

Preparation of Poly(divinylbenzene-*co*-*N*-isopropylacrylamide) Microspheres and Their Hydrogen-Bonding Assembly Behavior for Raspberry-Like Core-Corona Polymer Composite

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ABSTRACT: Narrow-disperse poly(divinylbenzene-*co*-*N*-isopropylacrylamide) (poly(DVB-*co*-NIPAM)) functional microspheres with the diameter in the range of 630 nm and 2.58 μ m were prepared by distillation-precipitation polymerization in neat acetonitrile in the absence of any stabilizer. The effect of *N*-isopropylacrylamide (NIPAM) ratio in the comonomer feed on the morphology of the resultant polymer particles was investigated in detail with divinylbenzene (DVB) as crosslinker and 2,2'-azobisisobutyronitrile (AIBN) as initiator. The monodisperse poly(DVB-*co*-NIPAM) microspheres with NIPAM fraction of 20 wt % were selected for the preparation of raspberry-like core-corona polymer composite by

the hydrogen-bonding self-assembly heterocoagulation with poly(ethyleneglycol dimethacrylate-*co*-acrylic acid) [poly(EGDMA-*co*-AA)] nanospheres. Both of the functional poly(DVB-*co*-NIPAM) microspheres and the core-corona particles were characterized with scanning electron microscopy (SEM), Fourier transform infrared spectra (FTIR), and elemental analysis (EA). © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1350–1357, 2007

Key words: distillation-precipitation polymerization; *N*-isopropylacrylamide; raspberry-like polymer composite; hydrogen-bonding

INTRODUCTION

The functional polymer microspheres with optimized characteristics, such as uniform size and shape, functionality of the base polymer, morphology of the polymer particles, and degree of crosslinking, have been widely used in various fields, such as biotechnology, metallic colloid stabilizer, chromatography separation, biomedical devices, coating additives, controlled release reservoirs, and in other areas.^{1–8} To date, work has been reported on the utilization of microspheres as microscopic markers for antigens and antibodies on the surface of the cells.⁹ The synthesis of hydrophilic microspheres with carboxylic acid, hydroxyl, and amino groups on the surface of the microspheres has been attempted by various techniques, in which the functional groups were used to covalently bind antibodies and other proteins to the particles. The control of the functionality, the size, and the uniformity of the

polymer microspheres has been a major area of interest, especially for the micron and nano-size range.

Recently, thermally responsive poly(*N*-isopropylacrylamide) (PNIPAM) microgels have attracted much attention because of their scientific importance and industrial applications.¹⁰ The NIPAM microspheres are commonly prepared by emulsion polymerization,^{11,12} dispersion polymerization,^{13,14} and precipitation polymerization.^{14,15} However, the surfactants in aqueous solution and stabilizers in organic solution are critical to stabilize the polymer phase and to avoid the aggregation of particles in dispersion and emulsion polymerizations, respectively. Precipitation polymerization is unique to afford polymer microspheres with uniform size and shape, which can lead to narrow-disperse particles free of any added surfactant or stabilizer. PNIPAM thermoresponsive hydrogels with low crosslinking degrees were often prepared by these methods in the range of nano- or submicrometer size for the application as biological carrier.¹⁶

The raspberry-like composites consisting of two kinds of particles have attractive characteristics, such as unique morphology, designed surface properties, large surface area, and high light-scattering ability when compared with the spherical microspheres. Raspberry-like core-shell composite particles were once synthesized by self-assembly technique through

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the electrostatic interaction between the positively charged polyferrocenylsilane microspheres with negatively charged silica particles.¹⁷ Heterocoagulation of large and small oppositely charged colloid particles, accompanied by spreading of small beads over the surface of large spheres, has offered a promising alternative to the synthesis of core-shell particles.¹⁸ The interaction between two different macromolecules plays an important role in a living system since biological phenomena such as enzymatic process and protein synthesis are indebted principally to specific intermacromolecular interactions and structural properties of the resultant macromolecular assemblies. Walt and coworkers have used the heterocoagulation technique through the specific chemical and biological interactions as a way to control the structure of the particle assembly.¹⁹ The hydrogen-bonding interaction has been utilized widely to fabricate the multilayer films of weak polyelectrolytes by self-assembly technique.^{20,21} These findings suggest the possibility to employ the hydrogen-bonding interaction as a useful driving force for the preparation of raspberry-like polymer composite particles.

