. According to IUPAC convention, they are classified as micro, meso, and macro having diameter <2 nm, between 2-50 nm and >50 nm, respectively [5,30]. The presence of all types of pores in the same material is referred as multiporous materials [31-36], having applications in the field of catalysis, chromatography, drug release, separation of large molecules, purification and recycling of municipal and industrial waste water, etc. [30,31,35,36].

In the literature, there are some reports of inorganic multiporous materials [31,35,37–39]; however, the polymeric multiporous materials are very few [32–34,40]. Again, the multiporous polymeric materials are mainly based on hydrophobic polymers, causing fouling due to the interaction of organics in the feed water with the typically hydrophobic pore surface [41]. But the fouling property arising from the hydrophobic one. However, low mechanical property,

poor thermal stability and high susceptibility towards chemicals are the causes of limitation for their application [41a] as a porous support of catalysts. So, multiporous materials with hydrophobic bulk and hydrophilic pore would be an ideal choice for the support of a catalyst. The multiporous materials find great application in heterogeneous catalysis as micro- and mesopores provide the size and shape selectivity for the guest molecules, and the macroporous channels permit improved access to active sites avoiding pore blocking by reagents or products.

We have chosen poly(vinylidene fluoride) (PVDF) as hydrophobic bulk material for its significant piezo and pyroelectric properties [42], good biocompatibility [43], excellent chemical resistivity, and good thermal stability [44]. One main strategy to modify PVDF surface is by grafting hydrophilic polymer to prepare amphiphilic PVDF [41,45,46] using atom transfer radical polymerization (ATRP) for its robust nature [47]. Recently, we have used solution based method to graft N,N-dimethylaminoethyl methacrylate (DMAEMA) by ATRP technique (Scheme 1) [48]. One strategy of preparing multiporous polymeric materials is making thermoreversible gels followed by careful drying while keeping the polymeric network intact [32,33,40]. Since PVDF produces thermoreversible gel with various >C=O containing organic gelators through the polymer-solvent complex formation from the interaction between >CF2 of PVDF and >C=O group of gelator [49,50a], it is also expected that PVDF-g-PDMAEMA(P-g-D), would form thermoreversible gel with camphor, (1,7,7-trimethylbicyclo[2,2,1]heptane-2-one), a bicyclic volatile solid gelator for PVDF. After removal of camphor in a proper way, multiporous polymeric materials with PVDF backbone and hydrophilic pore surface would be expected.





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^{1381-5148/\$ -} see front matter @ 2011 Elsevier Ltd. All rights reserved. doi:10.1016/j.reactfunctpolym.2011.07.006



Heterogeneous catalysis using multiporous polymeric materials is very uncommon, and recently, we have prepared palladium nanoparticles (Pd NPs) supported fibrillar network of porous β-PVDF from the novel gel nanocomposite route for efficient heterogeneous catalytic oxidation and reduction reactions [51]. However, during the cross-coupling of aryl-halides and aryl-boronic acids (Suzuki coupling), the catalyst fails. The poor dispersion of the catalyst in water and low catalytic activity towards aryl-bromides and chlorides due to hydrophobicity of PVDF and absence of any ligand may be the causes of above failure [52a]. We propose that in amphiphilic multiporous polymeric material with suitable functional group, the catalytic activity of a Pd-heterogeneous catalyst towards Suzuki coupling is expected to be very high in water, even in absence of external ligands. The presence of functional group(s) present in PDMAEMA part may bind and stabilize the reactive palladium species [52b], avoiding agglomeration or leaching through out the reaction in water and thus helping in Suzuki coupling of aryl halides. Among the other Pd catalyzed reactions, Suzuki coupling is the most easy and fundamental method in organic chemistry for the synthesis of pharmaceutically important bi-aryl derivatives which are the main components of biologically active and functional molecules [53a,b]. It promotes us to choose Suzuki coupling reaction to test the performance of the Pd NP catalyst embedded on amphiphilic porous polymer support.

