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Synthesis, Characterization and Aqueous Solution Behavior of a pH-responsive Double Hydrophilic Block Copolymer

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The pH-responsive double hydrophilic block copolymer poly(ethylene glycol)-*b*-poly(methacylic acid-*co*-4-vinyl benzylamine hydrochloride salt) (PEG-*b*-PMAA/PVBAHS) was synthesized. A series of PEG-*b*-PMAA/PVBAHS with different molecule weights and compositions were characterized by IR, ^{1}H-NMR, elemental analysis and TGA. With different MAA/VBAHS ratio, the PEG-*b*-PMAA/PVBAHS copolymers had the different isoelectric point (IEP). Supermolecular structures of the block copolymers could be formed by the interionic interactions at different solution pH. Experiment results showed that the structures of the pH-responsive copolymers in aqueous solution could be changed at different pH environments. The aggregation of this double hydrophilic block copolymer in aqueous solution was determined by both of solution pH and copolymer composition.

Keywords: pH-responsive, double hydrophilic, block copolymer, solution behavior

1 Introduction

Double hydrophilic block copolymers have attracted more attention in the past a few years because of their characteristics as applications in aqueous environment (1). This kind of polymers are widely applied as induced nanoreactors (2), gene and drug delivery systems (3–5), additives for crystal design (6–9) etc. These applications depended on the functional group the copolymer contained. With some functional groups, they would be certain stimuli-responsive polymers, which can self-assemble into one or more types of micelles aggregates in water upon selectively rendering one of the blocks water insoluble under proper external stimulation (10–22). Special emphasis has been given to a kind of polymers which can respond to the pH changes in aqueous solution, making a variety of self-assembled supermolecular structures. The studies about this aspect have been carried out by some researchers (23–25). All the polymers they synthesized at least possess one type of functional group which is stimulated to the variation of aqueous solution pH, just the pyridine group and carboxylate group. The variation of solution pH value has changed the solubility of polymer, therefore, some supermolecular structures would be observed at certain pH value in the aqueous solution.

In the present paper we report the synthesis of a new pH-responsive double hydrophilic block copolymer, namely poly(ethylene glycol)-*b*-poly(methacylic acid-*co*-4-vinyl benzylamine hydrochloride salt). The copolymer consists of two blocks with different chemical nature. The PEG block just promotes the water solubility of the copolymer, and the PMAA/PVBAHS block contains two functional groups which can be responsive to pH change. The copolymer is water-soluble in certain acidic or basic conditions, which is determined by the composition of the copolymer, namely the ratio of the two functional groups. The aggregation structure of the copolymer was investigated by dynamic light scattering and transmission electron microscopy.

2 Experimental

2.1 Materials and Characterization

Poly(ethylene glycol) monomethyl ether (mPEG) (M_n = 2000 g/mol, Shanghai Chemical Reagents Co.) was dried under vacuum at 40°C for 72 h. Methacylic acid (AR, Shanghai Chemical Reagents Co.) was purified by decompressed distillation. 4,4′-azobis(4-cyano pentanoic acid) (95%, Aldrich), 4-vinyl benzyl chloride (90%, Aldrich), triphenylphosphine (99%, Aldrich) were used without further purification). All the other solvents and reagents were of analytical grade and used without purification.

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The ^{1}H-NMR spectra of the block copolymers were measured on a Bruker AVANCE400 NMR spectrometer. D_2O was used for field-frequency lock, and the observed ^{1}H chemical shifts are reported in parts per million (ppm) relative to an internal standard (TMS, 0 ppm). FT-IR experiment was performed on a Bruker Vector-22 spectrometer with the sample prepared as KBr pellets. The spectra were acquired in the frequency range 4000-400 cm^{-1} at a resolution of 4 cm^{-1} with a total of 16 scans. The result of elemental analysis (N, C and H) obtained on a Vario EI III elemental analyzer. TGA experiments were done on a TA instrument SDT Q600 with a heating rate of 10°C/min from 30°C to 500°C in a dynamic nitrogen atmosphere (flow rate = 100 mL/min).

Multi-angle light scattering laser light scattering (MALLS, Wyatt Technology Corporation) detection was used to determine the hydrodynamic radius distributions. The pH values of samples were determined by a pHS-3C acidometer equipped with E-201-C Electrode. Absorption at different pH was determined by 752 type spectrophotometer with the wavelength at 560 nm. Transmission Electron Microscopy (TEM) observations were conducted on a Hitachi H-600 electron microscope at an acceleration voltage of 100 kV. The samples for TEM observations were prepared by placing 10 μL of solutions on copper grids stained with a 0.2% buffered phosphotunstic acid solution.

