

One-dimensional Janus Polymeric Vehicles^{*}

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Abstract We herein report a novel approach to fabricate poly(DVB-*co*-VBC) one-dimensional nanomaterials with varied composition. By adjusting the monomer DVB/VBC ratio and using inert solvents, after internal cavity of the nanotubes disappears and length of the nanotubes is decreased, thus nanorods are achieved. After quaternary ammoniation from the benzyl chloride group, the exterior surface becomes hydrophilic while the interiority preserves hydrophobic. The Janus nanorods can serve as a specific vehicle to selectively collect oils from their aqueous surroundings.

Keywords: Poly(DVB-*co*-VBC); Janus; Nanotube; Nanorod.

INTRODUCTION

One-dimensional (1D) nanomaterials have attracted growing interest in both fundamental research and practical applications^[1–4]. Polymer nanofibers or nanorods possess fascinating physical and chemical features determined by their microstructure and composition^[5, 6], which have been applied in many fields such as water treatment, catalysis, advanced materials and bionics^[7–11]. Meanwhile, polymer nanomaterials serve as ideal templates to derive composite functional nanofibers or nanorods^[12–14]. It is important to develop methods to large scale synthesize polymer nanofibers or nanorods in a simple way. One-dimensional polymer nanomaterials have been prepared by some methods including electro-spinning^[15, 16], template-guided synthesis^[17–21], self-assembly^[22] and micromachining^[23–26]. However, the previous methods are either expensive or inefficient. It remains challenging to large scale fabricate robust polymer one-dimensional nanomaterials.

We have recently proposed a simple way to large scale synthesize highly crosslinked polymer nanotubes of poly(divinylbenzene) (PDVB)^[27]. They have demonstrated promising performance in effective collection of spilled chemicals. The nanotubes are fabricated by a rapid cationic polymerization with immiscible liquid initiator nanodroplets. Morphology and composition of the nanotubes is controllable. More interestingly, the nanotubes are segmented with a bamboo-like structure. The synthesis process is highly efficient to complete the polymerization within 5 min. The nanotubes are very long about tens micrometers. It is difficult to obtain short nanorods. What's more, crosslinking degree of the nanofibers should be sufficiently high. Otherwise, it is impossible to achieve the polymer nanofibers.

Herein, we develop the approach to synthesize nanofibers with tunable crosslinking degree and length, especially short nanorods. It is significant to use inert solvents including *n*-hexane and *n*-heptane rather than the

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good solvent cyclohexane. A functional monomer of vinylbenzyl chloride (VBC) is added with divinylbenzene (DVB) to control crosslinking degree, which can also provide a starting point for further modification^[28, 29]. As an example of the modification, the exterior surface is transformed from hydrophobic to hydrophilic after modification with trimethylamine *via* quaternary ammoniation, while the interiority preserves hydrophobic. Janus nanomaterials are achieved. They are well dispersible in water, and selectively collect organic solvents into the hydrophobic interior sites. In comparison with other Janus spherical cages^[30–33], the one-dimensional Janus nanofibers or nanotubes will be much easier for separation.

EXPERIMENTAL

Materials

Divinyl benzene (DVB) and vinylbenzyl chloride (VBC) were purchased from Sigma-Aldrich. Boron trifluoride diethyl etherate ($\text{BF}_3\text{O}(\text{Et})_2$, CP) was purchased from Acros Organics. Ethanol, *n*-hexane, *n*-heptane and isooctane were purchased from Sinopharm Chemical Reagent Beijing. All chemicals are analytical grade. DVB and VBC were purified over Al_2O_3 column and then stored at low temperature prior to use. All other reagents were used as received without further purification.

Synthesis of Nanorods

At room temperature *e.g.* 20 °C, 150 mg of BFEE was immediately added into 100 mL of *n*-heptane containing 2.0 wt% of VBC/DVB monomer mixture under stirring to initiate the cationic polymerization at varied time. After 10.0 g of ethanol was added to terminate the polymerization, the system becomes white and turbid. After centrifugation and washing with ethanol, the products were obtained after ambient drying.