Although a number of solid materials have been employed as supports for palladium heterogeneous catalysts in the coupling reactions of aryl bromides or iodides [53–57]; only a very limited number of such palladium catalysts have been reported for coupling reactions with aryl chlorides [58–61]. This may be due to the fact that, the activation of C—Cl bond is much difficult than C—Br and C—I bonds, and in general requires drastic reaction conditions like very high temperature, tailored ligands, hazardous organic solvents, etc. To our knowledge, there are no reports of using amphiphilic multiporous polymeric materials as solid supports for Pd NPs in Suzuki coupling. There are some reports [56b–d] discussing the advantage of Pd nanoparticles (NPs) on catalysis over usual Pd catalysts. Particularly, the Pd NPs show enhanced catalytic efficiency over the bulk Pd material due to their better electron transfer ability during coupling reactions and large surface-to-volume ratio [56b-d]. The use of palladium complexes such as pincer complexes [57b] or phosphine-based complexes [57c] in catalysis is also reported in the literature although a strong and toxic chelating agent and highly non-aqueous medium is required due to their moisture sensitivity and so harmful for environment. In addition they are difficult to recycle. Thus ligand free, aqueous mediated coupling reaction catalyzed by recyclable porous polymer-capped-Pd NPs is a green method, fruitful from both environmental as well as economical points of view. Here we report amphiphilic multiporous polymeric materials prepared from P-g-D graft co-polymer using camphor as a solid gelator followed by leaching with cyclohexane. The presence of DMAEMA causes the material to be well dispersed and high binding capability with Pd²⁺ in water. Finally, a use of this Pd NPs embedded amphiphilic multiporous material as an efficient heterogeneous catalyst for aerobic ligand free Suzuki coupling of aryl halides (X = I, Br and Cl) in aqueous medium is demonstrated. The catalyst not only activates aryl iodides at 30 °C and aryl bromides at 100 °C in absence of cetyl trimethyl ammonium bromide, CTAB (and at 30 °C in presence of CTAB) but also activates aryl chlorides at 100 °C in presence of CTAB in water.

2. Experimental section

2.1. Materials

PVDF (Aldrich, USA, $\overline{M}_n = 7.0 \times 10^4$, polydispersity index 2.57, head to head (H–H) defect = 4.33 mol%) was purified by recrystallization from its 0.2% (w/w) solution of acetopheone. The monomer DMAEMA (Acros Organics, New Jersey, USA) was purified by passing through basic alumina column. *N*-methyl-2-pyrrolidone (NMP) (Loba Chemicals, Mumbai) was distilled and stored in argon atmosphere. 4,4'-dimethyl-2,2'-dipyridyl (DMDP, Aldrich, USA) was used as received. CuCl (Aldrich) was purified by washing with 10% HCl in water followed by methanol and diethyl ether in a Schlenk tube under a nitrogen atmosphere. DL-camphor (S.D. Fine Chem Ltd., Mumbai) was purified by a sublimation procedure. Palladium acetate [Pd(OAc)₂], aryl halides and boronic acids (Aldrich) were used as received without further purification.

2.2. Preparation of PVDF-g-PDMAEMA graft co-polymer

A nitrogen purged reaction vessel containing 20% (w/v) NMP solution of PVDF, DMDP and CuCl were added. The mole ratio of PVDF, DMDP and CuCl was 0.07:3.2:1. The monomer DMAEMA (volume ratio of NMP and DMAEMA 1.25:1) was next introduced into the tube followed by nitrogen purging for 15 min after which the tube was closed with a rubber septum. The tube was then placed in an oil bath (90 °C) with constant stirring. After 24 h, the content of the tube was diluted with small amount of NMP and poured into excess pet ether (60–80 °C). The separated polymer was isolated, re-dissolved in NMP and precipitated into pet ether. The polymer was then washed repeatedly with double distilled water followed by drying in vacuum at room temperature The average graft length of the graft copolymer is 30 monomer unit, graft density (i.e., grafting sites per PVDF chain) = 15.6. The molecular weight of the graft copolymer is 142,000 [48].

2.3. Preparation of multiporous material

The multiporous material was prepared in a two step processes.

2.3.1. Gelation

The amphiphilic P-g-D graft co-polymer and camphor with appropriate amounts were taken in a thick-walled glass tube and was sealed. The sample in the sealed tube was then melted at 195 °C in an oil bath for 20 min with intermittent shaking using a rotor (Remi, Cyclo-Mixer) to make transparent homogeneous solution followed by quenching to 30 °C to form the gel.

2.3.2. Drying of gel

The P-g-D/camphor gel is kept immersed in cyclohexane for 8–10 days to replace camphor by cyclohexane. To drive the above replacement process quickly, the cyclohexane was replaced by a fresh batch after every 12 h. After total extraction of camphor, it was first dried in air and finally in vacuum at 30 °C for 3 days.

2.4. Immobilization of Pd NPs

In a 50 ml flask 20 mg Pd(OAc)₂ and 15 ml double distilled water were taken with nitrogen purging for 30 min and then the flask was closed with a rubber septum, followed by sonication in a ultrasonic bath (60 W, model AVIOC, Eyela) for 2 h and stirring overnight in dark. 1 g of amphiphilic multiporous P-g-D polymer was then added and stirring is continued in dark in nitrogen atmosphere. After 24 h, the polymer was separated, washed with double distilled water (10 times) and the total filtrate thus obtained was used for Atomic Absorption Spectroscopy (AAS) study for indirect calculation of $Pd(OAc)_2$ bound by porous polymer. The $Pd(OAc)_2$ bound polymer is then dispersed in 50 ml distilled water, 2 ml of hydrazine was added followed by stirring at 50 °C for 2 h. The color of the porous polymer turned into brownish-black, indicating the formation of Pd NPs. After 2 h, the polymer was separated out, washed with double distilled water for 10 times and the total filtrate thus obtained was boiled with concentrated HNO₃ and used again for AAS study, no Pd was detected in the filtrate. The Pd NPs embedded porous materials was finally dried in vacuum at 30 °C for 3 days for further catalytic applications.