2.2 Synthesis of Macroinitiator (MAI)

The macroinitiator (MAI) was prepared by mPEG and 4,4′-azobis(4-cyano pentanoic acid) as described elsewhere (26). 4,4′-Azobis(4-cyano pentanoic acid) (1.4 g, 5.0 mmol) and thionyl chloride (1.0 mL, 13.7 mmol) was dissolved in water-free toluene (5.0 mL), and the reaction mixture stirred at room temperature for 6 h. The produce of 4,4′-azobis(4-cyano pentanoic acid chloride) was purified by cold ether and cyclohexane mixed solvent (1:3 by volume ratio) three times and dried in vacuum (yield 75%).

4,4′-Azobis(4-cyano pentanoic acid chloride) was dissolved by dichloromethane (10 mL) and slowly dropped into the mPEG (10.0 g, 5.0 mmol, dissolved in 100 mL dichloromethane) in the presence of triethylamine (1.5 mL, 10.8 mmol) at 0–5°C. Then, the reaction was kept for 8 h. The product was washed by a saturated solution of sodium carbonate and precipitated from petroleum ether. The resulting product was dried in vacuum, the yield was 92%.

2.3 Synthesis of 4-Vinyl Benzyl Amine Hydrochloride Salt (VBAHS)

4-vinyl benzyl amine hydrochloride salt was synthesized by three-step procedure with 4-vinyl benzyl chloride, sodium azide and triphenylphosphine (27). 4-Vinyl benzyl chloride (4.58 g, 30 mmol) reacted with sodium azide (3.9 g, 60 mmol) in DMF (20 mL) and produced 4-vinyl benzyl azide. The produce of 4-vinyl benzyl azide was reduced by triphenylphosphine (6.0 g, 23 mmol) to give reactive primary amine compound. Then it was purified and converted to 4-vinyl benzylamine hydrochloric salt using concentrated hydrochloric acid. The yellowish product was obtained by pump filter and vacuum drying, the yield was 89%.

Table 1. The feeding composition and yield of PEG-*b*-PMAA/PVBAHS

Sample	*MAA (g)*	*VBAHS (g)*	*Yield (%)*
PEG-*b*-PMAA/PVBAHS-1	1.003	0.121	68.0
PEG-*b*-PMAA/PVBAHS-2	1.015	0.270	67.6
PEG-*b*-PMAA/PVBAHS-3	0.732	0.375	68.9
PEG-*b*-PMAA/PVBAHS-4	0.364	0.459	65.5

2.4 General Polymerization of PEG-*b*-PMAA/PVBAHS

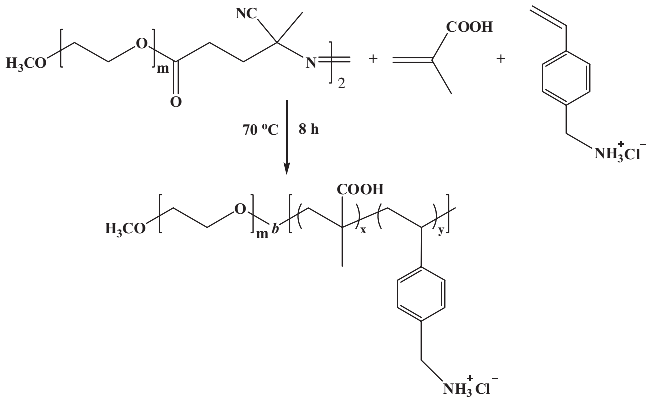
Typical procedures employed for the preparation of PEG-*b*-PMAA/PVBAHS was as follows. Methacylic acid and 4-vinyl benzyl amine hydrochloride salt with certain ratios were added to a round-bottomed flask and dissolved in proper H_2O, stirred for 10 min. MAI was added into the mixed solution. Nitrogen flow was inserted to the solution and kept for 30 min in order to remove oxygen. Then the flask was sealed with a sealing belt and dipped into 70°C oil bath equipped with durative magnetic stirring. After 8 h, the reaction solution was poured into 200 mL cool acetone, and the white precipitate was obtained. The product was purified by repetitious precipitation with cool acetone, and dried under vacuum at 40°C for more than 72 h. The feed with different content for the synthesis of block copolymers was shown in Table 1.

