Functionalization of Poly(divinylbenzene) Microspheres by Combination of Hydrobromination and Click Chemistry Processes: A Model Study

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Abstract

Fluorescent pyrene-functional poly(divinylbenzene) (PDVB) cross-linked core microspheres were synthesized using the click chemistry strategy as a model study. First, the core monodisperse microspheres were prepared by precipitation polymerization using 2,2'-azobisisobutronitrile (AIBN) as initiator in acetonitrile in the absence of any stabilizer. Residual double bonds were converted to azide-functions by hydrobrominated with hydrogen bromide followed by azidation with NaN₃ in DMF solution. Propargyl pyrene was prepared independently as a fluorescent click component. Finally, azide-functionalized microspheres were coupled with propargyl pyrene with high efficiency by click chemistry. The modified PDVB microspheres are characterized by using FT-IR spectroscopy, UV-Vis absorption spectroscopy, fluorescence spectroscopy and fluorescence microscopy.

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Keywords

Click chemistry, hydrobromination, polymerization, poly(divinylbenzene), characterization, microspheres

1. Introduction

Monodisperse polymer microspheres with uniform size and shape have been extensively studied for their potential applications in coatings, biotechnology, and as chromatographic packing materials. A number of methods including water-based emulsion, seeded suspension, non-aqueous dispersion polymerization and precipitation polymerization were successfully employed for preparation of such monodisperse microspheres [1–4]. Among them, precipitation polymerization, which can be performed in the absence of any added surfactant or stabilizer [5–12], appeared to be an attractive route to obtain microspheres with uniform size and shape. Typically, monodisperse and highly cross-linked poly(divinylbenzene) (PDVB) surfactant-free microspheres (with diameters between 2 and 5 μ m) were prepared by us-

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ing only monomer (commercial divinylbenzene, DVB55), radical initiator (2,2'azobisisobutronitrile, AIBN) and solvent (acetonitrile) [5]. Interestingly, PDVB microspheres formed by this method contained significant residual double bonds in the particle and on the surface of the particle [13]. The residual double bonds located at the surface allowed further growth and modification of particles. The properties of polymeric particles are considerably changed by surface modification which is frequently achieved in core-shell fashion through incorporation of functional groups and new monomer(s). Within the past decade, development of controlled/living polymerization methods [14, 15], and new synthetic coupling routes have allowed functionalization of polymer particles, planar surfaces and block co-polymeric backbones. For example, a variety of monomers were grafted from cross-linked PDVB core microspheres [16] by using controlled radical polymerization methods including radical addition fragmentation polymerization [17] and atom transfer radical polymerization (ATRP) [18–20] processes. Very recently, a combination of reversible addition fragmentation chain transfer polymerization and hetero Diels-Alder (HDA) chemistry has been utilized to successfully generate functional core-shell microspheres by Barner and co-workers [21]. In addition to radical route, hydroxyl functional core shell microspheres were prepared by anionic ring-opening polymerization [22].

The click reactions [23, 24], in particular Cu(I)-catalyzed 1,3-dipolar Huisgen cycloaddition reactions between an azide and an alkyne, have gained a great deal of attention due to their high specificity and nearly quantitative yields in the presence of many functional groups. This coupling process has been widely used for the modification of polymeric materials [25–30]. In our laboratory, copper-catalyzed Huisgen 1,3-dipolar azide/alkyne as well as Diels–Alder cycloaddition click reactions have been successfully used for functionalization of polymers [31–33], clays [33] and silsesquioxanes [34] with thermal- [35–37], photo- [38] and electro-active [34] groups. The azide–alkyne click reaction has also been used to modify surfaces of various solid supports including silica spheres [39–41], carbon nanotubes [42, 43], and even electrode surfaces [44].

Recently, PDVB microspheres were functionalized [45] by polymeric chains using two click reactions, namely thiol-ene chemistry and azide–alkyne cycloaddition reaction. While the thiol-ene approach provided direct route to modify the surfaces of the microspheres through the reaction of SH-functionalized polymers with the accessible double bonds on the surface, the latter approach required two successive click reactions, i.e., thiol-ene chemistry was used to attach azide group on the surface of microsphere and alkyne endfunctional polymers were then reacted with the azide-modified surface *via* Huisgen 1,3-dipolar cycloaddition.

Pyrene containing polymers have received interest because of their potential use as semiconductors, photoresist materials, and fluorescent probes [46]. Various methods have been developed to attach pyrene moieties to polymers. For instance, living anionic [47–49], conventional and atom transfer radical polymerization [50–

52], olefin metathesis polymerization [53] and click chemistry [32] processes were successfully applied to prepare pyrene-functionalized polymers.