2.5. Spectral characterization

2.5.1. UV-vis

The UV-vis spectra of aqueous dispersion of the multiporous P-g-D material, $Pd(OAc)_2$ bound porous material and Pd NPs embedded porous material were taken from 190 to 1100 nm in

1 cm quartz cell using a UV-vis spectrophotometer (H.P, model 8453).

2.5.2. FT-IR

The FTIR spectra of the PD/camphor gel and different porous materials are obtained from a Shimadzu FT-IR (model 8400S) instrument. The sample was mixed with solid KBr and pellets were used to scan the sample.

2.5.3. AAS

Atomic Absorption Spectroscopic (AAS) measurements were carried out by using a Shimadzu AA-6300 AAS spectrometer fitted with a double beam monochromator.

2.6. Wide-angle X-ray scattering (WAXS)

The wide-angle X-ray diffraction experiments of the gel and different porous materials were performed with a Bruker AXS D8 Advanced diffractometer using Cu K α (λ = 0.15406 nm) radiation. The instrument was calibrated with a standard silicon sample. The samples were scanned from $2\theta = 2^{\circ}-37^{\circ}$ at the step scan mode (step size 0.03°, preset time 2 s), and the diffraction pattern was recorded using a scintillation counter detector.

2.7. Microscopy

(i) The morphology of the P-g-D/camphor systems was studied from a thin portion of the dried gels after platinum coating in a field emission scanning electron microscope (FESEM; JEOL, JSM-6700F). (ii) For TEM study, a drop of aqueous dispersion of Pd NPs was taken on a carbon coated copper grid (200 mesh) followed by drying in air and finally in vacuum at 30 °C. The micrographs were taken through a high-resolution transmission electron microscope (JEOL, 2010 EX). The instrument was operated at an acceleration voltage of 200 kV without staining. A CCD camera was used to record the pictures. The diameter of the nanoparticles was measured using photoshop software and taking average over 100 particles from different spots.

2.8. Thermal measurements

The thermal behavior of the systems was investigated by a differential scanning calorimeter (DSC, Diamond DSC-7, Perkin–Elmer, USA) under nitrogen atmosphere. The gels were prepared in Perkin–Elmer large volume capsules (LVC) by taking a weighed amount of polymer, and camphor and the capsules were tightly sealed with a quick press. They were homogenized at 200 °C for 10 min and were quenched to 50 °C where it was equilibrated for 20 min. They were heated at the scan rate of 10° and 40°/min from 50 to 200 °C. Cooling runs were also taken from the melt at 200– 50 °C at the rate of 5 °C/min. The weight of the sample pan was checked after each experiment. The melting temperature and enthalpy of fusion values were measured with the help of PYRIS software (version 7.0).

2.9. Porosity measurements

Both mercury intrusion porosimetry (MIP) and N₂ adsorption porosimetry were used, the former was used to measure pore diameter >6 nm using the instrument Poremaster 60 (Quantachrome), and the later was used for pore diameter <6 nm using Autosorb 1-2C instrument (Quantachrome). In the MIP two pressure ranges e.g., low-pressure range (0.5–50 psi) and high-pressure range (20–34,000 psi) were used to measure pores >10 μ m and pores <10 μ m, respectively. Blank correction was made using α -Al₂O₃ beads. The sample was taken in a penetrometer (stem volume 0.5 cm³) was kept at first at the low-pressure chamber, and both intrusion and extrusion runs were recorded. After completion of the experiment the penetrometer was transferred to a highpressure chamber with the replacement of a little mercury at the stem by silicon oil, and the pressure was applied by hydraulic means. MIP is based on the principle that nonwetting liquids intrude into the capillaries under pressure (P) following the Washburn equation:

$$r = \frac{-2\gamma\cos\theta}{P} \tag{1}$$

where *r* is the radius of the pore, γ is the surface tension, and θ is the contact angle of mercury (nonwetting liquid) with the solid sample. The fraction of volume per unit mass occupied by the pores having radii in the interval (r and r + dr) can be deduced from the volume of mercury that intrudes within the pressure range (P and P + dP)

$$dV = -D_V(r)dr \tag{2}$$

where $D_V(r)$ refers to the volume pore size distribution function defined as the pore volume per unit interval of pore radius per unit of mass. Combining Eqs. (1) and (2), we have

$$DV(r) = \left(\frac{P}{r}\right)\frac{dV}{dP} \tag{3}$$

In nitrogen adsorption porosimetry we measured the pore size and pore size distribution of the mesopores and micropores using the BIH (Barett-Jovner-Halenda) and HK (Horvath-Kawazoe) methods, respectively using Autosorb 1 software.