3 Results and Discussion

3.1 Synthesis of PEG-*b*-PMAA/PVBAHS

The block copolymers PEG-*b*-PMAA/PVBAHS were synthesized as schematically shown in Scheme 1. The copolymers synthesized with different content of MAA and VBAHS were shown in Table 1. PEG-*b*-PMAA/PVBAHS-1, -2, -3 and -4 were polymerized under identical conditions (1.0 g of MAI and 10 mL of H_2O) except for the ratio of feed mass. Yield of the block copolymers showed only slight variation with the ratio of feed mass.

Because of the interionic interaction between carboxylate and quaternary ammonium groups, PEG-*b*-PMAA/PVBAHS was hard to dissolve in neutral aqueous solution generally, but it was well dissolved in acidic and basic conditions. Figure 1 showed the ^{1}H-NMR spectra of PEG-*b*-PMAA/PVBAHS-3 in D_2O with the addition of hydrochloric acid. The corresponding peaks of the



Sch. 1. Synthesis of block copolymer PEG-*b*-PMAA/PVBAHS.

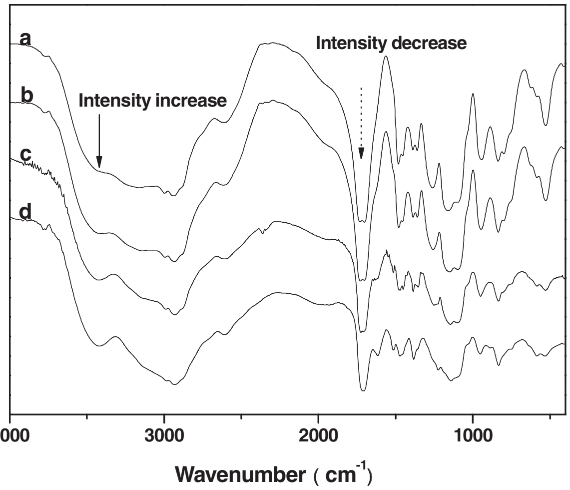


Fig. 2. FTIR spectra of PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d).

copolymer were marked on Figure 1 and the formation of PEG-*b*-PMAA/PVBAHS can be confirmed by the ^{1}H-NMR. The weight ratio of PEG, MAA and VBAHS were calculated from the integrals areas of peak 2 (3.63 ppm), peak 4 (0.86 ppm) and peak 7,8 (7.13 ppm) in ^{1}H-NMR spectra as listed in Table 2, and the weight ratio of VBAHS in the copolymers was also calculated from the nitrogen ratio determined by elemental analysis, which was in good agreement with the result obtained via ^{1}H-NMR spectra within experimental error. As the molecular weight of PEG block was known as 2000 g/mol, the copolymers molecular weights could be calculated from the weight ratio, which decreased with the PEG content. The results were shown in Table 2.

Figure 2 showed FTIR spectra of PEG-*b*-PMAA/PVBAHS-1 to -4 (the curves of a-d). The characteristic absorption peak at 3422 cm^{-1} was due to the N-H stretching vibration of VBAHS. The ratio of intensity of this peak increased gradually with an increasing amount of VBAHS (shown with solid arrows in Figure 2). PEG was defined by the absorption of C-O-C at 1088 cm^{-1}. The C=O of MAA characteristic absorption peak was observed at 1716 cm^{-1}. The intensity of this peak decreased with a decreasing amount of MAA (shown with dot arrow in Figure 2).

3.2 Thermal Properties of PEG-*b*-PMAA/PVBAHS

Figures 3 and 4 were the TGA and DTGA curves of PEG-*b*-PMAA/PVBAHS-1 to -4 (the curves of a-d). The copolymers showed two major weight loss steps under nitrogen atmosphere. The first transition occurred around 250°C, which might be caused by the loss of side groups. From the DTGA curves, it can be seen that the decomposition temperature increased with the decreasing mole ratio of MAA/VBAHS. It is due to the formation of inner salt by carboxylate and quaternary ammonium on the side groups of MAA and VBAHS. The mole percentage of MAA was much higher than VBAHS in the copolymers, with more VBAHS, more inner salt formed, which greatly improved the thermal stability of the side groups. The second transition occurred at about 440°C and was associated with the