Synthesis of Quaternary Ammoniation Modified Nanorods

1.0 g of the nanorods was dispersed in 100 mL of ethanol under ultrasonication. 5.0 g of aqueous trimethylamine (25 wt%) and 0.1 g of sodium hydroxide were added. The mixture was stirred at 20 °C for varied time, the products were separated by centrifugation and washing with ethanol. The quaternary ammonium functionalized products were obtained after ambient drying.

Characterization

Morphology of the samples was characterized using transmission electron microscopy (JEOL 100CX operating at 100 kV) and scanning electron microscopy (S-4800 at 15 kV). The samples for SEM observation were ambient dried and vacuum sputtered with Pt. The samples for TEM observation were prepared by spreading diluted dispersions in ethanol onto carbon-coated copper grids and dried at room temperature. Fluorescence microscopy images were taken using a confocal laser scanning microscope (CLSM, Leica TCS-sp2, Germany) with an excitation wavelength of 488 nm. FTIR spectroscopy was performed after scanning samples for 32 times using a Bruker EQUINOX 55 spectrometer with the sample/KBr pressed pellets.

RESULTS AND DISCUSSION

In our previous report on the synthesis of poly(DVB-*co*-VBC) nanotubes in cyclohexane, it is difficult to achieve nanotubes or nanofibers when the DVB content is at low levels^[27]. It is understandable that cyclohexane is a good solvent for linear poly(VBC). Alternatively, after cyclohexane is replaced with inert solvents such as alkanes, it is allowed to preserve the nanofiber structure even at low level of DVB content. Similarly, poly(DVB) nanotubes with an internal tubular cavity can be easily obtained in *n*-heptane (Figs. 1a and 1b). Bamboo-like nanotubes can be still achieved with an internal tubular cavity when co-monomer VBC is added at a VBC/DVB ratio of 1/1 (Fig. 1c). In comparison, it is impossible to achieve the nanotubes in cyclohexane. The cavity becomes thinner and much elongated when the VBC/DVB ratio increased to 2/1 (Fig. 1d). With further increasing the ratio to 3/1, the cavity becomes smaller or even disappears (Figs. 1e and 1f). Some short nanorods appear which are coexistent with long nanofibers. Especially, short nanorods are dominant at a high ratio of 10/1 (Fig. 1g). In the absence of DVB, the poly(VBC) nanorods become much shorter (Fig. 1h). In FTIR spectra (Fig. 2) the peak at 1630 cm^{-1} is assigned to C=C stretching vibration of poly(DVB) (curve a). Presence of the

poly(VBC) is confirmed by the bands at 1266 cm^{-1} and 676 cm^{-1} , which are assigned to the C–H bending vibration of phenyl ring connected with the $-\text{CH}_2\text{Cl}$ group and the C–Cl stretching vibration. The peaks become stronger in intensity with the increasing content of VBC, while the characteristic peak at 1630 cm^{-1} assigned to poly(DVB) becomes progressively weaker. In the case of poly(VBC), the peak of poly(DVB) disappears.