2.10. Catalytic application

2.10.1. Catalytic reaction and recycling

Arylboronic acid (1.2 mmol), aryl halide (1.0 mmol), an inorganic base (2 mmol) and surfactant (1 mmol) (not for aryl iodides) were taken in a 10 ml flask containing 2 ml distilled water followed by stirring to make a near homogeneous solution. Pd

NPs embedded amphiphilic multiporous material (15 mg) was then added and stirring was continued for homogeneous dispersion and the reaction mixture was kept in a bath of required temperature with constant stirring. The coupling reactions of aryl iodides and bromides were performed at 30 and 100 °C, respectively in absence of surfactant. In the presence of surfactant the reactions of aryl bromides and chlorides were performed at 30 and 100 °C, respectively. The progress of the reaction was monitored by thin layer chromatographic (TLC) analysis of the reaction mixture. After the desired time, the reaction mixture was diluted with 5 ml of water and the catalyst was separated by filtration. The catalyst was first washed with water and then with diethyl ether, dried in vacuum at room temperature for further use. The total filtrate thus obtained is extracted with dry Et₂O and the ether extract was washed with brine and water and was dried over Na₂SO₄. After evaporation of solvent, crude product was further purified by column chromatography over silica gel and the % conversion was determined. The purity of all compounds was also checked by ¹H NMR and ¹³C NMR. Majority of the products are well known compounds and hence, they are identified by comparing their spectroscopic data (¹H NMR and ¹³C NMR) with literature.

2.10.2. Heterogeneity test

A catalytic reaction, as described above was performed using phenylboronic acid, 4-bromo anisole, K₃PO₄ and CTAB at 30 °C. After 6 h (62% conversion) the catalyst was separated and the reaction was continued with the filtrate only for another 18 h but no reaction occurred due to the fact that there was no leached Pd-catalyst in the filtrate.

3. Result and discussion

3.1. Morphology

The FE-SEM pictures of dried gels at two different magnifications are presented in Fig. 1 and Suppl. Fig. 1 showing their porous

Cooling

200

180



Fig. 1. (a) Low- and (b) high-magnification FESEM pictures of the P-g-D/camphor system (WP-g-D = 0.1) after the removal of camphor. (c) DSC heating and cooling thermograms for the P-g-D/camphor system of composition WP-g-D = 0.1.

140

Temperature (⁰C)

120

168.3°C

160

91.1ºC

100

80

nature. Honeycomb type pores are present throughout the sample with pore diameter 18-25 µm as obtained from the low magnified picture of dried gel of composition $W_{P-g-D} = 0.1$. The morphology of low magnified picture of dried gel of composition $W_{P-g-D} = 0.25$ is somewhat different showing the presence of irregular honeycomb type pores (Suppl. Fig. 1a) and it is totally different for $W_{P-g-D} = 0.4$ where plum leaf type pores surrounded by large islands are observed (Suppl. Fig. 1c). The walls of pores and the islands are also porous, containing fibrillar network structure and nano-pores are observed from their higher magnified pictures (right hand side of Fig. 1 and Suppl. Fig. 1). In Fig. 1c the DSC heating and cooling thermograms of the P-g-D gel ($W_{P-g-D} = 0.1$) indicate reversible first order phase transition. The fibrillar net work structure and reversible first order phase transition characterize the system to behave as thermoreversible gel [50]. The lower transition temperatures are for the gel and the higher temperatures are for camphor. During gelation, a fraction of camphor molecules are involved to form P-g-D/camphor complex [34] and the rest of camphor molecules are crystallized in a honeycomb type array of caged camphor molecules inside the gel. Micro-pores are produced from P-g-D/camphor complexation whereas the macro-pores are originated from the removal of caged camphor molecules inside the gel [34]. In case of $W_{P-q-D} = 0.1$, minimum amount of camphor forms complex with P-g-D polymer leaving a large fraction as caged molecules remaining inside the gel. This contributes to the continuous honeycomb type pore formation and as the composition of gel gradually increases from $W_{P-g-D} = 0.1$ to $W_{P-g-D} = 0.4$, larger fraction of camphor forms complex and smaller amount of caged camphor remains inside the gel decreasing the honeycomb type pore formation and its size. The islands at lower magnification images are composed of fibrillar network structure being produced from polymer solvent complexation and removal of the complexed camphor yields nano-pores [34].

