Preparation of Poly(vinyl amine)-Grafted Crosslinked Poly(vinyl alcohol) Microspheres

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ABSTRACT: Crosslinked poly(vinyl alcohol) (CPVA) microspheres were first prepared via the suspension polymerization of vinyl acetate and the alcoholysis of poly (vinyl acetate). Afterwards, a two-step method involving graft polymerization and Hofmann degradation was used to prepare functional poly(vinyl amine)-grafted crosslinked poly(vinyl alcohol) (PVAm–CPVA) microspheres, onto which poly(vinyl amine) (PVAm) macromolecules were grafted. The graft polymerization of acrylamide (AM) on CPVA microspheres was performed with cerium salt as the initiator in an acidic aqueous medium, resulting in polyacrylamide (PAM)-grafted CPVA microspheres. Subsequently, the grafted PAM was transformed into PVAm via the Hofmann degradation reaction, and PVAm–CPVA microspheres were prepared. The effects of the main factors on the graft polymerization and Hofmann degradation were examined, and the reaction mechanisms were researched in depth. The experimental results showed that for the graft polymerization of AM on CPVA microspheres initiated by cerium salt, the acid concentration and the amount of cerium salt affected the grafting degree of PAM greatly. For the Hofmann degradation reaction of the grafted PAM, the amination degree of PVAm–CPVA microspheres was obviously affected by the amount of sodium hypochlorite in the presence of sodium hydroxide. The preliminary adsorption tests showed that PVAm–CPVA microspheres were multifunctional and had strong adsorption ability for Fe(III) ions by chelation action and for chromate ions (CrO_4^{2-}) by strong electrostatic interactions. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 3487–3494, 2009

Key words: adsorption; graft copolymers; polyamides; polyamines

INTRODUCTION

Polymeric carriers bearing amino groups are functional carrier materials. The chemical immobilization (or anchoring) of amino groups on polymer material can be realized via polymer reactions or graft polymerizations, and amino-functionalized carriers are obtained. Amino groups are very active groups, and a lot of chemical reactions can occur between amino groups and other chemical regents. Besides, amino groups can produce several kinds of secondary bond forces toward different substances. Thus, amino-group-bearing polymeric carriers are functional carrier materials, have special physicochemical properties, and have widespread applications in scientific and technical fields. For example, they can be used for the immobilization of biomacromolecules in biomedicine,[1,2] the removal and recovery of heavy metal ions in environmental protection,[3,4] the preparation of heterogeneous catalysts in synthetic chemistry,[5,6] the separation and purification of substances in material science,[7,8] and chromatogram stationary phases in analytical chemistry.[9,10]

Poly(vinyl amine) (PVAm) is a water-soluble polymer containing a mass of amino groups (primary amine groups). It is a functional polymer and has very important applications in scientific research and industrial production.[11–14] In this work, the monomer acrylamide (AM) was first grafted onto the surfaces of crosslinked poly(vinyl alcohol) (CPVA) microspheres, and this resulted in polyacrylamide-grafted crosslinked poly(vinyl alcohol) (PAM–CPVA) microspheres. Then, the grafted polyacrylamide (PAM) was transformed into PVAm via Hofmann degradation reaction, and poly(vinyl amine)-grafted crosslinked poly(vinyl alcohol) (PVAm–CPVA) microspheres were obtained. The influences of the main factors in the two-step preparation process of PVAm–CPVA were studied in depth. PVAm–CPVA microspheres are an amino-rich carrier material because there is one amino group in each chain unit of the grafted PVAm. The large number of amino groups affords the microspheres unique physicochemical characteristics, such as adsorption properties and reactivity. It can be expected that PVAm–CPVA microspheres as solid adsorbents will have wide application potential in

various fields, especially in biological and medical fields, because of the biocompatibility of the CPVA matrix. To our knowledge, a study on preparing PVAm-grafted CPVA micromolecules similar to this work has not been reported.