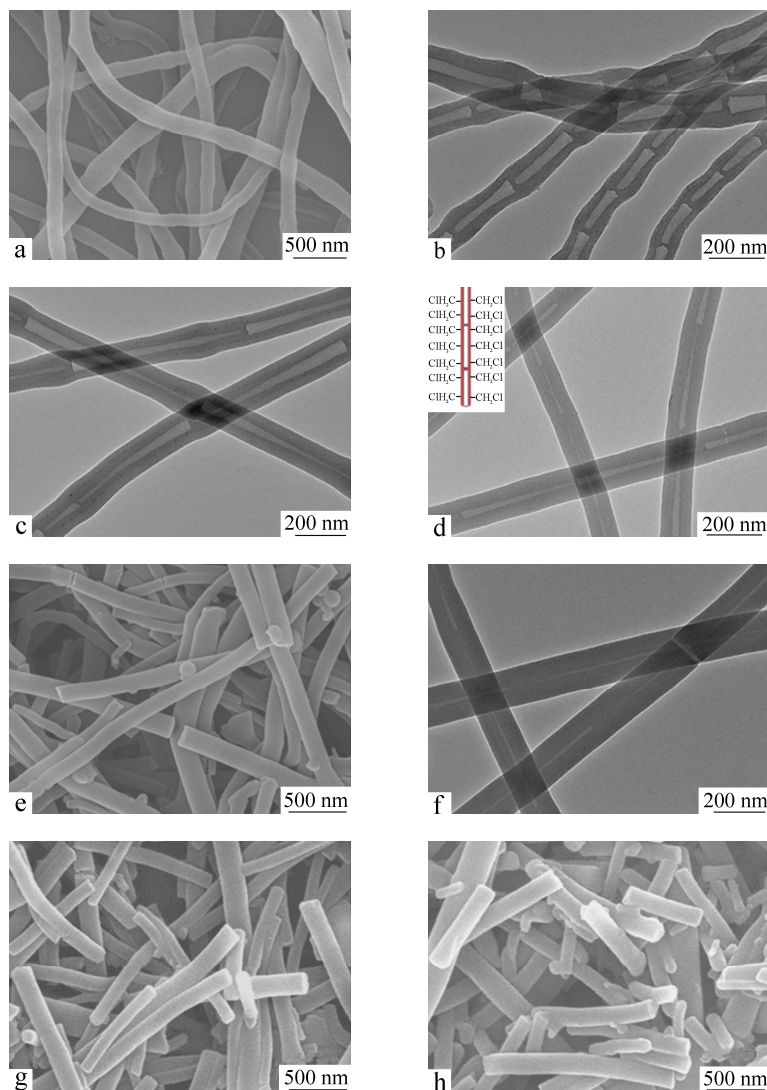


Fig. 1 (a, b) SEM and TEM images of poly(DVB) nanotubes; (c, d) TEM images of the poly(DVB-co-VBC) nanotubes synthesized at VBC/DVB ratio of 1/1 and 2/1, respectively; (e, f) SEM and TEM images of the poly(DVB-co-VBC) nanomaterials synthesized at VBC/DVB ratio of 3/1; (g) SEM image of the poly(VBC/DVB) nanomaterials synthesized at VBC/DVB weight ratio of 10:1; (h) SEM image of poly(VBC) nanomaterials (The synthesis is carried out in *n*-heptane at a monomer concentration of 2.0 wt%.)

It is seen that solvent is important to tune microstructure of the nanomaterials. At a given VBC/DVB monomer weight ratio of 10/1, short nanotubes with the internal cavity are achieved in *n*-hexane (Fig. 3a). In comparison, the internal hollow cavity disappears and short nanorods are obtained in longer alkane solvent such as isooctane (Fig. 3b).

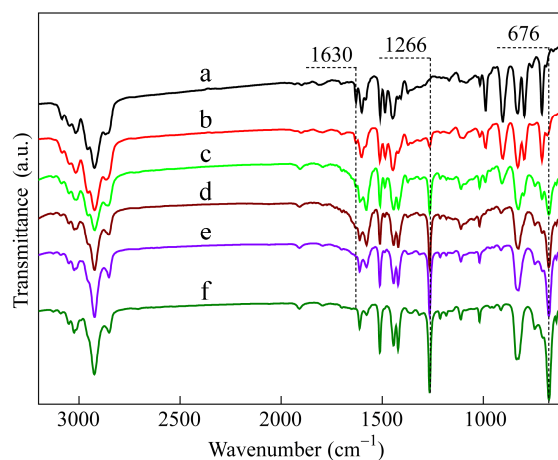


Fig. 2 FTIR spectra of the nanomaterials: (a) poly(DVB); poly(DVB-co-VBC) at varied monomer VBC/DVB ratios of (b) 1/1, (c) 2/1, (d) 3/1, (e) 10:1 and (f) poly(VBC)