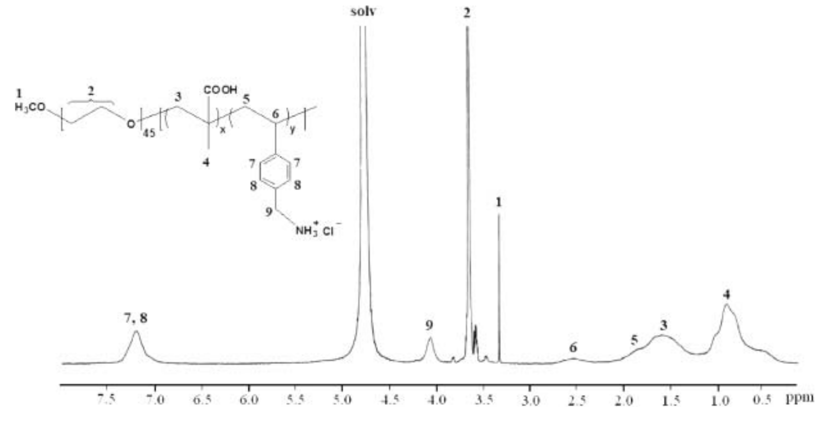


Fig. 1. ^{1}H-NMR spectrum of PEG-*b*-PMAA/PVBAH in D_2O with the addition of hydrochloric acid.

Table 2. The composition of PEG-*b*-PMAA/PVBAHS-1 to -4

	Elemental Analysis								
Sample	*C(wt%)*	*H(wt%)*	*N(wt%)*	*VBAHS*^{b} *(wt%)*	*VBAHS*^{a} *(wt%)*	*MAA*^{a} *(wt%)*	*PEG*^{a} *(wt%)*	*Mole Ratio (MAA/VBAHS)*^{a}	M_n^a *(g/mol)*
PEG-*b*-PMAA/PVBAHS-1	50.97	7.723	0.498	6.03	5.94	65.00	28.06	1/0.046	7056
PEG-*b*-PMAA/PVBAHS-2	51.81	7.810	1.008	12.20	12.41	53.96	33.63	1/0.117	5947
PEG-*b*-PMAA/PVBAHS-3	53.96	8.081	1.907	23.09	23.64	43.86	32.50	1/0.274	6154
PEG-*b*-PMAA/PVBAHS-4	54.97	7.859	3.110	37.65	37.12	29.45	33.43	1/0.640	5983

^{a}Determined via ^{1}H-NMR spectra, ^{b}Determined via elemental anylasis, M_n^a: Calculated molecular weight via ^{1}H-NMR spectra.

decomposition of the copolymer backbone, and the decomposition temperature decreased slightly with the increasing mole percentage of VBAHS, which might be attributed to the decreasing molecular weight of the copolymers. The weight loss percentage between 250°C and 440°C increased with the VBAHS ratio in copolymer; it is because, as the VBAHS ratio increases, the loss of side groups of VBAHS after the inner salts break up contributes to a greater weight loss percentage.

3.3 Aqueous Solution Behaviors of PEG-*b*-PMAA/PVBAHS

PEG-*b*-PMAA/PVBAHS was composed of two parts, one was PEG block and another was MAA and VBAHS copolymer, both of the two parts were hydrophilic. PEG only promoted the solubility of the copolymer, MAA and VBAHS contained carboxylate and quaternary ammonium groups, respectively. Because of the interionic interaction of the two groups, PEG-*b*-PMAA/PVBAHS was not easily solved when the solution pH is around isoelectric point (IEP). The copolymer could be suitably solved at a certain pH region, which was determined by the molecular ratio of MAA and VBAHS. The solubility at different pH was measured by a spectrophotometer. From the absorption and pH relation curves shown in Figure 5, we can see PEG-*b*-PMAA/PVBAHS-1 to -4 with a different molecular ratio of MAA and VBAHS had different IEP. The insoluble complexes formed at and around IEP. The IEP was not clearly detected because of the insolubility of the copolymers in the vicinity of this particular pH. As a crude approximation, the midpoint of the insoluble pH range was considered as the value of IEP (28, 29). For PEG-*b*-PMAA/PVBAHS-1, the insoluble pH range was around 3.2 to 3.6, so the approximate IEP was 3.4. With decreasing MAA and VBAHS ratio, the IEP moved to the higher pH, and the IEP for PEG-*b*-PMAA/PVBAHS-2 to -4 was respectively 4.2, 4.9 and 6.0. The result in Figure 4 also showed that the absorbance at the insoluble region decreased with increasing the VBAHS amount, which indicated the solubility of copolymers was promoted when containing more VBAHS. It was because the solubility of VBAHS was much better than MAA in water.