EXPERIMENTAL

Materials and equipment

CPVA microspheres were self-prepared, and the mean size was 180 μm. AM (Beijing Chemical Reagent, Inc., Beijing, China) was analytical-grade and was recrystallized from acetone. Ammonium cerous sulfate (Bode Chemical Engineering, Inc., Tientsin City, China) was analytical-grade. Sodium hypochlorite (NaOCl; 10 wt % aqueous solution; Damao Chemical Reagent Plant, Tianjin, China) was analytical-grade. The other reagents were commercial, analytically pure chemicals and were purchased from Chinese companies.

The instruments used in this study were as follows: a PerkinElmer 1700 infrared spectrometer (PerkinElmer Co., Waltham, MA), a Leo 438 VP scanning electron microscope (Leo Co., Cambridge, United Kingdom), a THZ-92C constant-temperature shaker equipped with a gas bath (Shanghai Boxun Medical Treatment Equipment Factory, Shanghai, China), a Unic 2602 ultraviolet–visible spectrophotometer (Unic Co., Shanghai, China), and a PHS-3C pH meter (Shanghai Precision Scientific Apparatus, Inc., Shanghai, China).

Preparation of CPVA microspheres with the suspension polymerization–alcoholysis method

CPVA microspheres were prepared with the suspension polymerization–alcoholysis method, and a typical procedure was as follows. Line-type poly(vinyl alcohol) (1.5 g) as a disperser was dissolved in a 100-mL aqueous solution of NaCl, and the continuous phase (water phase) was constituted. The water phase was poured into a four-necked flask. The monomer vinyl acetate (10 mL) and 3 mL of the crosslinker divinyl benzene were mixed and dissolved in each other, 0.1 g of the initiator azobisisobutyronitrile was dissolved in this solution, and the dispersed phase (oil phase) was composed. The oil phase was added to the water phase, and the contents were fully stirred to enable the two phases to be sufficiently dispersed each other. The suspension polymerization was carried out at a constant temperature of 65°C with stirring under an N_2 atmosphere for 7 h, resulting in white crosslinked poly(vinyl acetate) microspheres. The dried crosslinked poly(vinyl acetate) microspheres (5 g) were added to a 30-mL methanol solution of sodium hydroxide (NaOH; 4

wt %), the alcoholysis reaction was carried out at 40°C for 15 h, and CPVA microspheres were obtained. The morphology of CPVA microspheres was observed with scanning electron microscopy (SEM), and their mean size was measured. In this research, CPVA microspheres with a mean size of 180 μm were prepared and used.

Preparation of grafted PAM–CPVA microspheres

CPVA microspheres (0.6 g), 1.9 g of AM, and 50 mL of distilled water were added in turn to a four-necked flask equipped with a mechanical stirrer, a condenser, and an N_2 inlet. After the microspheres were soaked for 10 h so as to be fully swollen, 0.2 g of ammonium cerous sulfate and 0.5 mL of concentrated sulfuric acid were introduced, and the temperature was raised to 45°C. The graft polymerization was performed under an N_2 atmosphere at the constant temperature of 45°C for 6 h. By filtration, grafted PAM–CPVA microspheres were collected. These microspheres were soaked and washed with distilled water to remove a little PAM physically attached to the microspheres, and they were dried *in vacuo* to a constant weight. The grafting degree (wt %) of PAM of PAM–CPVA microspheres was determined with weighing method, and their chemical structure was characterized with infrared spectroscopy. In this study, the prepared and used PAM–CPVA microspheres had a grafting degree of 27.13%.

The concentrations of cerium salt and concentrated sulfuric acid were changed in series, and the graft polymerizations were conducted with other reaction conditions fixed to examine the effects of the two factors on the graft polymerization and to research the mechanism of the graft polymerization initiated by cerium salt.

