

SYNTHESIS OF MONODISPERSE HOLLOW POLYMER MICROSPHERES WITH FUNCTIONAL GROUPS BY DISTILLATION PRECIPITATION POLYMERIZATION*

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Abstract Monodisperse hollow polymer microspheres having various functional groups on the shell-layer, such as carboxylic acid, pyridyl and amide, were prepared by two-stage distillation precipitation polymerization in neat acetonitrile in the absence of any stabilizer or additive, during which monodisperse poly(methacrylic acid) (PMAA) afforded from the first-stage polymerization was utilized as the seeds for the second-stage polymerization. The shell layer with different functional groups was formed during the second-stage copolymerization of either divinylbenzene (DVB) or ethyleneglycol dimethacrylate (EGDMA) as crosslinker and the functional comonomers, in which the hydrogen-bonding interaction between the carboxylic acid group of PMAA core and the functional groups of the corresponding comonomers, including carboxylic acid, amide and pyridyl, played an essential role for the formation of monodisperse core-shell functional microspheres. The hollow polymer microspheres were then developed after the subsequent removal of PMAA cores by dissolution in ethanol under basic condition. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to determine the morphology of the resultant PMAA core, functional core-shell microspheres and the corresponding hollow polymer microspheres with different functional groups. FT-IR spectra confirmed the successful incorporation of the various functional groups on the shell layer of the hollow polymer microspheres.

Keywords: Hollow polymer microsphere; Distillation precipitation polymerization; Functional microsphere; Hydrogen-bonding interaction.

INTRODUCTION

The polymer particles with different structures including core-shell^[1, 2], microdomain^[3], hollow sphere^[4, 5], core-corona^[6, 7] and interpenetrating polymer network^[8] are attractive for a wide number of applications for separation science^[9], biomedical devices^[10], coating additives^[11] and controlled-release reservoirs^[12]. Among them, hollow micro- and nano-spheres behave unique properties with various applications in the fields of medicine and materials as product encapsulator for controlled-release drugs^[13], dyes and inks^[14], enzymes^[13, 14] and paints^[13], and as a precursor of light-sensitive compounds^[14] and heterogeneous catalysts^[15].

Many chemical and physicochemical techniques, such as hetero-phase polymerization together with a sol-gel procedure^[16], emulsion/interfacial polymerization process^[17], surface living polymerization method^[18], seeded polymerization of tetraethoxysilane on the surface of polystyrene particles followed by calcinations^[19], coating colloidal core templates with altering layers of oppositely charged nano-particles and polymers^[20], have been used to prepare hollow spheres comprising of polymeric or ceramic materials. In most cases, it is difficult to afford the hollow polymer microspheres with uniform shape and regular shell structures because the

* This work was financially supported by the National Natural Science Foundation of China (No. 20874049).

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Received June 8, 2009; Revised August 15, 2009; Accepted August 21, 2009

doi: 10.1007/s10118-010-9089-7

polymerization is not restricted to the surface of the templates.

In our previous work, distillation precipitation polymerization has been developed as a facile and powerful technique for the synthesis of monodisperse polymer microspheres with different functional groups free of any additive^[21–26], the functional core-shell polymer microspheres^[27, 28] and the further development of hollow polymer microspheres with gold nanoparticles on the interior surfaces^[29]. More recently, PDVB hollow microspheres with pyridyl groups located on the interior surface were prepared by a facile two-stage distillation precipitation polymerization with the aid of the vinyl group on the surface of PMAA core incorporated through the hydrogen-bonding interaction between the carboxylic acid group and pyridyl group of 4-vinylpyridine (VPy)^[30]. The present paper reports on the preparation of the hollow functional microspheres by two-stage distillation precipitation polymerization with subsequent removal of the PMAA core, in which the crosslinked shell-layer having different functional groups was formed by the second-stage polymerization with the aid of the hydrogen-bonding interaction between the carboxylic acid groups on the surface of PMAA core and the functional groups of the comonomers, such as carboxylic acid, amide and pyridyl.