Recently, we reported the distillation-precipitation polymerization as a novel technique to afford monodisperse poly(divinylbenzene) (polyDVB)²² and hydrophilic polymer microspheres with carboxylic acid groups²³ in neat acetonitrile in the absence of any stabilizer or surfactant. Furthermore, the anomalous polymer particles with raspberry-like structure having uneven surfaces were prepared by a self-assembly heterocoagulation of poly(ethyleneglycol dimethacrylate-*co*-acrylic acid) [poly(EGDMA-*co*-AA)] nanospheres on poly(divinylbenzene-*co*-styryl methyl pyridinium chloride) [poly(DVB-*co*-StMPyCl)] surfaces based on a charge compensation mechanism through the affinity complex between carboxylic acid and pyridinium group.²⁴ In the present article, monodisperse polymer microspheres having PNIPAM component were prepared by distillation-precipitation polymerization of divinylbenzene (DVB) as crosslinker and *N*-isopropylacrylamide (NIPAM) with 2,2'-azobisisobutyronitrile (AIBN) as initiator in neat acetonitrile in the absence of any stabilizer or surfactant and the core-corona composite polymer particles with raspberry-like morphology having uneven surfaces were afforded by the self-assembly of poly(EGDMA-*co*-AA) nanospheres on poly(DVB-*co*-NIPAM) surfaces based on hydrogen-bonding interaction.

EXPERIMENTAL

Chemicals

Divinylbenzene (DVB80, 80% DVB isomers, Shengli Chemical Technical Factory, Shandong, China) was washed with 5% aqueous sodium hydroxide, water, and

dried over anhydrous magnesium sulfate prior to use. *N*-isopropylacrylamide (NIPAM) was purchased from Acros and recrystallized from hexane. Ethyleneglycol dimethacrylate (EGDMA) was obtained from Aldrich Chemical and utilized without any further purification. Acrylic acid (AA) was purchased from Tianjin Chemical Reagent II and purified by vacuum distillation. 2,2'-Azobisisobutyronitrile (AIBN) was analytical grade available from Chemical Factory of Nankai University and was recrystallized from methanol. Acetonitrile (analytical grade, Tianjin Chemical Reagents II) was dried over 4 Å molecular sieves and purified by distillation before utilization. The other reagents were of analytical grade and utilized without any further purification.

Preparation of poly(DVB-*co*-NIPAM) microspheres

Crosslinked poly(DVB-*co*-NIPAM) microspheres were prepared by distillation-precipitation polymerization of DVB80 and NIPAM with AIBN as an initiator in neat acetonitrile in absence of any additive or surfactant. A typical procedure for the distillation-precipitation polymerization: DVB80 (1.7 mL, 1.6 g, 12.3 mmol), NIPAM (0.4 g, 3.5 mmol) (total loading of comonomer as 2.5 wt % of the reaction medium) and AIBN (0.04 g, 0.24 mmol, 2 wt % relative to the total comonomers) were dissolved in 80 mL of acetonitrile in a dried two-necked flask attaching with a fractionating column, Liebig condenser, and a receiver. The flask was submerged in a heating mantle and the reaction mixture was heated from ambient temperature till boiling state within 30 min, and the reaction system was kept under refluxing state for 20 min. Then, the solvent began to be distilled from the reaction system. The initial homogeneous reaction mixture became milky white after boiling for 15 min. The reaction was ended after 40 mL of acetonitrile and was distilled from the reaction system within 1.5 h. The resulting polymer microspheres were separated by vacuum filtration over a G-5 sintered glass filter and washed successively with THF, ethanol, and ether for three times. Then, the polymeric particles were dried at 50°C in a vacuum oven till constant weight.

The procedures for the other distillation-precipitation polymerizations were much similar to that of the typical one by altering the comonomer ratio of DVB80 and NIPAM, while the total comonomer feed and AIBN initiator were kept at 2.5 wt % of the reaction medium and 2 wt % corresponding to the whole comonomers, respectively. The reproducibility of the results was confirmed through several duplicate and triplicate experiments.

Preparation of raspberry-like polymer composite by self-assembly process

Monodisperse poly(EGDMA-*co*-AA) polymer microspheres were prepared according to our previous

work²³ by distillation–precipitation polymerization of EGDMA and AA (EGDMA/AA = 4/6 as volume ratio in the comonomer feed) with AIBN initiator in neat acetonitrile. The loading capacity of the accessible carboxylic acid group on the polymer microspheres was determined by acid–base titration.

Self-assembly heterocoagulation of poly(EGDMA-*co*-AA) nanospheres and poly(DVB-*co*-NIPAM) microspheres was performed as follows: 0.05 g of crosslinked poly(DVB-*co*-NIPAM) core particles were dispersed in 5 mL of suspension of poly(EGDMA-*co*-AA) nanospheres (10 mg/mL) in ethanol on a SHA-B shaker. The self-assembly heterocoagulation was carried out at room temperature with gentle agitation by rolling the bottles in a horizontal position to ~40 rpm overnight. The resultant heterocoagulates were separated by centrifugation and dried in a vacuum oven at room temperature overnight.