3.2. Porosity

To obtain a quantitative result of porosity, both MIP and N_2 adsorption porosimetry for the dried gel of composition $W_{P-\sigma-D} = 0.1$ are made. From our previous work it is known that, the surface area of a dilute gel is always larger than that of concentrated gel [34]. Since we are interested to use the porous material for heterogeneous catalysis and surface area has important role on catalysis, we have chosen the dilute gel, $W_{P-g-D} = 0.1$, for this purpose. In Suppl. Fig. 2 the MIP histograms for both high pressure and low pressure runs are presented and in the inset of Suppl. Fig. 2a low pressure MIP histogram for larger pores is shown. The low pressure MIP histogram is sharp in nature whereas for high pressure it is somewhat broad. The sharp nature indicates that the sample has narrow pore size distribution for larger pores. The pore size distribution histograms for high pressure and low pressure runs are plotted in Fig. 2. There is only one sharp peak at around 23 µm in the low pressure pore size distribution histogram indicating that though there are pores of different sizes, majority of pores have an average diameter of 23 µm. These results match well with that obtained from the lower magnification FES-EM picture of the sample. In the high pressure pore size distribution histogram there are peaks at 0.6, 4.9, 5.9 and 7.1 μ m, indicating the existence of smaller pores. In the inset of Fig. 2, the high pressure pore size distribution histogram of very small pores is shown indicating that pores of diameter ~6 nm are also present in the sample.

To understand the interesting feature of micro-pores and mesopores arising from polymer–solvent complexation [34], we have done the N_2 adsorption porosimetry (Fig. 3a) showing the presence of small hysteresis between intrusion and extrusion isotherms due to the interconnectivity among the pores or due to the presence of



Fig. 2. MIP (a) low-pressure and (b) high-pressure pore-size distribution histograms of the pure dry gel sample [inset of (b): MIP high-pressure pore-size distribution curves of same sample in a different region].

pores of ink-bottle-type structure. The BJH pore size distribution curve is presented in Fig. 3b and it is apparent that there are pores having pore diameter around 3.3 nm–28.6 nm in the sample. To understand the presence of pores of lower diameter we have plotted the HK pore size distribution curve (Fig. 3c) which shows micropores of diameter 0.74, 1.15, 1.4, 1.51 and 1.73 nm. The sample has BET surface area $32.5 \text{ m}^2 \text{ g}^{-1}$.

3.3. Structure

The structure of dried gels is determined from the WAXS diffraction patterns (Suppl. Fig. 3) and there are peaks at $2\theta = 17.9^{\circ}$, 18.6°, 20.2° and 26.8° corresponding to the α polymorph of PVDF [62–64]. We have also used FT-IR spectroscopy as an alternate tool for this purpose (Suppl. Fig. 4) and the FT-IR spectra of solvent subtracted gel and dried gel clearly indicate that PVDF mainly exists in the α form both in the gel as well as in the dried gel (corresponding peak at 532, 613 and 796 cm⁻¹) with the existence of a small fraction as β form also (corresponding peak at 510, 600 and 841 cm⁻¹) [65,66].

3.4. Characterization of Pd NPs captured porous material

Due to the presence of $-NMe_2$ group in the hydrophilic part of the pore surface, the amphiphilic multiporous graft co-polymer (1 g) can bind 6.4×10^{-2} mmol (72% of 20 mg) palladium from



Fig. 3. (a) BET adsorption and desorption isotherms, (b) BJH pore-size distribution curves and (c) HK pore-size distribution plots for the pure dry gel and the Pd NP-captured dried gel samples.

Table 1

Atomic-Absorption Spectroscopy data of Pd in 1 gm of mutiporous polymeric material.

Amount of	Amount of Pd in the	Amount of Pd in the
Pd taken	filtrate (after immobilization	polymer (after immobilization
(mmol)	of Pd ²⁺) (mmol)	of Pd ²⁺) (mmol)
89×10^{-3}	24.9×10^{-3}	$64.1 \times 10^{-3} \equiv 72\%$