EXPERIMENTAL

Chemicals

Divinylbenzene (DVB, 80% divinylbenzene isomers) was supplied as a technical grade by Shengli Technical Factory, Shandong, China, which was washed with 5% aqueous sodium hydroxide and then dried over anhydrous magnesium sulfate prior to use. Ethyleneglycol dimethacrylate (EGDMA) was a chemical grade reagent from Heshibi Chemical Co., Shanghai, China and used without further purification. Methacrylic acid (MAA) was purchased from Tianjin Chemical Reagent II Co. and purified by vacuum distillation. 4-Vinylpyridine (VPy) was available from Acros and distilled under vacuum. Acrylamide (AAm, Tianjin Chemical Reagent II Co.) was recrystallized from acetone. 2,2'-Azobisisobutyronitrile (AIBN) was provided by Chemical Factory of Nankai University and was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagent II Co.) was dried with calcium hydride and purified by distillation before use. The other reagents were analytical grade and used without any further purification.

Preparation of Monodisperse PMAA Core

Monodisperse PMAA core was prepared by the first-stage distillation precipitation polymerization according to our previous paper in the absence of any crosslinker without any additive or surfactant in neat acetonitrile with AIBN as initiator^[31]. For a typical polymerization procedure, MAA (2.0 mL, 2.0 g, 22.0 mmol, relative to 2.5 vol% of the whole reaction medium) and AIBN (0.04 g, 0.24 mmol, 2 wt% corresponding to the monomer) were dissolved in 80 mL of acetonitrile in a dried 100 mL of two-necked flask attaching with a fractionating column, Liebig condenser and a receiver. The flask was immersed in a heating mantle, and the reaction mixture was heated from ambient temperature to the boiling state within 20 min. Then the solvent began to be distilled from the reaction system. The initially homogeneous reaction mixture became opalescent and then deepened in color as a milky white dispersion after boiling for 20 min. The reaction was ended after 40 mL of acetonitrile was distilled from the reaction system within 1.5 h. The resultant PMAA microspheres were suspended in the residual acetonitrile without further treatment and kept in refrigerator for the second-stage distillation precipitation polymerization. During the first-stage polymerization, the conversion of MAA to PMAA microspheres was 73%.

Preparation of Monodisperse Core-Shell Functional Polymer Microspheres

The PMAA core was prepared as described above during the first-stage distillation precipitation polymerization, in which the conversion of MAA was only about 70% at that period. A typical procedure for the second-stage polymerization was as following: 0.30 mL of DVB together with 0.012 g AIBN in 30 mL of acetonitrile was introduced into 10 mL of PMAA core suspension in a 50 mL two-necked flask equipped with a fractionating column, condenser and a receiver. The flask was submerged in a heating mantle and the reaction system was heated from ambient temperature till boiling state within 15 min and then the solvent began to be distilled out of

the reaction system. The copolymerization of DVB and the residual MAA monomer from the above suspension was continued under the distilling state and was ended after 30 mL of acetonitrile was distilled off the reaction mixture within 1.5 h. After the polymerization, the resultant polymethacrylic acid/poly(divinylbenzene-*co*-methacrylic acid) (PMAA/P(DVB-*co*-MAA)) core-shell particles were isolated by vacuum filtration over a G-5 sintered glass filter and was washed successively three times with THF, acetone and ether. The core-shell functional polymer microspheres were dried at 50°C in vacuum oven till constant weight.

A series of parallel synthesis using different EGDMA as crosslinker and the copolymerization of DVB with functional comonomers, including AAm, VPy, were carried out in the presence of PMAA particles as seeds to afford the core-shell polymer microspheres with different functional groups, such as carboxylic acid, pyridyl and amide.

Preparation of Monodisperse Hollow Polymer Microspheres with Various Functional Groups

Monodisperse core-shell microspheres with different functional groups on the shell layer were immersed in an aqueous solution with pH of 10 adjusted by 1 mol/L NaOH solution in ethanol with ultrasonic bathing at room temperature for the selective dissolution of PMAA cores. Hollow polymer microspheres with different functional groups were formed by subsequent washing with ethanol and ultracentrifugation to remove the residual PMAA species and NaOH from the surface. The final hollow functional microspheres were dried at room temperature in vacuum oven till constant weight.