Preparation of functional microspheres of PVAm–CPVA

Functional microspheres of PVAm–CPVA were prepared via the Hofmann degradation reaction of the grafted PAM. Ref. 15 was used, and some procedures were improved. Grafted PAM–CPVA microspheres (0.5 g) were soaked in 10 mL of distilled water containing dimethyl sulfoxide for 10 h so as to be fully swollen. The mixture was added to a three-necked flask, and this was followed by the addition of 15 mL of an aqueous NaOH solution, the concentration of which was 14 wt %. In the system, the molar ratio of NaOH units to AM units of the grafted PAM remained at 30 : 1. The contents in the flask were cooled to −3°C in a cryohydrate bath, and 4.5 mL of an aqueous NaOCl solution was added. The degradation reaction of the grafted PAM was carried out for 11 h with stirring. By filtration,

PVAm–CPVA microspheres that were produced were collected, washed many times with distilled water, and dried *in vacuo* to constant weight. The infrared spectrum of PVAm–CPVA microspheres was determined with the KBr pellet method, and the chemical structure was characterized.

The amination degree (mmol/g) of functional PVAm–CPVA microspheres was determined with the acid–base titration method, and the detailed procedure was as follows. A certain amount of PVAm–CPVA microspheres, weighed accurately, was soaked in a standard solution of HCl with a certain volume for 5 h; subsequently, the residual HCl was back-titrated with a standard NaOH solution, and the amination degree was calculated with the consumed volume of the NaOH solution.

The amount of NaOCl and the reaction temperature were varied in series, and the Hofmann degradation reaction was conducted with other reaction conditions fixed. The effects of the two main factors on the degradation reaction of the grafted PAM were examined, and the mechanism of the Hofmann degradation reaction was further researched.

Preliminarily testing of the adsorption characteristics of PVAm–CPVA microspheres

Examination of the adsorption ability of PVAm–CPVA toward Fe^{3+} ions

Aqueous solutions of $Fe(NO_3)_3$ with different concentrations at pH 4 were prepared in the range of 0.001–0.01 mol/L. $Fe(NO_3)_3$ solutions (100 mL) with different concentrations were placed in several conical flasks. Functional PVAm–CPVA microspheres (0.025 g), weighed accurately, were added to these solutions. These mixtures were shaken in a constant-temperature shaker at 30°C for 5 h. After a period of static standing, the supernatants (5 mL) were withdrawn, diluted, and made to have a constant volume. The concentration of Fe^{3+} ions of these supernatants was determined with a spectrophotometric method (with sulfosalicylic acid as a color-developing agent). The amount of adsorption [Q (g/100 g)] of PVAm–CPVA microspheres for Fe^{3+} ions was calculated according to eq. (1), and the adsorption isotherm was determined:

$$Q = \frac{(C_0 - C_1)V}{1000m} \tag{1}$$

where C_0 is the concentration of Fe^{3+} ions of the initial $Fe(NO_3)_3$ solution (g/L), C_1 is the concentration of Fe^{3+} ions of the supernatant (g/L), V is the volume of the adsorbate solution of $Fe(NO_3)_3$ (mL), and m is the weight of the adsorbent PVAm–CPVA microspheres (g).

Examination of the adsorption properties of PVAm–CPVA toward CrO_4^{2-} ions

Aqueous solutions of K_2CrO_4 with different concentrations at pH 4 were prepared in the range of 0.005–0.1 mol/L. K_2CrO_4 solutions (100 mL) with different concentrations were placed in several conical flasks. Functional PVAm–CPVA microspheres (0.025 g), weighed accurately, were added to these solutions. These mixtures were shaken at 30°C for 3 h. After a period of static standing, the supernatants (5 mL) were withdrawn, diluted, and made to have a constant volume. The CrO_4^{2-} ion concentration of these supernatants was determined with a spectrophotometric method (with diphenylcarbazide as a color-developing agent). The adsorption amount (g/100 g) of PVAm–CPVA microspheres for CrO_4^{2-} ions was calculated according to eq. (1) (the corresponding concentrations were changed as those of CrO_4^{2-} ions), and the adsorption isotherm was also determined.