Characterization

The morphology of the polymer microspheres and the resultant raspberry-like composite heterocoagulates was studied by scanning electron microscopy (SEM) using a Scanning Electron Microscope Quanta-200. All of the SEM size data reflect the averages about 100 particles each, which are calculated according to the following formula:

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

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

where, U is the polydispersity index, D_n is the number–average diameter, D_w is the weight–average diameter, and D_i is the diameter of the determined microspheres.

Transmission electron microscopy (TEM) was determined by a Tecnai G² 20 S-TWIN Microscope.

Fourier transform infrared analysis was performed on a Bio-Rad FTS 135 spectrometer with scanning over the range of 400–4000 cm⁻¹. Elementary analysis was determined on a PerkinElmer 2400 instrument to determine the nitrogen content of the resulting polymer microspheres.

RESULTS AND DISCUSSION

PolyDVB²² and poly(divinylbenzene-*co*-chloromethylstyrene) (poly(DVB-*co*-CMSt))²⁵ were prepared in our previous works by distillation–precipitation polymerization, in which the crosslinker such as DVB and monovinyl comonomers used were styrenic and hydrophobic in nature. Here, we intend to utilize this technique to prepare monodisperse hydrophilic microspheres with thermoresponsive component NIPAM

and investigate the self-assembly behavior of the resultant poly(DVB-*co*-NIPAM) with poly(EGDMA-*co*-AA) nanospheres to afford core-corona raspberry-like polymer composites based on a hydrogen-bonding process.

Preparation of poly(DVB-*co*-NIPAM)

Crosslinked polymer networks afforded by free radical polymerization of NIPAM with crosslinker, such as methylene bisacrylamide (MBA), were found attractive as microgel colloidal particles, which exhibited thermosensitive properties with a dramatic change of their colloidal behavior (particle size, electrophoretic, and colloidal stability) above the low critical solubility temperature (LCST).^{15,26–30}

A series of experiments were initially designed to investigate the effect of NIPAM fraction in the comonomer feed on the morphology of the poly(DVB-*co*-NIPAM) particles resulting from the distillation–precipitation polymerization. The SEM micrographs of the poly(DVB-*co*-NIPAM) particles with different NIPAM fractions in the range of 0–40 wt % were illustrated in Figure 1.

Figures 1(a–d) showed the images of monodisperse microspheres obtained with the NIPAM fraction of 0, 5, 30, and 40 wt %, respectively. All these polymer particles had nearly perfect spherical shape with non-segmented surfaces. With NIPAM increasing further toward 30 wt %, irregular particles with a broad size distribution were obtained as shown in Figure 1(c). A few of second-initiated particles were observed when NIPAM fraction in the comonomer feed was higher than 30 wt % as shown in Figure 1(d) with NIPAM fraction of 40 wt % as a sample. This may be because of the different reactivity between DVB and NIPAM during the radical polymerization and the different solubility of polyDVB and PNIPAM in acetonitrile media, which was much similar to the case of the distillation–precipitation polymerization of DVB and AA in our previous work.²³ The solubility parameters of polyDVB, PNIPAM, and CH₃CN are 17.6, 21.2, and 24.3 MPa^{1/2}, respectively,³¹ which lead to the easier precipitation of oligomer of DVB than that of NIPAM from the reaction system. With the polymerization occurring with NIPAM feed higher than 35 wt %, the surface of the initially formed poly(DVB-*co*-NIPAM) microspheres cannot capture all the newly formed oligomers with more NIPAM fragments in the later stage because of the lower ability of the residual double bonds on the surface to capture the oligomers from the reaction system, which caused the second-initiated particles. On the other hand, the number of the nuclei formed during the polymerization decreased with increasing the NIPAM fraction in the comonomer feed (decreasing the crosslinking degree), which retarded the formation of nuclei and the parti-