The characteristic band at 1630 cm^{-1} is assigned to $\text{C}=\text{C}$ stretching vibration, the characteristic band at 1266 cm^{-1} is assigned to the $\text{C}-\text{H}$ bending vibration of phenyl ring connected with the $-\text{CH}_2\text{Cl}$ group. The characteristic band at 676 cm^{-1} is assigned to the $\text{C}-\text{Cl}$ stretching vibration.

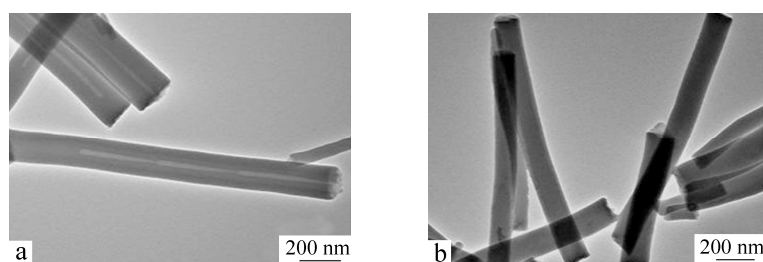


Fig. 3 TEM images of (a) the polymer hollow nanorods synthesized in *n*-hexane and (b) the polymer solid nanorods synthesized in isooctane (VBC/DVB monomer ratio is fixed at 10/1.)

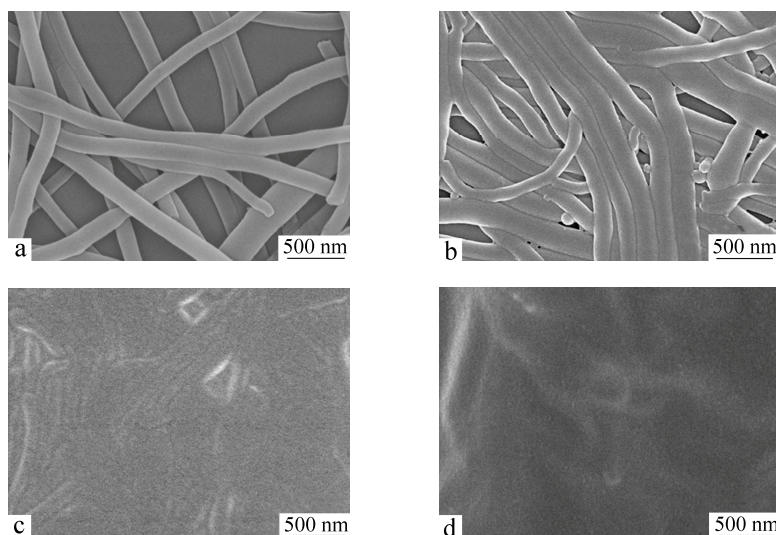


Fig. 4 Morphologies of the poly(DVB-co-VBC) nanomaterials in toluene, synthesized at varied DVB/VBC ratios: (a) 1/1, (b) 1/2, (c) 1/3 and (d) 1/10

The polymer nanofibers composed of higher VBC contents will become less resistant to good solvents such as toluene. Highly crosslinked poly(DVB-*co*-VBC) (1/1) nanotubes can well preserve the original morphology after immersion in toluene (Fig. 4a). The nanofibers of poly(DVB-*co*-VBC) (1/2) start to coalesce together (Fig. 4b). At VBC/DVB ratio of 3/1, nanofiber structure becomes weakening (Fig. 4c). At higher ratio of 10/1, no fibrill structure is preserved (Fig. 4d).