RESULTS AND DISCUSSION

Reaction process for the preparation of PVAm–CPVA microspheres

A great number of hydroxyl groups exist on the surfaces of CPVA microspheres. According to the redox initiation mechanism of cerium salt,[16] a complex reaction between Ce^{4+} ions and the hydroxyl groups on CPVA will first occur, forming a complex. Subsequently, an oxidation process of a single electron transfer will occur, and the complex will soon be disproportionated, forming free radicals on the carbon atoms bearing the hydroxyl groups. Therefore, the graft polymerization of AM on CPVA microspheres is initiated, resulting in grafted PAM–CPVA microspheres. The Hofmann degradation reaction of the grafted PAM macromolecules on PAM–CPVA is conducted with NaOCl as the reaction reagent in the presence of excessive NaOH, and the grafted PAM is transformed into the grafted PVAM, resulting in the formation of PVAm–CPVA microspheres. The entire process to prepare PVAm–CPVA microspheres is expressed schematically in Scheme 1.

Characterization of the three kinds of microspheres

Morphology of CPVA microspheres

Figure 1 displays an SEM photograph of CPVA microspheres. The sphericity of the microspheres is excellent, and the grain diameter is more uniform. By the adjustment of the copolymerization conditions, microspheres with different grain diameters can be prepared.

(1) Graft polymerization of AM on CPVA microspheres initiated by cerium salt
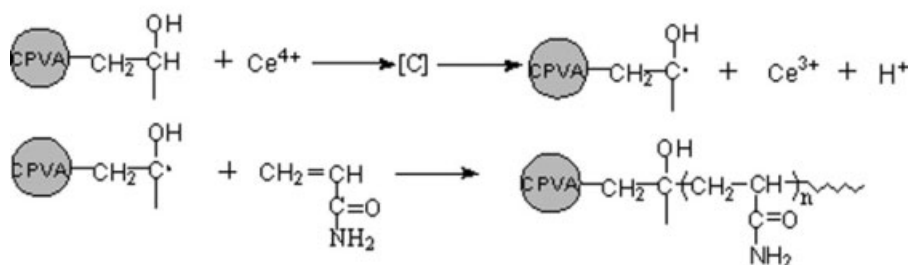
(2) Hofmann degradation reaction of grafted polyacrylamide
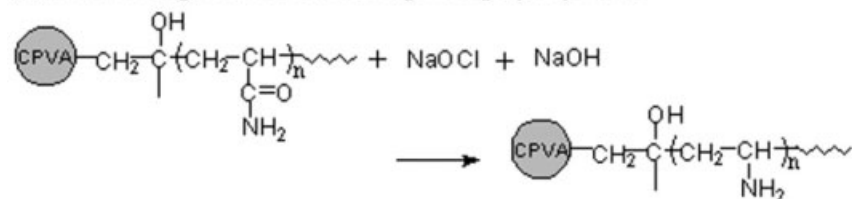
Scheme 1 Reaction process to prepare functional PVAm–CPVA microspheres ([C] = complex).

Infrared spectra of PAM–CPVA and PVAm–CPVA microspheres

Figure 2 presents the spectra of two kinds of microspheres, PAM–CPVA and PVAm–CPVA. In the spectrum of PAM–CPVA microspheres, the characteristic absorbance bands of PAM appear at 3444, 1710, and 1621 cm^{-1}. The first band can be ascribed to the stretching vibration of $-NH_2$ in the amido group, the second band can be attributed to the vibration absorption of carbonyl (C=O) in the amido group, and the last band should correspond to the deformation vibration absorption of $-NH_2$ in the amido group. The presence of these characteristic bands shows that PAM has been grafted onto CPVA microspheres, and the grafted microspheres PAM–