Characterization

The morphology of the resultant PMAA core, core-shell functional polymer microspheres and hollow polymer microspheres with various functional groups were determined by transmission electron microscopy (TEM) using a Tecnai G20 S-TWIN on a copper grid coated with carbon membrane and scanning electron microscopy (SEM) using a Scanning Electron Microscope (Philips-XL-30). All the size and size distribution reflect the average of 100 particles, which are calculated according to the following formula:

$$U = D_w / D_n \quad D_n = \sum_{i=1}^k n_i D_i / \sum_{i=1}^k n_i \quad D_w = \sum_{i=1}^k n_i D_i^4 / \sum_{i=1}^k n_i D_i^3$$

where, U is the polydispersity index, D_n is the number average diameter, D_w is the weight-average diameter, D_i is the diameter of the determined microsphere. The thickness of the shell layer was determined as the half of the difference in diameters between PMAA core and the core-shell functional polymer microspheres.

Fourier transform infrared spectra were determined on a Bio-Rad FTS 135 FT-IR spectrometer over potassium bromide pellet and the reflectance spectra were scanned over the range of 400–4000 cm^{-1} .

RESULTS AND DISCUSSION

In our previous work, the crosslinked PDVB core in the functional core-shell structure polymer microspheres^[27, 28] cannot be selectively removed by dissolution with solvent for the preparation of hollow polymer microspheres. The TEM micrograph of PMAA microspheres obtained in the first-stage distillation precipitation polymerization was shown in Fig. 1(a), which would be used as seeds for the synthesis of the functional core-shell microspheres, and the subsequent removal of the cores of non-crosslinking nature may result in hollow functional polymer microspheres. The results indicated that the PMAA microspheres had spherical shape and smooth surface with an average diameter of 160 nm and a monodispersity index (U) of 1.007 as summarized in Table 1.

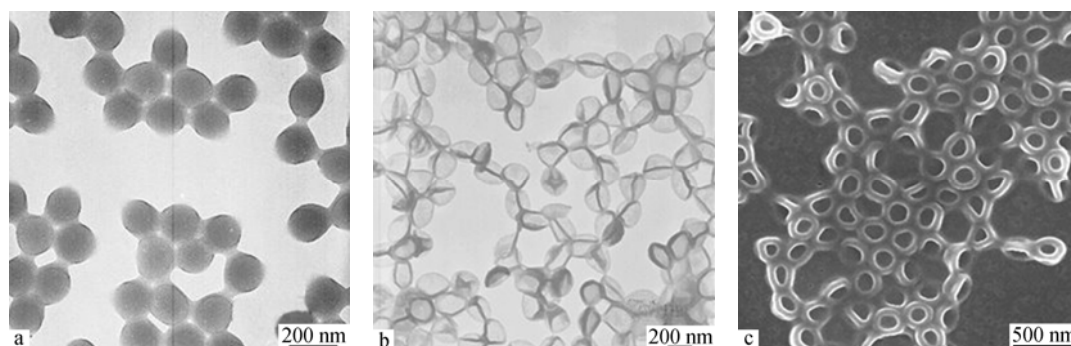


Fig. 1 Micrographs for polymer particles: (a) TEM for PMAA core, (b) TEM for hollow P(DVB-*co*-MAA) microspheres, and (c) SEM for hollow P(EGDMA-*co*-MAA) microspheres

Table 1. Reaction conditions for the synthesis of core-shell microspheres, the size and size distribution of the resultant core-shell microspheres

Entry	Microsphere	Monomer feed (mL)	D_n (nm)	Shell thickness	U
1A	PMAA	2.0	160		1.007
1B	Hollow P(DVB- <i>co</i> -MAA)	0.30		30 nm	
1C	Hollow P(EGDMA- <i>co</i> -MAA)	0.25		60 nm	
3A	PMAA/P(DVB- <i>co</i> -VPy)	0.20 DVB 0.05 VPy	194		1.005
3C	PMAA/P(DVB- <i>co</i> -AAm)	0.30 DVB 0.20 g AAm	216		1.011
3B	Hollow P(DVB- <i>co</i> -VPy)			25 nm	
3D	Hollow P(DVB- <i>co</i> -AAm)			35 nm	
3E	PMAA/PDVB	0.20		Irregular particles	