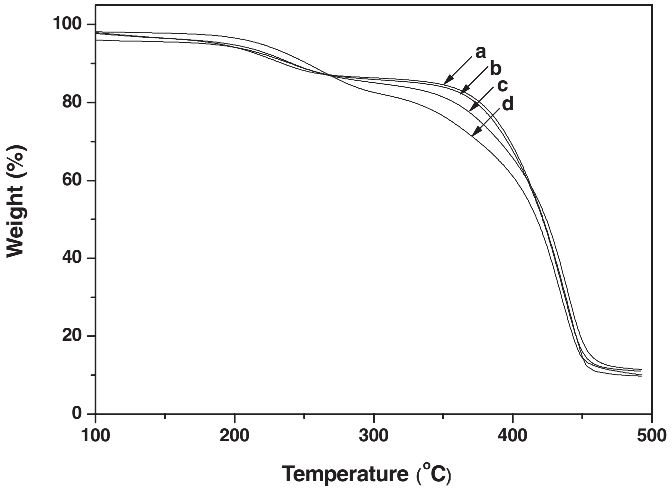


Fig. 3. TGA curves of PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d).

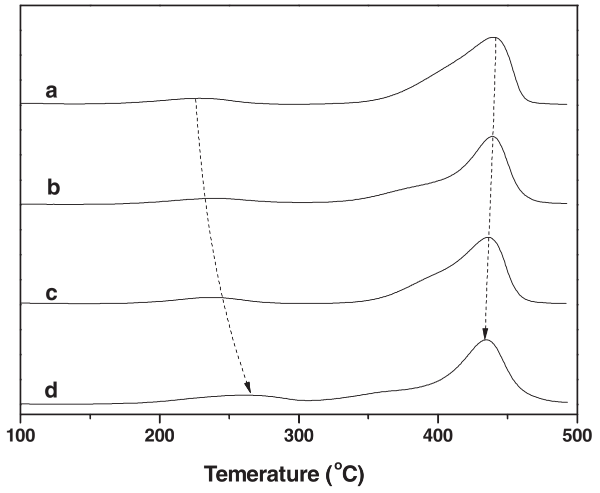


Fig. 4. DTGA curves of PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d).

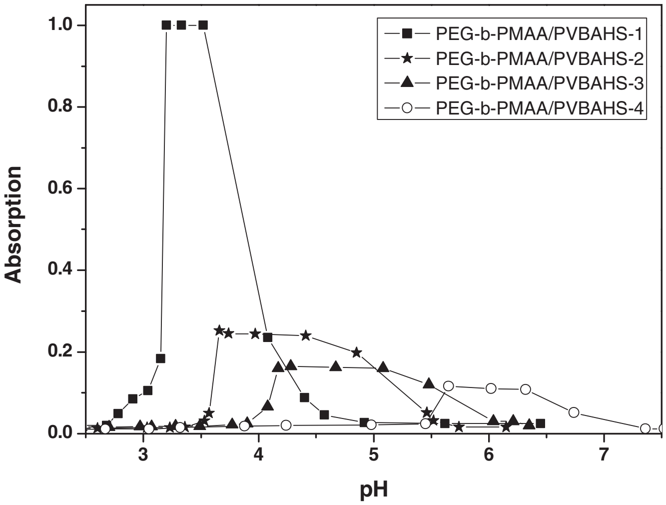


Fig. 5. Absorption vs pH for 0.5 g/L PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d).