CPVA have formed via the graft polymerization of AM initiated by cerium salt. In the spectrum of PVAm–CPVA microspheres, the vibration adsorption of carbonyl (C=O) of the amido group at 1710 cm^{-1} has been weakened greatly, and some new bands have appeared. The deformation and stretching vibration adsorptions of the primary amine groups ($-NH_2$) appear at 1645 and 3435 cm^{-1}, respectively, and another new band at 1109 cm^{-1} should be attributed to the stretching vibration adsorption of the C—N bond of the primary amine groups ($-NH_2$). These spectrum variations show that the amido groups of the grafted PAM have been transformed into primary amine groups via the Hofmann degradation reaction, and the functional PVAm–CPVA microspheres have been formed.
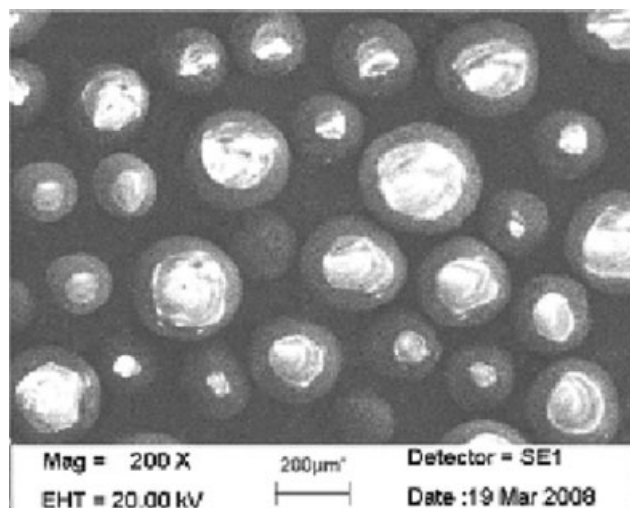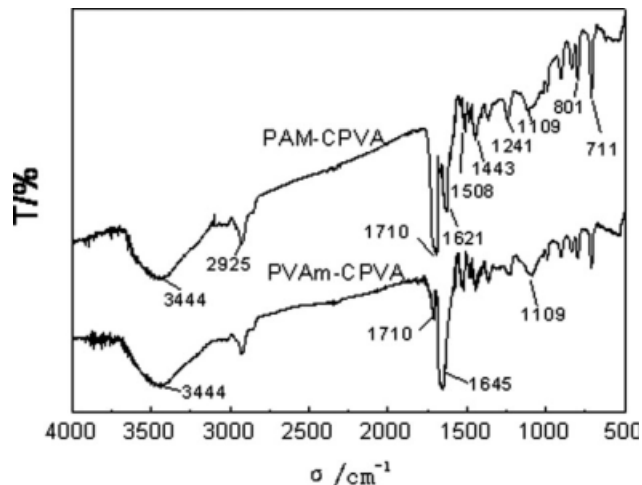

Figure 1 SEM image of CPVA microspheres.

Figure 2 FTIR spectra of PAM–CPVA and PVAm–CPVA microspheres (T = transmittance; σ = wavenumber).
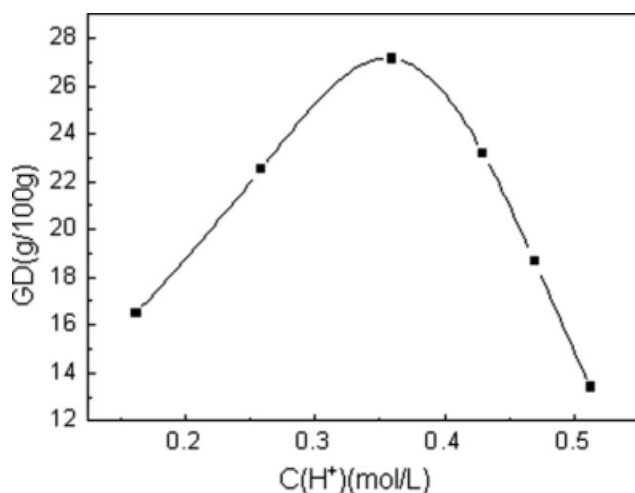
Figure 3 Grafting degree (GD) of PAM for PAM–CPVA microspheres as a function of the H^+ concentration [$C(H^+)$; conditions: cerium salt concentration = 5.98 $\times$ 10^{-3} mol/L; reaction temperature = 45°C; reaction time = 6 h].