It is interesting to consider whether the azide-modified surface of microspeheres could be obtained directly without additional thiol-ene coupling reaction requiring specifically designed and synthesized molecule possessing both azide and thiol functions.

This report describes our advances in the functionalization of PDVB microspeheres by the copper-catalyzed Huisgen 1,3-dipolar cycloaddition click reaction with a small fluorescent molecule, alkyne, modified pyrene as a model compound. In our approach, the azido functional microspheres were prepared directly by simple organic reactions using commercially available, cheap compounds. Propargyl pyrene was deliberately selected as the other click component for functionalization of the microspheres so as to have efficient characterization of cross-linked microspheres through its attractive fluorescent properties.

2. Experimental

2.1. Materials

Divinylbenzene (DVB55, 55% mixture of isomers, technical grade, Aldrich) was used as received. Acetonitrile (99%, Aldrich) was distilled over CaH₂ before use. 2,2'-Azobis(isobutyronitrile) (AIBN, Fluka) was recrystallized from methanol. N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich) was distilled before use. Dichloromethane (CH₂Cl₂, 99% Lab-Scan) was distilled over P₂O₅. N,N-Dimethylformamide (DMF, \geq 99%, Aldrich), sulfuric acid (95–97%, Fluka), potassium bromide (\geq 99.5%, Merck), sodium azide (\geq 99%, Merck), sodium chromate (Merck), silver nitrate (Merck), CuBr (98%, Acros), sodium hydride (98%, Fluka), propargyl bromide (80 vol% in toluene, Fluka), 1-pyrene methanol (98%, Aldrich), methanol (99%, Reiden-de Haën), diethylether (98%, Carlo-Erba) and tetrahydrofuran (THF, 99% Lab-Scan) were used as received.

2.2. Characterizations

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Fluorescence measurements were carried out using a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Particle shapes and sizes of the product were determined by optical photography using an image analyzing system consisting of a microscope (XSZ single zoom microscope), a CDD digital camera (TK 1381 EG) and a PC with the data analyzing system Image-Pro Plus. Fluorescence image of the microscope were obtained using a Olympus Bx60 Transmitted-Reflected Light Microscope equipped with a Nikon digital camera. It has UplanFL $10 \times /0.30$, UplanFL $20 \times /0.50$, UplanFL $40 \times /0.75$, UplanFL $100 \times /1.3$ oil objectives and all objectives have DIC optics. In order to obtain uniformly distributed microspheres for light microscopy imaging, microspheres were dispersed in CH₂Cl₂, and then applied onto glass microscope slides.

2.3. Synthesis of Polydivinylbenzene PDVB Microspheres

PDVB microspheres were prepared by precipitation polymerization technique as described in the literature [5]. For this purpose, AIBN (0.2 g, 1.22 mmol, 4 wt% relative to DVB55) was added to the solution of DVB55 (11 ml, 76.8 mmol, 4 vol% relative to total volume) and 274 ml acetonitrile in a dry 500-ml three-necked flask equipped with a mechanical stirrer and a nitrogen inlet. The flask was placed in thermostated oil bath and the temperature was adjusted to 70°C. The nitrogen flow was stopped and the reaction was conducted for 48 h at this temperature under continuous stirring (32 rpm). The reaction content was cooled to room temperature and polymer precipitated was filtered, washed with tetrahydrofuran (20 ml), acetone (20 ml) and methanol (20 ml). The product was dried at 45°C under vacuum for overnight. The yield was 3 g (30%).

2.4. Hydrobromination of PDVB Microspheres

Hydrobromination was performed according to a procedure as described in the literature [54]. PDVB microspheres (2 g) were suspended using 80 ml n-heptane in a 250-ml round-bottom flask, and dibenzoyl peroxide (0.18 g, 0.74 mmol) was added to the mixture under magnetic stirrer. Hydrogen bromide (HBr) was generated by drop-wise addition of concentrated sulfuric acid (15 ml, 0.28 mol) to solid KBr (59.5 g, 0.50 mol) in a separated vessel was introduced to the mixture by means of a delivery tube. After 8 h, the generation of HBr was stopped and the stirring was maintained for another 2 h. The suspension mixture was filtered and product was purified by washing with dichloromethane, methanol and diethylether before drying in a vacuum oven at 40°C for overnight. The yield of dried product was 2.4 g.

The amount of bromine on the particles was determined by titration; the brominated particles (0.1 g) were mixed with magnesium oxide (1 g, 25 mmol) and sodium carbonate (0.5 g, 4.71 mmol) and fused at 550°C for 10 h as described in the literature [55]. Sodium bromide in the cooled mixture was transferred into a 100-ml volumetric flask by appropriate dilutions and washings and slightly acidified (pH 5) by adding nitric acid (65%). This solution was titrated with AgNO₃ in presence of sodium chromate as color indicator. This estimation revealed a bromine content of 1.46 mmol/g.