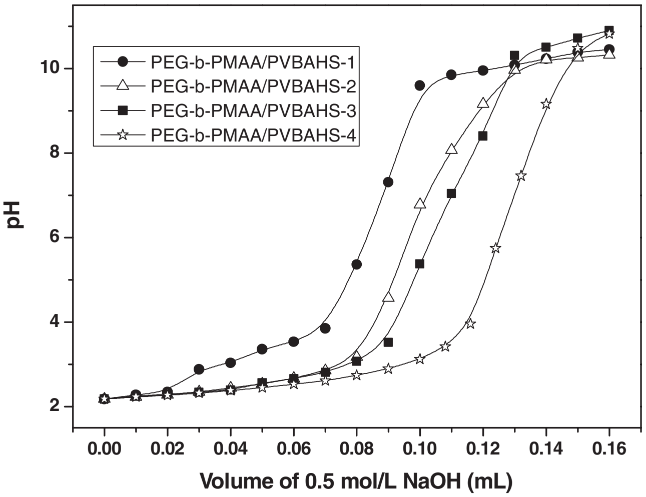


Fig. 7. Experimental titration of 0.5 g/L PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d) using 0.5mol/L NaOH.

The copolymer could be well dissolved in certain acidic and basic conditions, owing to the presence of a large amount H^+ or OH^- which greatly weakened the interaction between carboxylate and quaternary ammonium groups. There was a charge balance in the copolymer aqueous solution. When the solution pH was lower than the IEP, the copolymers had a net positive charge, and it turned out to be a net negative charge when the pH was higher than the IEP. At and around IEP, the cross-link structure was formed by the strong ionic interaction between intermolecules and made the copolymer insoluble. Figure 6 showed the schematic association models of the copolymers at different pH in aqueous solution. When the pH was much lower or much higher than the IEP, the copolymer chains mainly had the same charge. The repulsive force made the copolymer chains stave off each other and were hard to associate, so the copolymer became soluble.

Figure 7 showed the titration curves for PEG-*b*-PMAA/PVBAHS-1 to -4 in their 0.5 g/L aqueous solution. The initial pH of PEG-*b*-PMAA/PVBAHS solutions were all adjusted to 2.18, and then titrated with 0.5 mol/L NaOH (mL). As known, PEG-*b*-PMAA/PVBAHS had two different functional groups with different pK_a. The pK_a of VBAHS with quaternary ammonium groups was greater than the pK_a of MAA with carboxylate group. From the result in Figure 7, it can be seen the pK_a of PEG-*b*-PMAA/PVBAHS-1 to -4 increased, which agreed with the change of MAA/VBAHS ratio. The pK_a was greater when it contained more VBAHS.

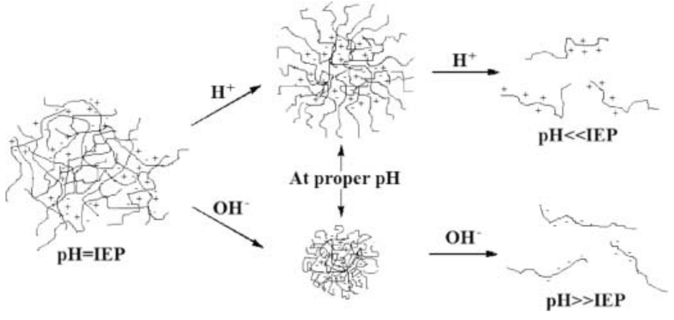


Fig. 6. Schematic association models of PEG-*b*-PMAA/PVBAH at different pH in aqueous solution.

PEG-*b*-PMAA/PVBAHS can be dissolved in both basic and acidic aqueous solutions. But the strong electrostatic interactions between the carboxylate and quaternary ammonium groups allow the formation of aggregates under suitable conditions. In order to investigate the supermolecular structures of PEG-*b*-PMAA/PVBAHS at different solution pH values, dynamic light scattering was used to measure the hydrodynamic radius in their aqueous solution. The distribution of hydrodynamic radius of PEG-*b*-PMAA/PVBAHS-1 to -4 at different pH values obtained by the dynamic light scattering was shown in Figure 8. From the result in Figure 8a for PEG-*b*-PMAA/PVBAHS-1, the hydrodynamic radius was much larger at acidic solution than at neutral or basic solution, and the radius was bigger at pH 2.87 than at 2.05. From the high values of hydrodynamic radius compared with the rather low copolymer molecular weight, it could be concluded that the supermolecular structures formed in solution, and the supermolecular structures formed at pH 2.87 were largest. Figure 8b for PEG-*b*-PMAA/PVBAHS-2 also showed the same regulation. For PEG-*b*-PMAA/PVBAHS-3 in Figure 8c, the hydrodynamic radius was large at both acidic and basic conditions but small at neutral conditions; it indicated that the supermolecular structures formed at