Effects of the main factors on the graft polymerization of AM

Effect of the sulfuric acid concentration

In the graft polymerization system initiated by cerium salt, the concentration of sulfuric acid was changed in series with other reaction conditions kept fixed, and the grafting degree of PAM as a function of the sulfuric acid concentration (expressed as the concentration of H^+ ions) is shown in Figure 3.

Figure 3 shows that along with the increase of the concentration of H^+ ions, the grafting degree of PAM exhibits a variation trend of first increasing and then decreasing. When the concentration of H^+ ions is equal to 0.36 mol/L, there is a maximum grafting degree. These facts can be explained as follows. The Ce^{4+} ion has a stronger hydrolysis property (see the following expressions), so to suppress the hydrolysis of the Ce^{4+} ion, the graft polymerization should be performed in an acidic medium. In a certain concentration range of H^+ ions, the higher acid concentration will bring about a higher Ce^{+4} species concentration and a higher graft polymerization rate, which will result in the increase in the grafting degree of PAM. On the other hand, in the initiation step, H^+ ions will be produced (see the following expressions), and an overly high H^+ ion concentration will inhibit the initiation step[17] (this will make the second equilibrium in the following expressions shift to the left), leading to the reduction of primary free radicals. Therefore, the overly high concentration of sulfuric acid is disadvantageous for the graft polymerization of AM. By this token, in the graft polymerization system initiated by cerium salt, there is an adequate acid concentration. For this

study system, the suitable concentration of H^+ ions is 0.36 mol/L, and over this concentration, the grafting degree will decrease with a continuous increase of the sulfuric acid concentration:

Hydrolysis of Ce^{4+} ions

$$Ce^{4+} + H_2O \rightleftharpoons Ce(OH)^{3+} + H^+$$

Formation of primary free radicals in initiation step

$$Ce^{4+} + ROH \longrightarrow \overset{\bullet}{R}OH + Ce^{3+} + H^+$$

Effect of the cerium salt concentration

The graft polymerizations of AM were carried out with different concentrations of cerium salt, and the relationship curve of the grafting degree with the concentration of the initiator, ammonium cerous sulfate, is presented in Figure 4.

Figure 4 shows that the grafting degree of PAM initially increases with the cerium salt concentration increasing up to 5.98 $\times$ 10^{-3} mol/L and then decreases. For this experimental result, a reasonable explanation involves the mechanism of the free-radical polymerization initiated by cerium salt. In the free-radical polymerization process initiated by cerium salt, except for the biradical and disproportionation terminations for the growing chains, there is another termination mode, oxidation termination,[18,19] as shown in the following expressions. For the graft polymerization of monomers on the surfaces of CPVA microspheres, the oxidation termination should be only a termination mode. Besides, in the graft polymerization system, the primary free radicals are also inactivated, probably because of
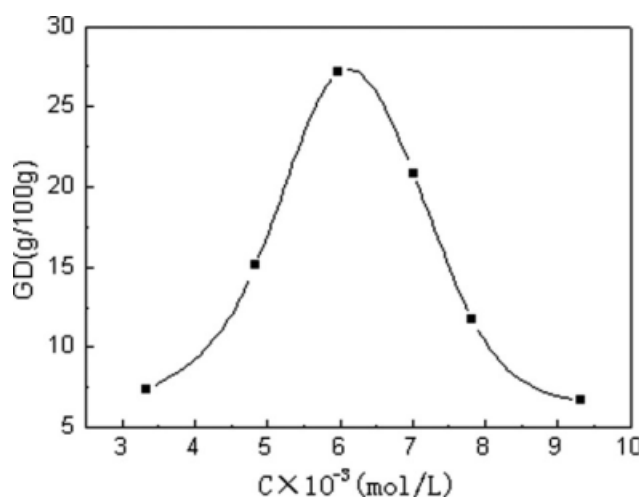