Monodisperse Hollow Polymer Microspheres with Different Polarity

A series of core-shell structure polymer microspheres with various functional groups were synthesized by two-stage distillation precipitation polymerization in our previous paper, in which the shell was formed during the second-stage polymerization *via* the capture of monomer and the oligomers from the reaction system with the aid of the residual vinyl groups on PDVB cores due to the poor solvent and much low monomer concentration used for the first-stage polymerization^[27, 28]. In the present work, the PMAA microspheres without any crosslinker were used as cores for the preparation of the functional core-shell microspheres, in which the vinyl group was absent from the surface of PMAA seeds. The mechanism for the distillation precipitation polymerization of MAA in neat acetonitrile driven by the hydrogen-bonding interaction was investigated in detail in our previous paper^[31]. The conversion of MAA reached only about 70% due to the low monomer concentration for the first-stage distillation precipitation polymerization in the present work. There were many residual MAA monomer and soluble MAA oligomers in the reaction system at this stage. Accordingly, addition of the second-comonomer either DVB or EGDMA as crosslinker during the second-stage copolymerization with the residual MAA species would result in the desired core-shell functional polymer microspheres with the aid of the hydrogen-bonding interaction between the carboxylic acid groups on the surface of PMAA cores and the carboxylic acid group of residual MAA species in the solution.

The polarity of the polymer microspheres is an essential concern for many applications. Here, we intended to explore the possibility for the formation of crosslinked hollow polymer microspheres with different polarity by the second-stage copolymerizations of DVB or EGDMA as crosslinker together with the residual MAA species in the reaction system after the first-stage polymerization. PMAA cores of the resultant PMAA/poly(divinylbenzene-*co*-methacrylic acid) (PMAA/P(DVB-*co*-MAA)) and PMAA/poly(ethyleneglycol dimethacrylate-*co*-methacrylic acid) (PMAA/P(EGDMA-*co*-MAA)) core-shell microspheres were selectively removed by dissolution of PMAA segments under basic conditions in ethanol to afford the corresponding

P(DVB-*co*-MAA) and P(EGDMA-*co*-MAA) hollow microspheres, respectively. The driving force for such selective removal was due to the solubility of linear PMAA in ethanol, especially with the aid of the base. The micrographs of hollow P(DVB-*co*-MAA) from TEM observation and SEM characterization for P(EGDMA-*co*-MAA) hollow microspheres are shown as in Figs. 1(b) and 1(c), respectively. The P(DVB-*co*-MAA) hollow microspheres having convincing hollow-sphere structures in the presence of circular rings of sectioned spheres and a cavity in the interior were observed in Fig. 1(b), which were obtained with DVB feed of 0.10 mL for the formation of the shell layer. The thickness of the shell-layer for the resultant P(DVB-*co*-MAA) hollow microspheres was determined as 30 nm from TEM characterization. The successful encapsulation of P(DVB-*co*-MAA) over PMAA core resulting in core-shell microspheres and the further development as P(DVB-*co*-MAA) hollow microspheres were confirmed by FT-IR spectra as illustrated in Fig. 2 spectrum b, in which the peak at 710 cm^{-1} was attributed to the C—H bond of stretching vibration of the phenyl group in PDVB component and the peak at 1713 cm^{-1} was corresponding to the stretching vibration of the carboxylic acid group.

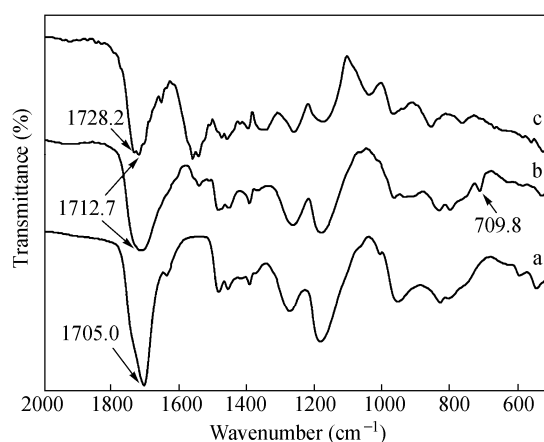


Fig. 2 FT-IR spectra of the polymer microspheres: (a) PMAA core, (b) hollow P(DVB-*co*-MAA) microsphere, and (c) hollow P(EGDMA-*co*-MAA) microspheres