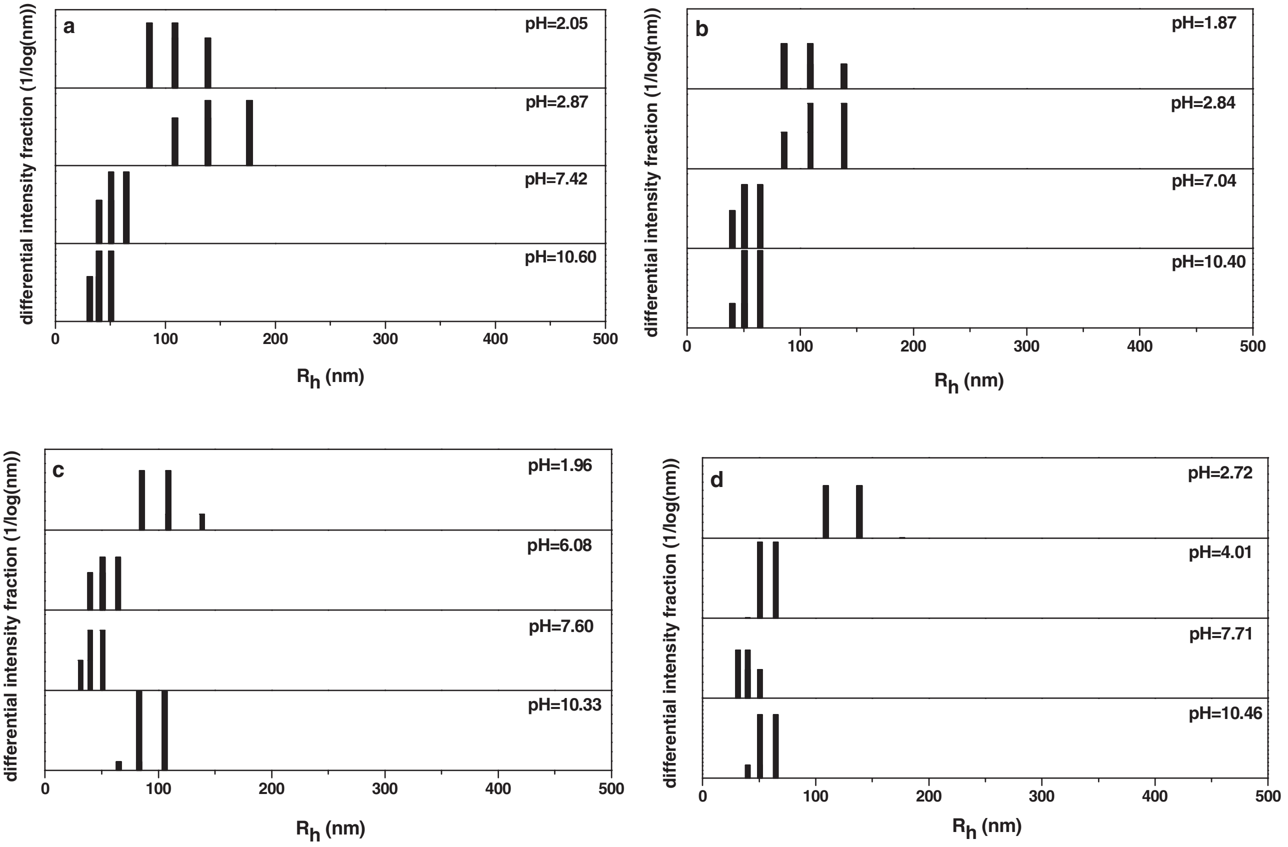


Fig. 8. The hydrodynamic radius distributions at different pH for PEG-*b*-PMAA/PVBAH-1 (a), PEG-*b*-PMAA/PVBAH-2 (b), PEG-*b*-PMAA/PVBAH-3 (c) and PEG-*b*-PMAA/PVBAH-4 (d).

neutral conditions were small. In Figure 8d, the smallest value appears at neutral conditions. From the results in Figure 8, it could be speculated that despite the different composition of PEG-*b*-PMAA/PVBAHS-1 to -4, they can all form supermolecular structures at different pH in aqueous solutions.