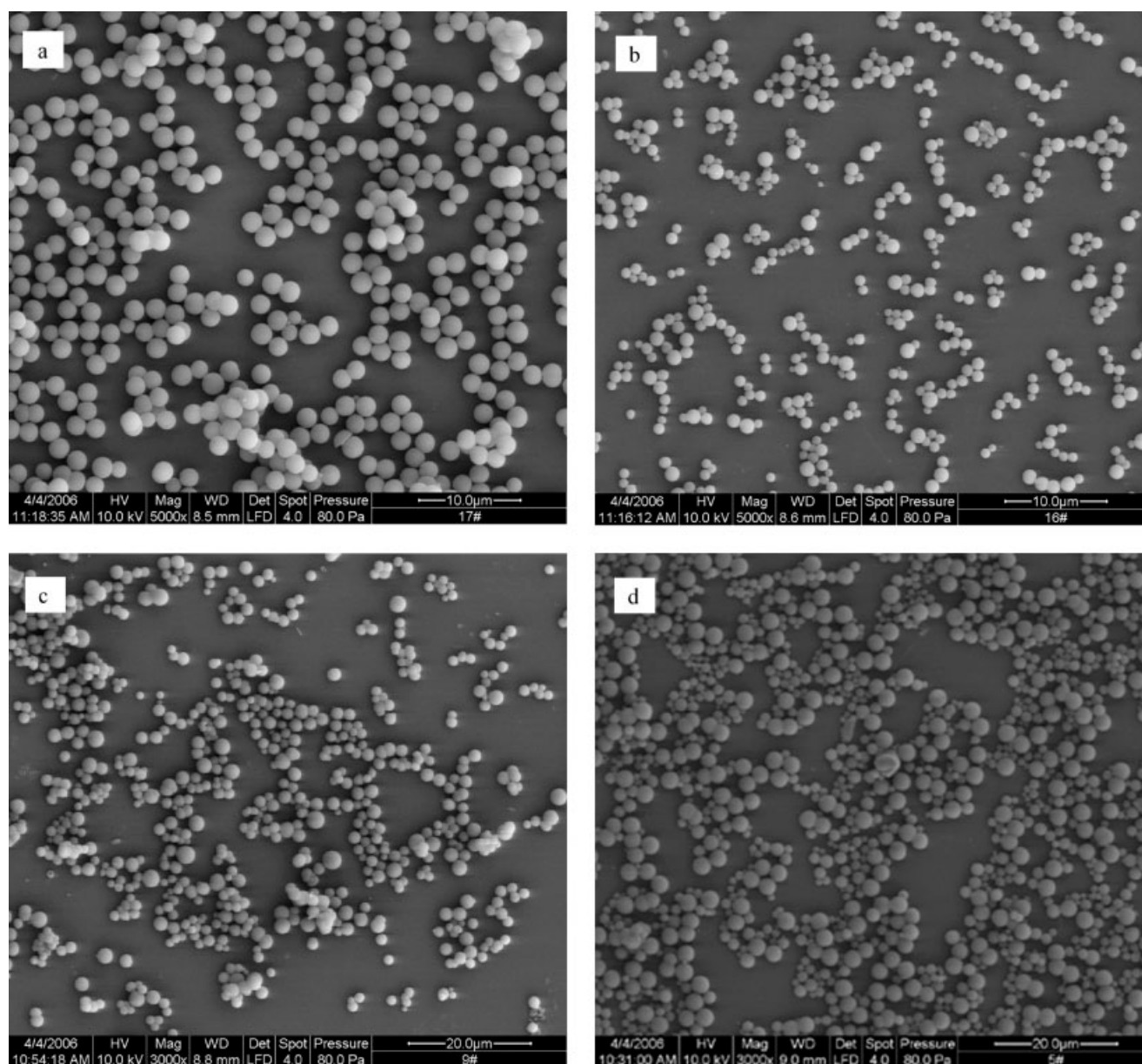


Figure 1 SEM micrographs of poly(DVB-co-NIPAM) microspheres with various NIPAM fraction in the comonomer feed: (a) 0; (b) 5; (c) 30; and (d) 40 wt %.

cle nucleation to result in the polymer particles with a broader distribution. When the NIPAM fraction in the comonomer feed was higher than 80 wt %, no precipitant was formed at all and only a significant sol fraction was isolated.

The size, size distribution, and the yield of poly(DVB-co-NIPAM) particles with different NIPAM fractions in the comonomer feed were summarized in Table I.

The size of the microspheres increased significantly from 1.29 μm at NIPAM of 0.05–2.58 μm at NIPAM of 20 wt % with the polydispersity index (U) around 1.002. Then, the size decreased with further enhancing NIPAM fraction to 25 wt %, especially in the case of

NIPAM fraction of 30 wt % originating from the broad size distribution with U of 1.340. The solubility parameters of the solvent played a significant role in disseminating the resultant polymer microspheres with a stable spherical shape in dispersion polymerization^{31,32} as well as precipitation polymerization.³³ The final particle size was determined by the conversion of the comonomers and the number of nuclei formed during the polymerization. With increasing NIPAM fraction in the polymer network, it can retard the formation of the nuclei because of the good solubility of PNIPAM fragment in acetonitrile to result in larger size for the polymerization. In other words, more nuclei were formed with higher crosslinking degree of DVB at the