Figure 1(c) indicated that P(EGDMA-*co*-MAA) hollow microspheres had convincing hollow-sphere structures with circular rings and a cavity in the interior, in which most of the hollow P(EGDMA-*co*-MAA) microspheres were interconnected each other with few sectioned spheres. Such result may be due to the softer surface of P(EGDMA-*co*-MAA) microspheres than that of P(DVB-*co*-MAA) particles, in which the pendent residual vinyl group on the gel-layer of P(EGDMA-*co*-MAA) microspheres was much easier to access for the growth of the core-shell structure microspheres through the capture of the newly formed oligomers and monomers from the reaction system. This was investigated in detail for the distillation precipitation polymerization of EGDMA in neat acetonitrile in our previous paper^[32]. The presence of a strong peak at 1728 cm^{-1} in FT-IR spectrum as shown in Fig. 2 spectrum c assigning to the carbonyl group of the ester segment in PEGDMA together with a strong peak at 1713 cm^{-1} corresponding to the carbonyl group of carboxylic acid in PMAA component indicated that the successful coating of P(EGDMA-*co*-MAA) over PMAA cores.

The FT-IR spectra in Fig. 2 had a peak in the range of $1705\text{--}1712\text{ cm}^{-1}$ corresponding to stretching vibration of the carbonyl bond of carboxylic acid groups, in which such peak in spectrum a for PMAA was much stronger than those in spectra b and c for P(DVB-*co*-MAA) and P(EGDMA-*co*-MAA) hollow microspheres. These results indicated the presence of the carboxylic acid group on the shell-layer of the resultant P(DVB-*co*-MAA) and P(EGDMA-*co*-MAA) hollow microspheres and the efficient removal of PMAA core in ethanol.

Hollow Polymer Microspheres with Pyridyl and Amide Groups on the Shell-layer

The PMAA core particles were prepared as described above in the first-stage polymerization, which were

obtained after the treatment with successive washing with acetonitrile and ultracentrifugation to remove the residual soluble MAA species on the surface of PMAA cores.

The shell layer was formed through the copolymerizations of DVB as crosslinker and the functional comonomer, such as VPy and AAm, having hydrogen-bonding interaction with the carboxylic acid group on the surface of PMAA cores to incorporate the corresponding pyridyl and amide groups on the shell-layer. The TEM micrographs of the resultant PMAA/poly(divinylbenzene-*co*-4-vinylpyridine) (PMAA/P(DVB-*co*-VPy)) and PMAA/poly(divinylbenzene-*co*-acrylamide) (PMAA/P(DVB-*co*-AAm)) core-shell functional microspheres are shown as Figs. 3(a) and 3(c), respectively. Figure 3(a) indicated that PMAA/P(DVB-*co*-VPy) core-shell microspheres had spherical shape and slightly rough surface. The capsule structure of PMAA/P(DVB-*co*-AAm) core-shell microspheres was observed in TEM micrograph as shown in Fig. 3(c), which may be due to the different shrinkage characteristics between the non-crosslinked PMAA core and crosslinked P(DVB-*co*-AAm) shell. The non-crosslinked PMAA core tended to shrink much more during the drying process of the resultant core-shell microspheres than the crosslinked shell, during which the P(DVB-*co*-AAm) shell was likely to remain its previous size and shape. In such way, the capsule structure with a small void between PMAA core and P(DVB-*co*-AAm) shell was developed as observed in TEM characterization.