2.5. Azidation of PDVB Microspheres

The bromoethyl group on PDVB microspheres was converted into ethyl azidefunction by condensation with NaN₃. For this purpose, PDVB microsphere (1 g) was suspended in 20 ml dimethylformamide and NaN₃ (0.5 g, 7.7 mmol) was added to the mixture. Then, 0.1 ml distilled water was added to enhance solubility of sodium azide. The flask was closed and covered with aluminum foil to protect from light exposure and shaken for 24 h at room temperature. The bead product was isolated by filtration and successive washings with water $(20 \times 2 \text{ ml})$, methanol (20 ml) and diethylether (20 ml) and dried overnight under vacuum at room temperature.

2.6. Synthesis of Propargyl Pyrene

Acetylene-functional pyrene was synthesized according to a procedure as described in the literature [32]. To a solution of pyrene methanol (1.0 g, 4.30 mmol) in dry 20 ml of THF was added to sodium hydride (60 wt% dispersion in oil) (0.11 g, 4.73 mmol) and the reaction mixture was stirred at 0°C under nitrogen for 30 min. A solution of propargyl bromide (0.56 g, 4.73 mmol) in toluene was added portion wise to the solution. The mixture was kept stirring at room temperature for 24 h. Then it was refluxed for 3 h in the dark. The resulting mixture cooled to room temperature and evaporated to half of its volume. The solution was extracted with ethyl acetate, and the organic layer was dried over anhydrous MgSO₄. Evaporating ethyl acetate afforded a light yellow product. The crude product was dissolved in toluene and was passed through a column of silica gel to remove unreacted pyrene methanol. Toluene was removed by evaporating and the residue was dried in a vacuum oven (yield 55%).

2.7. Pyrene-Functionalized PDVB Microspheres via Click Reaction

PDVB microspheres (80 mg, containing 0.116 mmol azide groups) were suspended in 2 ml DMF in a Schlenk tube. Propargyl pyrene (60 mg, 0.233 mmol), CuBr (16.7 mg, 0.11 mmol) and PMDETA (24.4 μ l, 0.11 mmol) were added and the reaction mixture was degassed by three freeze–pump–thaw cycles and left *in vacuo*. The mixture was stirred at 40°C for 48 h. The solid was separated from the mixture by centrifugation. The collected solid was redispersed in DMF and separated by centrifugation. This purification cycle was repeated three times for dilute acidic methanol solution and THF. After purification, the resulting products were dried overnight under vacuum, and a sample of pyrene-functionalized PDVB microspheres (100 mg) was obtained.

3. Results and Discussion

Nearly monodisperse (approx. 2.5 μ m) spherical PDVB beads were prepared by precipitation polymerization technique and the residual double bonds on the surface were activated to primary bromine by anti-Markovnikov addition of hydrogen bromide according to the procedure described in the literature [54]. After the reaction, the brominated particles with 1.46 mmol/g of bromine (estimated by titration method [55]) were obtained. Ethyl bromide groups formed this way were then converted into azide-functions by condensation with NaN₃ in DMF solution (Scheme 1). The magnified photo-images of the starting bead polymer and its derivatives obtained by the modification in each steps show nearly perfect microspheres (Fig. 1).



Scheme 1. Hydrobromination and azidation of PDVB microspheres. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp



Scheme 2. Synthesis of pyrene-functionalized PDVB microspheres *via* click chemistry. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp



Figure 1. Optical microscope images of (a) PDVB, (b) brominated PDVB and (c) azide-functionalized PDVB microspheres. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

The chemical structure of propargyl pyrene was confirmed by both ¹H-NMR and FT-IR. The ¹H-NMR spectrum of propargyl pyrene showed two signals at 4.34 and 5.25 ppm which are assigned to CH₂ protons adjacent to the pyrene ring and propargyl moiety, respectively. Notably, the acetylene proton of the propargyl moiety and DMSO overlap and appear at 2.50 ppm. Also, aromatic protons of pyrene were detectable at 7.04–8.42 ppm (Fig. 2). In the FT-IR spectrum, propargyl group was evidenced by characteristic bands appeared at 3277 and 2121 cm⁻¹.

Chemical transformations in each step were monitored by FT-IR spectroscopy. Typical stretching vibration band of the vinyl groups is observed at 1628 cm⁻¹ and other peaks at 1405, 1014 and 989 cm⁻¹ are associated with in-plane and out-of-plane deformation bands of the vinyl group (Fig. 3a). After hydrobromination, of these peaks almost disappear from the spectrum (Fig. 3b), indicating a high yield of transformation in this step. A new peak appears at 1172 cm⁻¹, which can be



Figure 2. ¹H-NMR spectra of propargyl pyrene in DMSO.