TABLE I
Size, Size Distribution and the Yield of Poly(DVB-co-NIPAM) Microspheres

Entry	Fraction of NIPAM (wt %)	D_n (μm)	D_w (μm)	U	Nitrogen content (wt %)	Yield (%)	
E ₀	0	1.99	2.03	1.019	0.83	31	
E ₅	5	1.29	1.41	1.098	0.69	13	
E ₁₀	10	1.45	1.71	1.180	0.93	14	
E ₁₅	15	1.91	2.21	1.159	0.93	10	
E ₂₀	20	2.58	2.58	1.002	1.20	14	
E ₂₅	25	2.37	2.50	1.054	1.37	9	
E ₃₀	30	0.63	0.84	1.340	1.30	12	
E ₄₀	40	Second-initiated particles					

initial stage of polymerization, which tended to decrease the particle size. On the other hand, the conversion of the comonomers for the polymerization decreased dramatically from 31% of PDVB to around 12% of poly(DVB-co-NIPAM) system, which may be because of the increasing solubility of the oligomers with NIPAM fraction in acetonitrile. The resultant diameter of the polymer particles was determined by these two competitive factors. Therefore, the size of the poly(DVB-co-NIPAM) fluctuated in the range of 1.29 and 2.58 μm with the maximum size at NIPAM fraction of 20 wt % in the comonomer feed. With crosslinking degree decreasing further to 30 wt % (entry E₃₀, Table I), the smaller particles with a broad size distribution were afforded because of the much late formation of nuclei and slow particle nucleation during the polymerization.

Nitrogen content of the resultant poly(DVB-co-NIPAM) microspheres from elemental analysis (EA) increased considerably from 0.83 wt % of PDVB (the residual part from the AIBN initiator) to 1.37% of poly

(DVB-co-NIPAM) (DVB/NIPAM = 70/30 in mass ratio). The presence of the residual cyano group from AIBN initiator on the polymer microspheres was proven by the typical peak at 2236 cm^{-1} in Fourier transform infrared spectra (FTIR) spectra as shown in Figure 2(a) (E₀) assigning to the stretching vibration of cyano group. The successful incorporation of NIPAM to the poly(DVB-co-NIPAM) microspheres was confirmed further by FTIR spectra as shown in Figure 2(b–d) (E₁₀–E₃₀) with the characteristic peaks at 1675 cm^{-1} as well as 3425 cm^{-1} corresponding to the vibration of the second-amide group in NIPAM fragment. However, the nitrogen contents proved that the NIPAM content incorporated was much less than the feed composition. Such results may be originated from the higher reactivity of DVB crosslinker compared to that of NIPAM during distillation-precipitation polymerization with AIBN as initiator.

The residual double bonds on the surface of polymer microspheres played an important role for the formation and extension of monodisperse particles, which can capture the soluble oligomers and monomers to grow the polymer particles and prevent the coagulation during the distillation-precipitation polymerization. All the FTIR spectra of the resultant poly(DVB-co-NIPAM) microspheres had a weak peak at 1628 cm^{-1} because of the vibration of the residual double bonds on the surface, a strong peak at 1675 cm^{-1} corresponding to the vibration of the amide group in NIPAM fragment, a strong peak at 2929 cm^{-1} assigning to the vibration of the benzyl backbone, respectively. The ratios of peak area 1628/2929 and 1675/2929 cm^{-1} for all the polymer microspheres calculated by Kubelka-Munk units were summarized in Table II.

The results indicated that A_{1675}/A_{2929} (amide group in NIPAM) increased significantly from 0 of PDVB to 0.090 wt % of poly(DVB-co-NIPAM) (DVB/NIPAM = 30/70 as mass ratio in comonomer feed) with simultaneous decrease of A_{1628}/A_{2929} from 0.021 to 0.008 (residual double bonds). All these results demonstrated that the loading of the NIPAM on the poly(DVB-co-NIPAM) microspheres increased signifi-