aqueous solution of palladium acetate at 24 h as indicated from Atomic-Absorption Spectroscopy (AAS) data (Table 1). The binding of Pd²⁺ is supported by UV-vis spectrum (Suppl. Fig. 5). It is reported that aqueous solution of Pd(OAc)₂ shows a UV-vis absorption band at approximately at around 256 nm [67]. The UV-vis spectrum clearly indicates that the aqueous dispersion of multiporous P-g-D showed two well absorption bands at around 297 and 307 nm for π - π * transition coupled with n- π * transition, whereas the Pd²⁺ captured porous materials shows two additional small peaks at 246 and 256 nm which may be due to the Pd(II)-polymer complexation (246 nm) with PDMAEMA part along with some adsorbed $Pd(OAc)_2$ (256 nm) onto the graft polymer matrix. Bernechea et al. also obtained similar type of new band at lower wavelength region due to palladium(II)-dendrimer complexation [67]. Upon reduction with hydrazine the color of the polymer changed from light yellow to brownish black indicating the formation of Pd NPs inside the porous material. The formation of Pd NPs in the porous materials is established from the absence of the absorption band at 246 nm and 256 nm in the UV-vis spectrum. The formation of Pd NPs in the porous material is confirmed from TEM images (Fig. 4a) and the histogram (Fig. 4b) shows two major intense regions at approx. 2.92 nm and ~4.0 nm. Probably, Pd(II)-polymer complexation is responsible for the formation of smaller Pd NPs (2.92 nm) and the larger NPs (3.89-4.02 nm) are produced from the adsorbed Pd $(OAc)_2$. In this polymer-supported Pd catalyst, there are two types of capping agents for Pd NPs. One is the PVDF backbone which has capped the Pd NPs by simple adsorption [51] and the other is >NMe₂ group of grafted PDMAEMA which has capped the Pd NPs through complexation. The capping by complexation makes the PDMAEMA shell more compact, hence there is difficulty in diffusion of Pd atoms, causing lower dimension. Anyway, the dispersity of Pd NPs is really small. The lattice spacing value (0.224 nm) matched very well with that of 1 1 1 lattice plane of Pd metal [51,68] as evidenced from the HRTEM image (Suppl. Fig. 6a). The EDXS spectrum of the material indicates the presence of metallic palladium in the multiporous polymeric material (Suppl. Fig. 6b). The gel structure and polymorph of PVDF remain unchanged after complexation with Pd²⁺ and its reduction to produce Pd NPs as evidenced from the WAXS pattern (Suppl. Fig. 7) and FTIR spectra (Suppl. Fig. 8) of Pd²⁺ and Pd NPs captured dried gels.

The Pd NPs captured dried gel ($W_{P,g-D} = 0.1$) is also porous and to obtain a quantitative idea of porosity, we have performed both MIP and nitrogen adsorption porosimetry of it. Though the low pressure MIP intrusion histogram of pure gel has one sharp peak,





Fig. 4. (a) TEM image of the Pd NPs in the porous material and (b) histogram of the Pd NPs

it is broad in case of Pd NPs captured dried gel (Suppl. Fig. 9a), indicating the presence of wide range of large pores in the sample whereas the high pressure MIP intrusion histogram of Pd NPs captured died gel (Suppl. Fig. 9b) is very similar with that of pure dried gel. In the inset of Suppl. Fig. 9a, the low pressure MIP intrusion histogram is plotted for Pd NPs captured dried gel which is an indication for the presence of pores of larger diameter. From the low pressure pore size distribution histogram of Pd NPs captured dried gel (Fig. 5a) it is clear that there is a peak at about 22 μ m, which is 1 µm less than that of low pressure pore size distribution histogram of pure dried sample (23 μ m). In addition of this, two humps are present in the Pd NPs captured sample at around 12 µm and 17 µm, indicating the presence of smaller pores which are absent in pure dry gel.

The porous material has a bi-functional hydrophilic side chain which is responsible for the binding of Pd^{2+} from aqueous $Pd(OAc)_2$ solution. In the cyclohexane leached dried gel, all the hydrophilic parts may not be present in the pore surface, but in aqueous medium most of them endeavor at the pore surface (phase inversion). Upon drying, the hydrophilic parts form a layer at the inner surface of the pore, reducing the pore diameter than that of cyclohexane dried pure gel. However, high pressure pore size distribution histogram of Pd NPs captured sample has four peaks at 0.4, 5.3, 6.4 and 7.3 μ m which are slightly higher than that of pure gel (0.6, 4.9, 5.9 and 7.1 µm). The BET adsorption isotherm of the Pd NPs captured dried gel (Fig. 3a) is at lower position than that of pure gel indicating some micropores are blocked due to inclusion of Pd NPs. The BET surface area of pure gel is higher $(32.5 \text{ m}^2 \text{ g}^{-1})$ than that of



Fig. 5. MIP (a) low-pressure and (b) high-pressure pore-size distribution histograms of the Pd NP-captured dry gel sample.

the Pd NPs captured dried gel (24.3 $m^2 g^{-1}$). Due to the presence of pd nanoparticles in the Pd NPs captured dried gel, some pores are blocked which is the main reason for lower BET surface area of the sample than the pure gel. The BJH and HK pore size distribution of Pd NPs captured dried gel, shown in Fig. 3b and c, are similar with those of pure gel but at lower position due to the blocking by Pd nanoparticles as stated above.

3.5. Catalytic tests

With the P-g-D amphiphilic multiporous polymeric materials supported Pd NPs in hand; we explore its catalytic activity towards aerobic ligand free Suzuki coupling of aryl halides (X = I, Br and Cl) in aqueous medium. We have tested the catalytic activity over various electron-withdrawing and electron-donating aryl halides at high temperature (100 °C) as well as at room temperature (30 °C).