Thanks to the presence of benzyl chloride groups at the nanomaterials surface, it becomes very easy to further modify the nanomaterials to render functional performances. In order to demonstrate the concept, the nanomaterials are treated with trimethylamine for the quaternary ammoniation for varied time. The quaternary ammoniation starts from the outer surface of the nanomaterials, the modification degree is controlled by alteration of ammoniation time. At low ammoniation degree, the interior nanomaterial preserves hydrophobic. Morphology of the nanomaterials is not influenced by the modification (Fig. 5a). The internal hollow cavity is preserved (Fig. 5b). After the modification, some new peaks appear at 1633 cm^{-1} and 1382 cm^{-1} which are assigned to the strong stretching vibration of C—N bond and the bending vibration of $-\text{CH}_2$ group connected to the nitrogen cation (Fig. 5c). The pristine poly(DVB-*co*-VBC) nanomaterials are not dispersible in water but floating at the top layer (left Fig. 5d). After modification, the nanomaterials become well dispersible in water (right Fig. 5d). The nanomaterials are capable to integrate the hydrophobic interiority and hydrophilic exterior

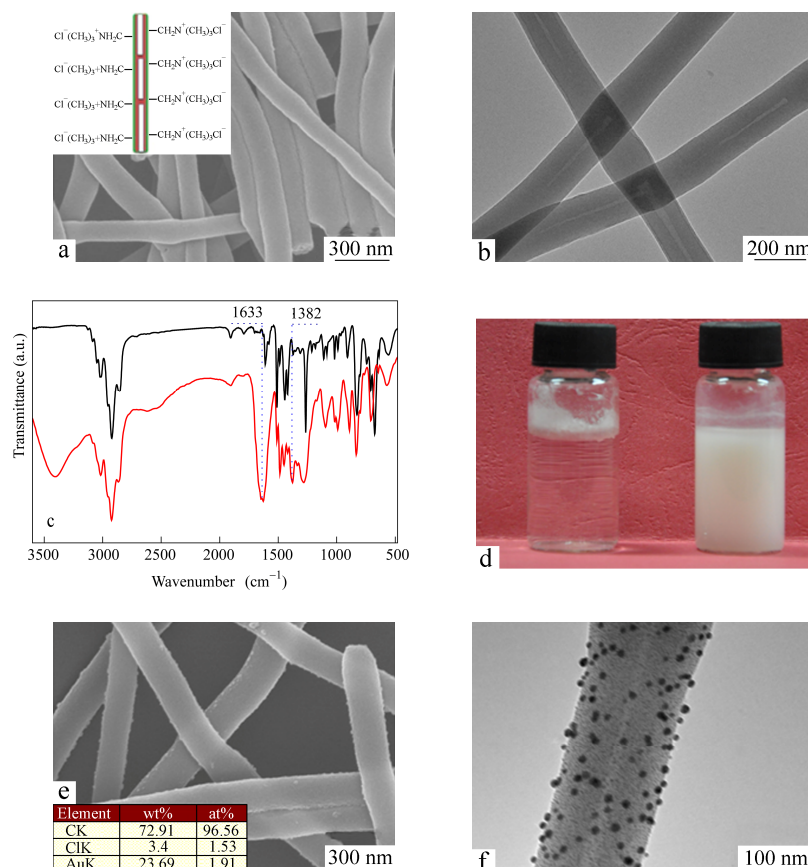


Fig. 5 (a, b) SEM and TEM images of the poly(DVB-*co*-VBC) nanomaterials after quaternary ammoniation; (c) FTIR spectra of the pristine sample (black curve) and the modified one (grey curve) (d) aqueous dispersions of the poly(DVB-*co*-VBC) nanorods (left) and the quaternary ammonium nanorods (right). (e, f) SEM and TEM images of Au NPs labelled quaternary ammonium poly(DVB-*co*-VBC) nanorods by *in situ* reduction (inset EDX result)

surface, which is regarded as Janus performance. Au NPs are *in situ* grown at the quaternary ammonium site for a selective labeling. A preferential absorption of $[\text{AuCl}_4]^-$ within the quaternary ammonium site is performed after the modified nanomaterials are immersed in an aqueous solution of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ for 24 h. After growth of Au NPs, the surface becomes slightly coarsening (Fig. 5e). Presence of Au NPs is confirmed by EDX result (inset Fig. 5e). TEM image indicates the NPs are mainly distributed at the skin layer of the nanomaterials (Fig. 5f).