The supermolecular structures of copolymer can be observed by transmission electron microscopy. The supermolecular structures were shapeless for PEG-*b*-PMAA/PVBAHS-1 and -4, and spherical structures formed by PEG-*b*-PMAA/PVBAHS-2 and -3 at certain conditions in solution. At proper pH value around the IEP, certain structures could form. For PEG-*b*-PMAA/PVBAHS-2 at 3.0 of the solution pH, a loose spherical structure with the diameter at about 120 nm was observed (as shown in Fig. 9a). And the micelle with the diameter at about 50 nm formed at pH 7.5 for PEG-*b*-PMAA/PVBAHS-3 in aqueous solution (as shown in Fig. 9b). The sizes of the

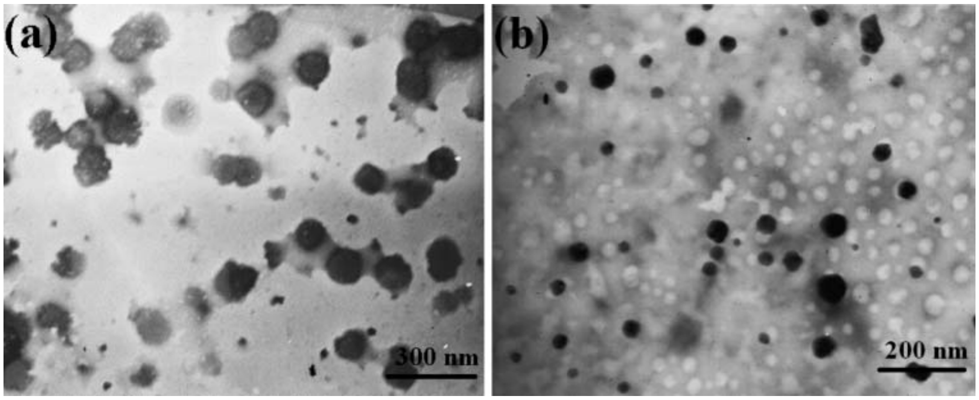


Fig. 9. TEM images for PEG-*b*-PMAA/PVBAH-2 aqueous solution at pH=3.0 (a), PEG-*b*-PMAA/PVBAH-3 at pH=7.5 (b).

loose spherical structure and micelle were agreement with the results measured by dynamic light scattering. When the PEG-*b*-PMAA/PVBAHS-2 solution pH was at 3.0, MAA in the copolymer partly ionized and interacted with the ionized VBAHS forming a hydrophobic core, and the PEG block formed a hydrophilic shell in aqueous solution. However, the lack of carboxylate anions, which interacted with quaternary ammonium cationic, made the supermolecular structure loose, and the loose spherical structure appeared. For the micelles formed in pH 7.5 of PEG-*b*-PMAA/PVBAHS-3 aqueous solution, the ionized MAA and VBAHS interacted tightly and formed a compact structure. The aggregation of PEG-*b*-PMAA/PVBAHS in aqueous solution had a great relationship with the composition of the copolymers. The transmission electron microscopy result showed that the MAA/VBAHS ratio should be kept in a proper region in order to form some regular supermolecular structures. If the MAA/VBAHS ratio was too high, there would not be enough ammonium cationic interaction with carboxylate anions no matter how the pH value of the solution changed. On the other hand, if the MAA/VBAHS ratio was too high, though the molecular ratio of MAA/VBAHS had not reached 1 for PEG-*b*-PMAA/PVBAHS-4, regular supermolecular structures would not appear either. It may due to the fact that the VBAHS was too easily soluble to form hydrophobic cores with MAA in aqueous solution. The results indicated that, besides the effect of solution pH, the character of the copolymers themselves determined by their compositions played basic roles in their aggregating behavior.

4 Conclusions

Poly(ethylene glycol)-*b*-poly(methacylic acid-*co*-4-vinyl benzyl amine hydrochloride salt) (PEG-*b*-PMAA/PVBAHS) with different compositions was synthesized and characterized. PEG-*b*-PMAA/PVBAHS was a pH-responsive copolymer, which can be dissolved in acidic or basic aqueous solution. With different compositions, the IEPs of the copolymers were different and increased with the VBAHS content. Supermolecular structures could form by the interionic interaction of the copolymers. With the variation of solution pH, different supermolecular structures appeared. When with proper compositions and pH values in the solution, micelle structure could be formed in the aqueous solution. The result showed that the aggregating behavior of PEG-*b*-PMAA/PVBAHS was determined by both the solution pH and copolymer compositions.

Acknowledgments

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