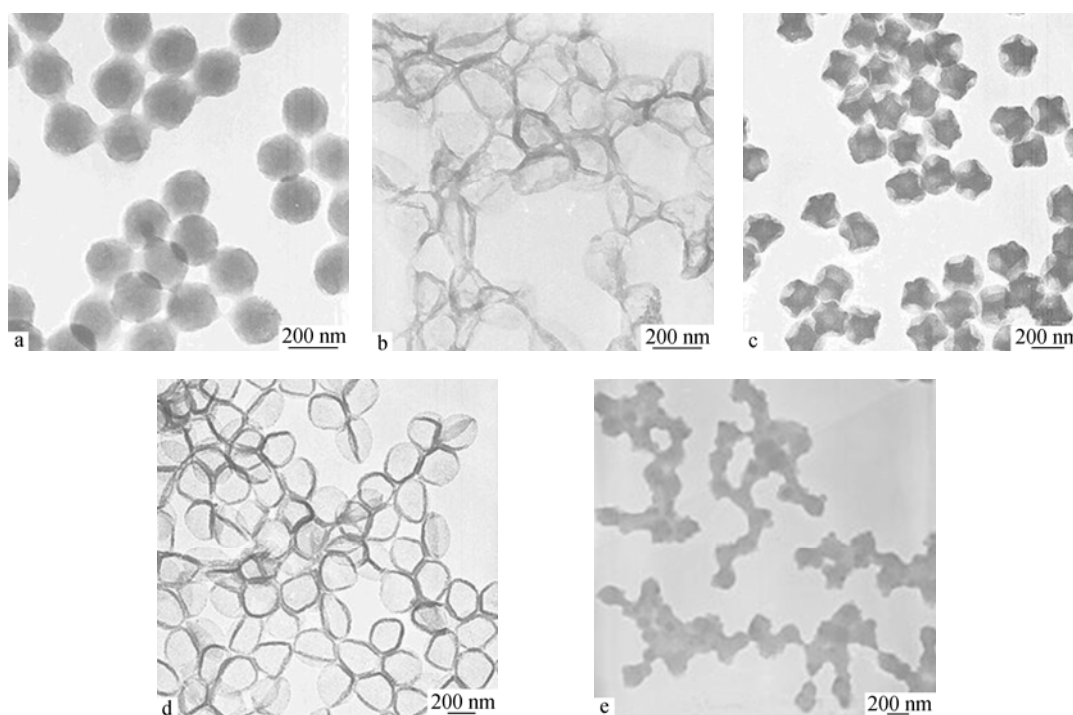


Fig. 3 TEM micrographs: (a) PMAA/P(DVB-*co*-VPy) core-shell microspheres, (b) P(DVB-*co*-VPy) hollow microspheres, (c) PMAA/P(DVB-*co*-AAm) core-shell microspheres, (d) P(DVB-*co*-AAm) hollow microspheres and (e) PMAA/PDVB irregular particles

The size and size distribution of the resultant PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres were summarized in Table 1. The average diameters were significantly increased from 160 nm of PMAA core to 194 and 216 nm for PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres, respectively. This meant that the sizes of the functional shell-layers were 34 and 56 nm after the second-stage polymerization for PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres, respectively.

The seeded-copolymerization of DVB as crosslinker and the functional comonomers, VPy and AAm, in the

presence of PMAA particles as cores leading to PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres was studied further by FT-IR spectra as shown in Fig. 4. The FT-IR spectrum of PMAA/P(DVB-*co*-VPy) has a peak at 710 cm^{-1} corresponding to the vibration of phenyl groups of PDVB segments and a peak at 1540 cm^{-1} attributing to the stretching vibration of pyridyl groups. The FT-IR spectrum in Fig. 4(c) behaves a very strong peak at 1716 cm^{-1} due to the stretching vibration of the carbonyl bond of the amide group and together with a peak at 3197 cm^{-1} attributing to the adsorption of N—H bonds of the amide group for PMAA/P(DVB-*co*-AAm) core-shell microspheres. The essential role of the hydrogen-bonding interaction between the carboxylic acid groups of PMAA cores with either the pyridyl groups of VPy or amide groups of AAm for the growth of the corresponding PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres was proven further by the formation of irregular particles in the presence of PMAA as core only for the second-stage polymerization of DVB as shown in Fig. 3(e) from TEM characterization. All these results demonstrated the successful preparation of the PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres.