To optimize the reaction conditions, a model coupling reaction between 4-bromoanisole and phenylboronic acid is chosen and it acts as a benchmark to compare the activity of different palladium catalysts in Suzuki reaction [53-57]. In 4-bromoanisole, the methoxy group present at the para position, which is the cause of difficulty in C-C bond formation via cross-coupling reaction, thus providing an opportunity for comparing the catalytic activity of different Pd-catalysts. The reaction is initially carried out with Na₂CO₃ as base in water at 100 °C with only 62% product in 24 h (Table 2, entry 1). In the coupling reactions the nature of base is very important and to obtain higher conversion, experiments using

Table 2

Standardization of base for the cross-coupling reaction of 4-bromoanisole (1 mmol) and phenylboronic acid (1.2 mmol) using 2 mmol base and 20 mg catalyst in 2 ml water.



Entry	Base (2 mmol)	Temperature (°C)	Time (h)	Yield (%)
1	Na ₂ CO ₃	100	24	62
2	K ₂ CO ₃	100	24	80
3	KF	100	24	78
4	КОН	100	24	65
5	CsF	100	24	88
6	K ₃ PO ₄	100	24	96
7	K ₃ PO ₄	100	16	94
8	K ₃ PO ₄	100	10	70
9	K ₃ PO ₄	50	16	52
10	K ₃ PO ₄	30	16	35

different types of base are performed and the results are compared in Table 2. From the table it is clear that the optimum yield (94%) is achieved with K₃PO₄ at 100 °C (Table 2, entry 7) for 16 h. of reaction time. It is well established that the higher temperature facilitates the debromination product leading to lower selectivity [69]. which is the main reason for recent trend to perform the coupling reactions at ambient temperature. The reaction (Table 2 entry 10) clearly indicates that the catalyst can activate the 4-bromoanisole even at room temperature (30 °C) with a lower yield (35%). The effect of surfactant on the coupling reaction with the mutiporous Pd catalyst in presence of K₃PO₄ is tested with addition of small amount (1 mmol) of them and the results are compared in Suppl. Table 1. Tetra butyl ammonium bromide (TBAB) has increased the reaction yield to 68%, (Suppl. Table 1, entry 1) from 35%. The addition of TBAB improves the solubility of the reactants in water [70]. However, the increase of yield using TBAB encourages us to carry out the model reaction at room temperature with better yield. Thus, four different surfactants namely TBAB, tetra octyl ammonium bromide (TOAB), cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfonate (SDS) have been employed out of which the addition of CTAB enhances the transformation significantly (Suppl. Table 1, entry 3) and the exact reason is unknown to us. The influence of the amount of CTAB in the coupling reaction is also optimized with the same model reaction showing a maximum yield with 1 mmol (Suppl. Table 2). Finally, we have tried to find out the minimum amount of catalyst to obtain maximum yield using optimized amount of K₃PO₄ and CTAB. The best result is obtained using 15 mg of catalyst (~10⁻³ mmol Pd) as indicated from Suppl. Table 3.

After optimizing the model reaction in terms of base, nature of surfactants, amount of surfactants and amount of catalyst, aryl halides of different structures are employed for cross-coupling reactions with phenylboronic acid using pre-optimized conditions to obtain different substituted biaryls. The results are summarized in Table 3 (characteristic NMR spectra of products in Suppl. Fig. 10a–n) where the presence of an electron-donating or withdrawing group on the aromatic ring of aryl bromides have shown independency of reactivity, producing very good yield in each case (>90%). We have also performed some reactions with various aryl iodides without surfactant and interestingly, we have

Table 3

Pd NPs catalyzed cross-coupling reactions of aryl halides (1 mmol) and arylboronic acid (1.2 mmol) using 2 mmol K₃PO₄, 15 mg catalyst (0.1 mol% Pd) and 1 mmol CTAB (except aryl iodides) in 2 ml of water.

-x +	
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Entry	R	Х	Reaction temperature (°C)	Reaction time (h)	Surfactant	Yield (%)	Turnover number
1	Н	Ι	30	14	No	90	900
2	4-Me	Ι	30	12	No	92	920
3	4-OMe	Ι	30	18	No	93	930
4	3-NO ₂	Ι	30	12	No	97	970
5	Н	Br	30	12	Yes	92	920
6	3-NO ₂	Br	30	10	Yes	93	930
7	4-NO ₂	Br	30	10	Yes	95	950
8	4-CHO	Br	30	12	Yes	96	960
9	4-COCH ₃	Br	30	10	Yes	98	980
10	4-OMe	Br	30	16	Yes	95	950
11	4-Me	Br	30	14	Yes	92	920
12	Н	Cl	100	24	Yes	44	440
13	4-COCH ₃	Cl	100	24	Yes	65	650
14	4-OMe	Cl	100	24	Yes	26	260
15	4-NO ₂	Cl	100	24	Yes	71	710
16	4-CHO	Cl	100	24	Yes	67	670



Fig. 6. Cyclic reaction diagram for Table 3, entry 10.

also obtained very high yield (>90%). With interest, we have also checked the water mediated catalytic activity using aryl chlorides under pre-standardized conditions at 100 °C. In this case, the catalyst can trigger only the activated aryl chlorides with electron withdrawing group showing moderate yield (65–71%), but the others show an yield as low as 26%.