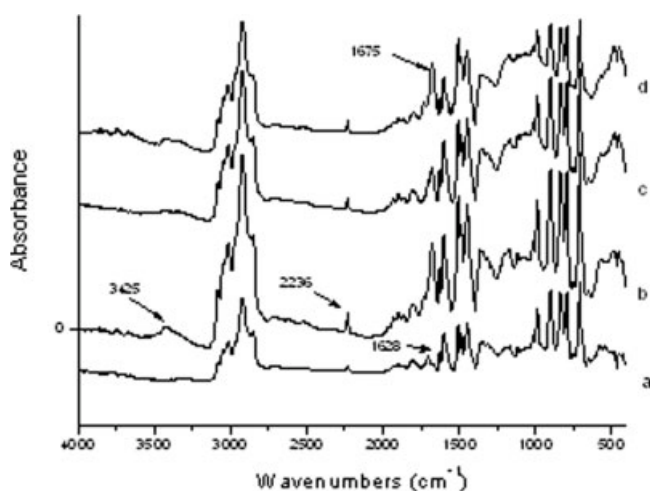


Figure 2 FTIR spectra of poly(DVB-co-NIPAM) microspheres with various NIPAM fraction in the comonomer feed: (a) 0; (b) 10; (c) 20; and (d) 30 wt %.

TABLE II
Area Ratios of Key FTIR Bands in Poly(DVB-co-NIPAM) Microspheres with Various NIPAM Fractions in the Comonomer Feed^a

Entry	A_{1628}/A_{2928}	A_{1675}/A_{2928}
a	0.021	0
b	0.017	0.045
c	0.013	0.069
d	0.008	0.090

(a) 0 wt %; (b) 10 wt %; (c) 20 wt %; (d) 30 wt %.

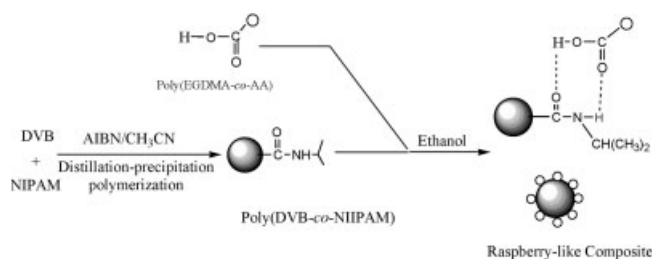
^a The peak areas adjusted according to the Kubelka-Munk method.

cantly with the increase of NIPAM fraction in the comonomer feed, which was consistent with the result of the EA.

Raspberry-like core-corona polymer composite via hydrogen-bonding self-assembly

It is critical to work with polymer particles rather than small molecules having only one limited spot for interaction because the microspheres provide many spots for interparticle interaction for the formation of a single integral polymer composite consisting of two different polymer microspheres. The hydrogen-bonding interactions as the driving force have been utilized to prepare ultra-thin films through layer-by-layer assembly.^{20,21,34} The resultant poly(DVB-co-NIPAM) microspheres were then used to prepare the raspberry-like core-corona composite through self-assembly heterocoagulation via hydrogen bonding interaction with poly(EGDMA-co-AA) nanospheres in ethanol as illustrated in Scheme 1.

It is well-known that PNIPAM and PAA are good hydrogen-bonding complementary partners, which have been used to fabricate the thermoresponsive thin films via self-assembly technique.³⁴ In the present work, the core-corona polymer composite with raspberry-like structure was produced based on an interparticle hydrogen-bonding mechanism as shown in Scheme 1. The hydrogen-bonding of the complementary partners between the amide group and carboxylic acid groups used in the present work were poly(DVB-co-NIPAM) (Entry E₂₀ in Table I) microspheres and poly(EGDMA-co-AA) nanospheres, in which poly(DVB-co-NIPAM) acted as core and poly(EGDMA-co-AA) behaved as corona, respectively. The typical SEM image of poly(DVB-co-NIPAM)/poly(EGDMA-co-AA) core-corona composites was shown in Figure 3(c), which was prepared from poly(DVB-co-NIPAM) [Fig. 3(a)] microspheres and poly(EGDMA-co-AA) nanospheres [Fig. 3(b)] with diameter of 180 nm and active carboxylic acid of 7.90 mmol/g determined by acid-base titration. The coverage was observed nearly constant after two particles was mixed immediately, which suggested



Scheme 1 The preparation of the raspberry-like core-corona polymer composite via hydrogen-bonding assembly heterocoagulation.

that their hydrogen-bonding assembly was a rapid process. In addition to the hetero-association between secondary amide and acid groups, the other aggregates also observed in Figure 3(c) may be because of the self-association in the presence of amide–amide and acid–acid interactions between poly(DVB-co-NIPAM) and poly(DVB-co-AA) particles, respectively.

The stability of the resultant heterocoagulates after ultrasonic treatment in ethanol was also investigated by TEM technique as shown in Figure 3(d). Poly(EGDMA-co-AA) particles were attached densely on the poly(DVB-co-NIPAM) surface, indicating the high stability characterization of raspberry-like composite and the strong affinity between the core and corona particles.