Figure 3. FT-IR spectra of (a) PDVB, (b) brominated PDVB, (c) azide-functionalized PDVB and (d) pyrene-functionalized PDVB microspheres. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp



Figure 4. UV-Vis absorbance spectra of propargyl pyrene $(2.9 \times 10^{-5} \text{ mol/l})$, azide-functionalized PDVB (2.5 µg/ml) and pyrene-functionalized PDVB microspheres (2.5 µg/ml) in CH₂Cl₂. The absorbance spectra have been normalized for clarity. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

ascribed to C–Br stretching vibration. In the FT-IR spectrum of the azidated sample (Fig. 3c), this peak disappears completely and the characteristic vibration band of N_3 group is observed as a sharp peak at 2100 cm⁻¹. These results establish occurrence of the proposed transformation in each step and presence of azide-functions on the bead particles.

The click reaction with propargyl pyrene and azide-modified PDVB microspheres was performed using Cu(I) catalyst in DMF at 40°C. After the coupling reaction, PDVB microspheres could be easily collected by centrifugation. The catalyst and the excess pyrene were removed by washing dilute acidic methanol and THF. These pyrene-functionalized microspheres were characterized by IR (Fig. 3d), where a reduction of the azide vibration peak at 2110 cm^{-1} was observed, concomitant with an increase in the aromatic C–H peaks at 3050 cm^{-1} and 1100 cm^{-1} that correspond to pyrene groups. Comparison of the peak areas at 2110 cm^{-1} before and after the click reaction shows that most of the azide groups have successfully reacted. As can be Fig. 4, UV-Vis spectroscopy also confirmed the presence of pyrene groups on the PDVB microspheres. In spite of the lower intensity typical of dispersed networks, pyrene-functionalized PDVB microspheres show characteristic absorbance of pyrene chromophore.

Playing the predominant role in functionalization of microspheres, the fluorescence properties of the pyrene units incorporated to PDVB are important and were also studied. Figure 5 shows a visual observation of the fluorescence properties

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Figure 5. Photograph of azide-functionalized PDVB, pyrene and pyrene-functionalized PDVB microspheres dispersed in CH_2Cl_2 which was taken when irradiated with a 366 nm UV lamp. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

of bare pyrene, azide- and pyrene-functionalized PDVB microspheres dispersed in CH_2Cl_2 which recorded when irradiated with a 366 nm UV lamp.

Moreover, Fig. 6 shows fluorescence excitation and emission spectra of the precursor propargyl pyrene and pyrene-functionalized microspheres recorded in CH_2Cl_2 .

The normalized excitation spectra of both compounds overlap with some broadening and slight red shift of the functionalized microsphere relative to the precursor propargyl pyrene. This indicates that the pyrene moieties present in the close proximity on the surface of the dispersed microsphere interact in the ground state. Interestingly, the fluorescence emission spectra of these two compounds are quite different. Peaks corresponding to the emission from propargyl pyrene at 380 and 400 nm appear as a weak broad band for the microsphere. In addition, the microsphere exhibits structureless excimer emission centered at 482 nm indicating strong interaction of pyrene groups also in the excited state.

Also, fluorescence microscopy presented in Fig. 7 shows that every microsphere exhibited fluorescence of similar intensities and distributed uniformly.

In conclusion, PDVB microspheres were prepared *via* precipitation polymerization and efficiently functionalized at their residual double bonds by click chemistry. This strategy has capability to provide a general methodology for the postmodification of microspheres with a variety of terminal alkyne-modified substrates. Our studies focusing on pyrene functionalization showed that the strong fluorescence properties of such monodisperse microspheres makes them useful candidates for various applications in biomolecular interactions including those between ligands and receptors, enzymes and substrates, and oligonucleotides and their complemen-



Figure 6. Normalized excitation (a, b) and emission (a', b') fluorescence spectra of propargyl pyrene (black, 2.9×10^{-5} mol/l) and pyrene-functionalized PDVB microspheres (blue, $2.5 \,\mu$ g/ml) in CH₂Cl₂ at room temperature. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp



Figure 7. Images of the microspheres from optical microscope, transmission images (a) and fluorescence images (b) of the same area with different optic zoom. This figure is published in colour in the online edition that can be accessed *via* http://www.brill.nl/dmp

tary sequences [56]. Immobilizing pyrene on the surface of the microspheres and interacting with a partner would allow their interaction to be measured as a change in fluorescence [57]. Further studies in this line are now in progress.

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Figure 7. (Continued.)

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