In general, the catalyst can activate all the aryl halides (X = I, Br and Cl) in water with moderate to very high yield. The reactions are very smooth and we have obtained different biaryls from aryl iodides and bromides at room temperature in water, which is a green approach; thus important from environmental as well as from industrial points of view. The catalyst is air stable as evidenced from our series of reactions performed in aerobic condition even up to five cycles (for reaction Table 3 entry 10) without any appreciable loss of efficiency, shown in Fig. 6. The catalyst is highly heterogeneous in nature and no dissolved catalyst is observed in the filtrate as verified from the failure of reactions using filtrate only.

Again the reactivity of immobilized Pd NPs on porous polymer is better than that of usual Pd NPs. As for example, the in situ generated Pd NPs can only activate the iodo- and bromo-aryl derivatives but not the chloro-aryl derivatives during aqueous mediated Suzuki coupling reaction in presence of K_3PO_4 as base [55c]. Here, we have used the same protocol with porous polymer grafted Pd NPs which can activate the chloro-aryl derivatives. Compared to the usual Pd catalysts or palladium complexes immobilized Pd NPs on amphiphilic porous polymer causes (i) easier dispersion of the catalyst in water, (ii) facilitates the reaction in a green condition, (iii) easy to process, (iv) the reaction is really fast and finally (v) the yield is very high. So this present catalyst is beneficial to the cross-coupling reactions and the present catalyst system is inexpensive, eco-friendly, more reactive and recyclable it offers a green method suitable for environment and industry.

4. Conclusion

PVDF-g-DMAEMA/camphor system produces thermoreversible gel and leaching of camphor with cyclohexane produces multiporous material as evident from SEM, MIP and nitrogen adsorption porosimetry. Analysis of the adsorption data indicates that the dried gels have pore diameters ranging from 0.74 nm to 283 μ m and there is hysterisis between extrusion and intrusion isotherms of nitrogen adsorption porosimetry indicating interconnection between mesopores and/or presence of inkbottle type pores. WAXS and FTIR data clearly indicate presence of mainly α -polymorph PVDF with a small fraction of β -PVDF in the material. Pd NPs are grown on this porous material by adsorption of $Pd(OAc)_2$ in its aqueous dispersion followed by reduction with hydrazine transforming the porous material brownish black. UV-vis spectra indicate the formation of Pd NPs on the porous material and the presence of Pd NPs within the amphiphilic porous material is confirmed from HRTEM images and EDXS spectra. The sizes of Pd nanoparticles vary from 2.5 to 4.5 nm. MIP low pressure pore size distribution histogram of Pd NPs captured dried gel exhibit pore diameters of ~12, 17 and 22 μ m, in contrast to a sharp peak corresponding to pore diameter of 23 μ m of pure dry gel. The BET surface area of the Pd NPs captured dried gel (24.3 m² g⁻¹) is lower than that of pure gel (32.5 m² g⁻¹). The BJH and HK pore size distribution of Pd NPs captured dried gel are similar with those of pure dried gel but at lower position due to reduced pore volume by Pd NPs.

The Pd NPs captured amphiphilic porous PVDF-g-DMAEMA act as an effective catalyst for aerobic ligand free Suzuki coupling of aryl halides (X = I, Br and Cl) in aqueous medium. The catalyst not only activates aryl iodides at 30 °C and aryl bromides at 100 °C in absence of CTAB (and at 30 °C in presence of CTAB) but also activates aryl chlorides at 100 °C in presence of CTAB in water. The catalyst shows very good recyclability and is very effective even in the absence of surfactant for aryl bromides and iodides. The higher activity of that catalyst in aqueous medium is attributed to the multiporous and hydrophilic nature of the polymer support.

Acknowledgments

We gratefully acknowledge Department of Science and Technology, New Delhi (Grant No. SR/S1/PC/26/2009) for financial support. R. K. L. thanks CSIR, New Delhi for the fellowship and we acknowledge. Mr. R. Dey of Organic Chemistry department for helping in reactions. We also acknowledge the help extended by Central Glass and Ceramic Research Institute, Kolkata for their help in MIP measurements.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.reactfunctpolym.2011.07.006.

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