In our previous work, raspberry-like composites were formed by the self-assembly of poly(EGDMA-co-AA) nanospheres and poly(DVB-co-StMPyCl) microspheres through a charge compensation mechanism.²⁴ Here, the hydrogen-bonding interaction of amide group in NIPAM and carboxylic acid complementary partners between the core and corona particles played a key role as the driving force during the heterocoagulation, which was much different from those reported in the literature.^{17–19,24} The synergistic interparticle hydrogen-bonding of polymer composites was probably associated with the hydrogen donor of the carboxylic acid group in poly(EGDMA-co-AA) corona and the second-amide group in poly(DVB-co-NIPAM) core, while the lone-pair electron of the oxygen atom in amide group of poly(DVB-co-NIPAM) core and the oxygen atom of the carboxyl group on poly(EGDMA-co-AA) corona behaved as electron-donating group as illustrated in Scheme 1. To understand the interaction mode between poly(DVB-co-NIPAM) and poly(EGDMA-co-AA) particles during the self-assembly process, FTIR spectra were measured for these two particles and raspberry-like composites as shown in Figure 4. For poly(EGDMA-co-AA) and raspberry-like composites, the adsorption band of the carboxylic acid had a strong peak centered at 1730 cm⁻¹ corresponding to the characteristic stretch vibration of the carbonyl