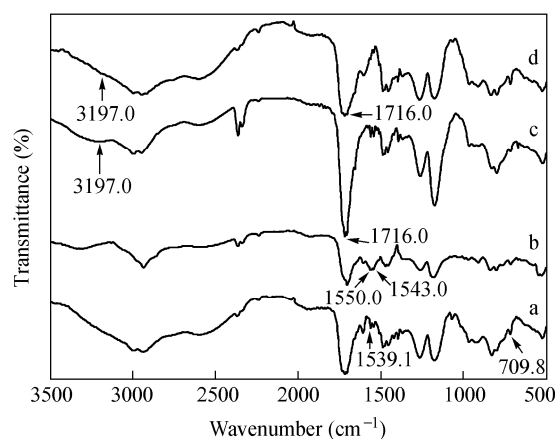


Fig. 4 FT-IR spectra of the polymer microspheres: (a) PMAA/P(DVB-*co*-VPy) core-shell microspheres, (b) P(DVB-*co*-VPy) hollow microspheres, (c) PMAA/P(DVB-*co*-AAm) core-shell microspheres and (d) P(DVB-*co*-AAm) hollow microspheres

The TEM micrograph of hollow poly(DVB-*co*-VPy) microspheres with shell thickness of 25 nm is shown in Fig. 3(b), in which the convincing hollow structures with circular rings and a cavity in the interior are observed. The deformed particles in Fig. 3(b) indicated that the P(DVB-*co*-VPy) shell layer was not thick enough to retain the shape of the cavity during the selective removal of PMAA cores. The hollow P(DVB-*co*-AAm) microspheres were obtained as shown in Fig. 3(d) with convincing hollow-sphere structures and the presence of circular rings of sectioned spheres and a cavity in the interior. These results demonstrated that the P(DVB-*co*-AAm) shell-layer was thick enough to support the cavity formed during the removal of PMAA cores.

The reservation of the pyridyl group on the shell-layer of P(DVB-*co*-VPy) hollow microspheres was confirmed further by FT-IR spectrum in Fig. 4, which had a strong peak at 1558 cm^{-1} contributing to the vibration of phenyl groups from PDVB species together with a peak at 1543 cm^{-1} corresponding to the typical stretching vibration of the pyridyl group. The presence of a strong peak at 1720 cm^{-1} may be due to the strong hydrogen-bonding interaction between the carboxylic acid group of PMAA core and the pyridyl group of P(DVB-*co*-VPy) shell, which caused part of PMAA core difficult to be removed during the formation of the hollow P(DVB-*co*-VPy) structure. The mechanism for the hydrogen-bonding interaction between the carboxylic acid group and pyridyl group has been investigated in detail by our previous works for the formation of the core-shell polymer microspheres^[30, 33] and the construction of raspberry-like polymer composites^[6]. The presence of amide groups in P(DVB-*co*-AAm) hollow microspheres was confirmed by FT-IR spectrum as shown in Fig. 4, which had a weak peak at 3197 cm^{-1} corresponding to N—H bonds of the amide group. The mechanism for the

hydrogen-bonding between amide groups and carboxylic acid groups has been investigated in detail by our previous work for the preparation of raspberry-like polymer composites^[34]. The carboxylic acid, pyridyl and amide-functionalized shell-layer of these hollow polymer microspheres will enable them suitable for the applications as micro-reactors in catalysis and adsorption.

CONCLUSIONS

Hollow P(DVB-*co*-MAA) and P(EGDMA-*co*-MAA) microspheres with different polarity were prepared by a facile route with a two-stage distillation precipitation polymerization and subsequent removal of PMAA core, in which the shell-layer was formed during the second-stage polymerization with the aid of the hydrogen-bonding interaction between the carboxylic acid group of PMAA cores and that of the residual MAA species in the reaction system. Hollow P(DVB-*co*-VPy) and P(DVB-*co*-AAm) microspheres with the shell-thickness of 25 and 35 nm were developed after the selective removal of PMAA cores from the corresponding PMAA/P(DVB-*co*-VPy) and PMAA/P(DVB-*co*-AAm) core-shell microspheres, during which the hydrogen-bonding interaction between the carboxylic acid group of PMAA cores with either the pyridyl group of VPy or the amide group of AAm played a key role for the formation of the monodisperse functional core-shell microspheres.

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