The modified nanorods are Janus. The hydrophilic surface ensures them to well disperse in water, while the hydrophobic interiority can collect oil from their aqueous surroundings. A toluene/water immiscible mixture is used to demonstrate the oil collection. A trace amount of dil-C18 dye is added to toluene for easier observation. The modified nanorods are added into the dyed mixture to collect oil under stirring. After the toluene containing nanorods are filtered from the mixture, morphology is observed under fluorescence microscope to evaluate oil collection content. At initial stage of the collection (2 min), there exist green discontinuous segmental domains along the nanorods (Fig. 6a). This implies that the oil collection amount is low. Meanwhile, small droplets of oil phase are trapped. With increasing collection time (5 min), the green nanorods become more bright and continuous (Fig. 6b). This is consistent with the increase of oil collection amount. Large oil droplets disappear, and amount of the individual oil droplets is greatly decreased. After 10 min collection, no oil droplets are found (Fig. 6c). Uniform long green nanorods are achieved. This indicates that the collection of oil by the Janus nanorods has reached saturation. Similarly, oil can be collected with the Janus nanorods from the oil-in-water emulsions which are stabilized with surfactants, and the corresponding dyed nanorods are created. Meanwhile, we provide a simple method to achieve optical active nanorods by selective collection of dyes with the Janus nanorods.

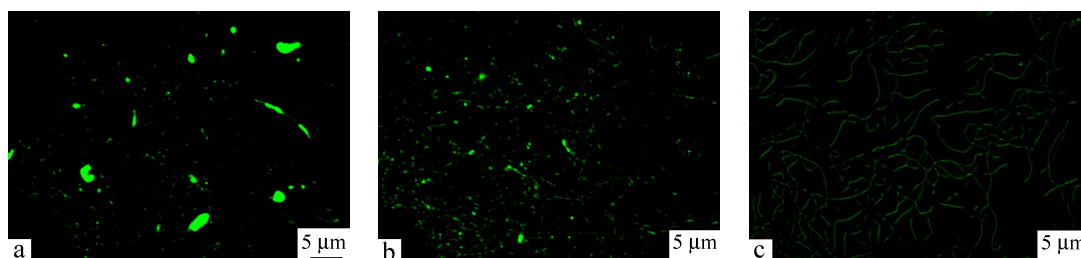


Fig. 6 Fluorescence microscopy images in the process of collecting oil with the quaternary ammonium poly(DVB-*co*-VBC) nanorods: (a) at the early stage (2 min), (b) after 5 min and (c) after 10 min. A trace amount of dil-C18 dye is added in toluene to label the phase. After the dyed toluene is mixed in water, the nanorods are dispersed in the mixture.

CONCLUSIONS

In summary, we have reported on simple synthesis of poly(DVB-*co*-VBC) copolymer nanofibers by cationic polymerization in inner solvent system. The microstructure and length of the nanofibers are tunable by changing the DVB/VBC monomer ratio. The nanofibers can be easily transformed into Janus structure after selective modification of their outermost surface for example by quaternary ammoniation, which become well dispersible in water. The interior part preserves hydrophobic and can selectively collect oil from aqueous surroundings. Onto the exterior surface, other functional materials can be selectively grown. The Janus nanorods can be manipulated if paramagnetic Fe_3O_4 nanoparticles are introduced.

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