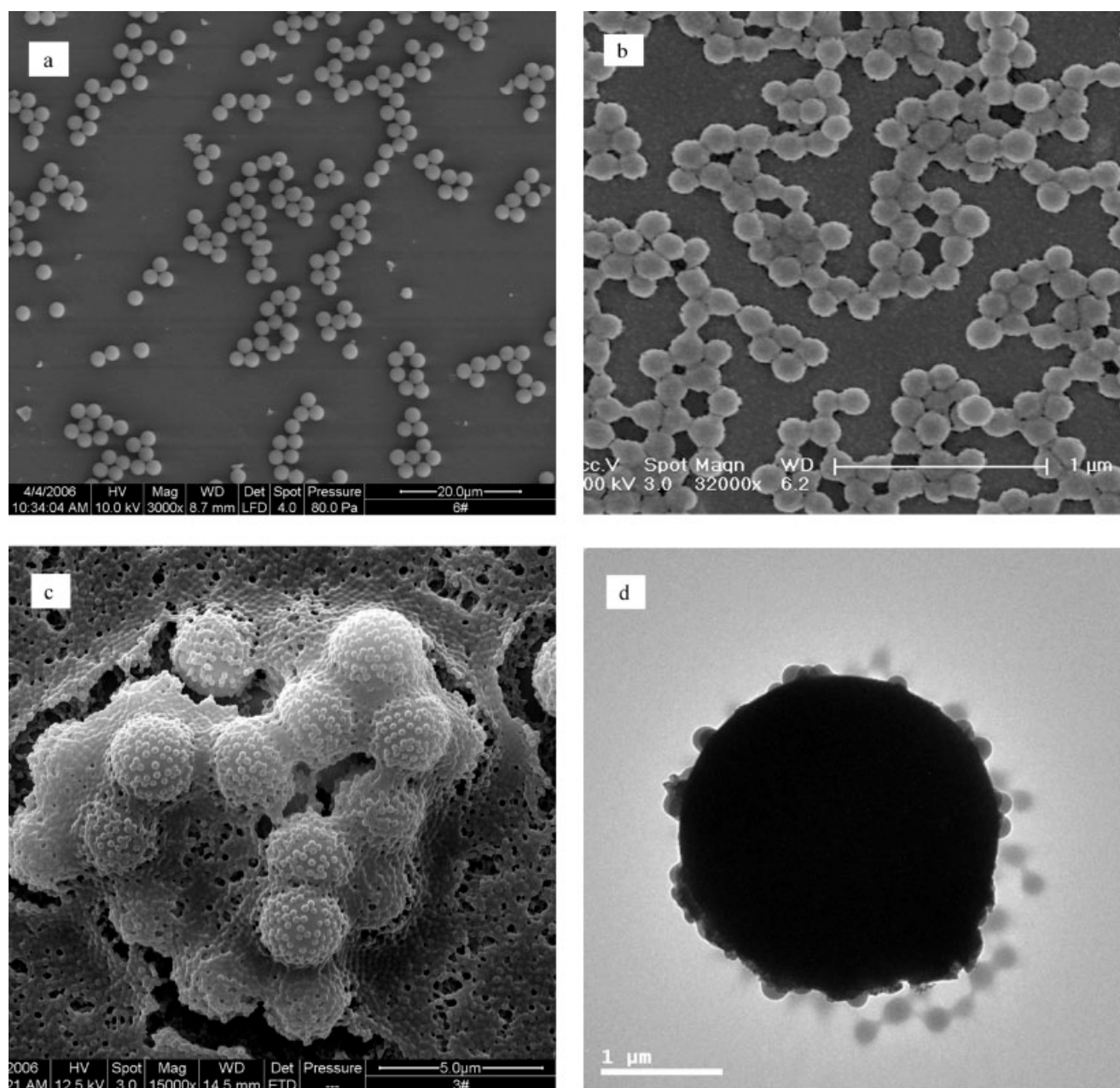


Figure 3 SEM micrographs of raspberry-like core-corona polymer composite: (a) poly(DVB-*co*-NIPAM) (NIPAM/DVB = 20/80 as mass ratio); (b) poly(EGDMA-*co*-AA) (EGDMA/AA = 40/60 as volume ratio); (c) raspberry-like core-corona composite; (d) TEM micrograph of polymer composite after ultrasonication bathing.

group in AA segment. For both of poly(DVB-*co*-NIPAM) and raspberry-like composites, the FTIR spectra contained a peak at 1675 cm^{-1} assigning to the characteristic vibration of carbonyl group in NIPAM segment. For the raspberry-like composites (curve c, Fig. 4), the appearance of a new peak at 1701 cm^{-1} demonstrated that the hydrogen-bonding existence occurred between the core and corona microspheres through the interparticle affinity complex interaction between the carboxylic acid and the secondary amide group. It was evident that such driving force originating from the interparticle

hydrogen-bonding for the self-assembly competed favorably with the existed-intramolecular association of carboxylic acid units within PAA segments at low pH.³⁵

The core-corona polymer assemblies have provided characteristics uniquely different from those in homogeneous media and film states, such as uneven surfaces with large area. It is evident that the hydrogen-bonding interaction can be used as a useful method to design the other composite with novel structure and surface. The resultant poly(DVB-*co*-NIPAM)/poly(EGDMA-*co*-AA) raspberry-like com-

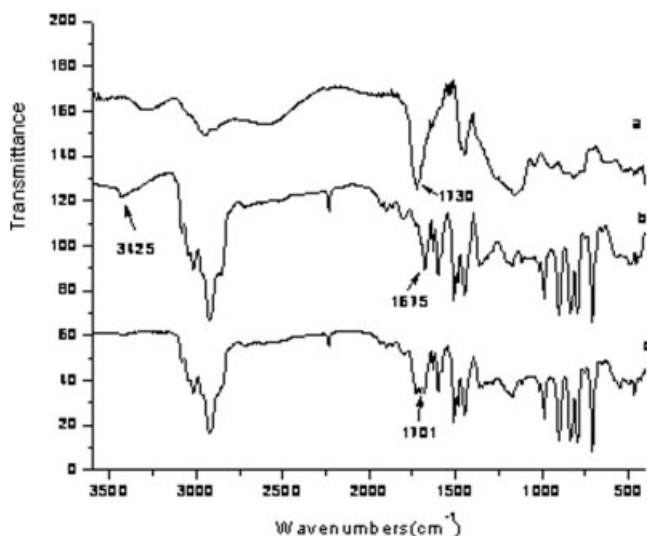


Figure 4 FTIR spectra: (a) poly(EGDMA-co-AA); (b) poly(DVB-co-NIPAM); and (c) raspberry-like polymer composite.

posite particles with hydrophilic carboxylic acid uneven surfaces may be expected to prepare superhydrophilic functional material because of the simplicity and efficiency of this procedure.

CONCLUSIONS

Narrowly dispersed poly(DVB-co-NIPAM) functional microspheres were prepared by distillation precipitation polymerization of NIPAM with DVB as crosslinker in neat acetonitrile without any additive or surfactant. The SEM images showed that the resultant poly(DVB-co-NIPAM) microspheres had a spherical shape with nonsegmented surfaces and narrow dispersion in the range of 1.45 and 2.58 μm in the presence of 0–25 wt % of NIPAM in the comonomer feed. The successful incorporation of NIPAM segment in the polymer microspheres was proven by EA and FTIR spectra, which increased considerably with increasing NIPAM fraction in the comonomer feed. The raspberry-like core-corona polymer composite based on the resultant poly(DVB-co-NIPAM) microspheres was prepared by self-assembly heterocoagulation with poly(EGDMA-co-AA) nanospheres through the synergistic hydrogen interaction between the second-amide group in core and the carboxyl group in the corona, which was confirmed further by FTIR spectra. The resultant raspberry-like composite was stable under ultrasonic treatment in ethanol.

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