Figure 4 Grafting degree (GD) of PAM for PAM–CPVA microspheres as a function of the cerium salt concentration [C (cerium salt); conditions: sulfuric acid concentration = 0.18 mol/L; reaction temperature = 45°C; reaction time = 6 h].
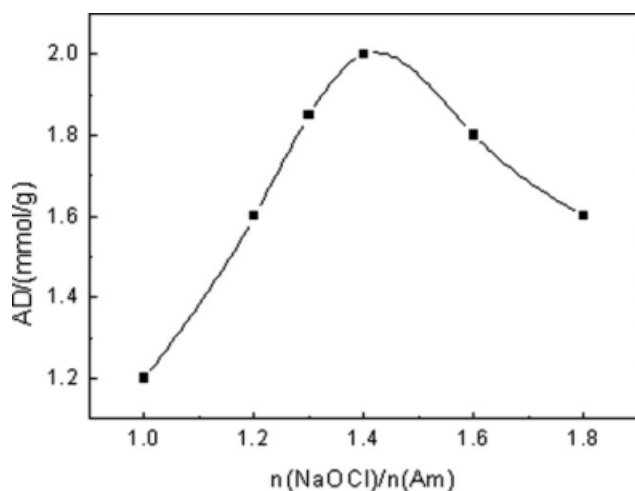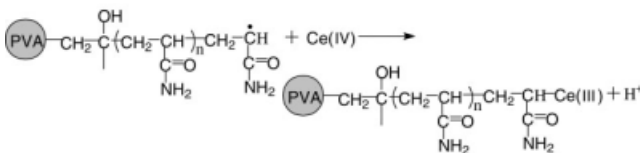
Figure 5 Effect of the molar ratio of NaOCl molecule to AM unit on the amination degree (AD) of PVAm–CPVA microspheres (conditions: reaction temperature = −3°C; reaction time = 11 h).

oxidation termination,[18] as displayed in the following expressions:

Oxidation termination for the propagation chains

Oxidation termination for the primary radicals

When the concentration of cerium salt is lower the number of primary free radicals on the surfaces of CPVA microspheres will increase with the concentration of cerium salt increasing, as shown in Scheme 1, and the graft polymerization will be accelerated; this will result in an increase in the grafting

degree of PAM. However, when the concentration of cerium salt is overly high (>5.98 × 10^{−3} mol/L), the oxidation termination step will be accelerated, and the oxidation termination process of the primary free radicals will be especially accelerated; this will lead to the reduction of the number of active sites on the surfaces of CPVA microspheres. Therefore, the graft polymerization will be hindered here, and the grafting degree of PAM will then gradually decrease with the concentration of cerium salt increasing. Thus, for the graft polymerization system initiated by cerium salt, there is a suitable cerium salt concentration. In this study system, the suitable cerium salt concentration is 5.98×10^{-3} mol/L, at which there is a maximum grafting degree of PAM of 27.13 g/100 g, as shown in Figure 4.

Effects of the main factors on the Hofmann degradation of grafted PAM

Effect of the amount of NaOCl

The effect of the molar ratio of NaOCl molecule to AM unit of the grafted PAM on the Hofmann degradation of grafted PAM on PAM–CPVA was examined with other conditions fixed and the added amount of NaOCl varied. The amination degree of PVAm–CPVA microspheres as a function of the molar ratio is displayed in Figure 5.

Figure 5 shows that the amination degree of PVAm–CPVA first increases and then decreases with the molar ratio of NaOCl molecule to AM unit of the grafted PAM increasing, and there is a maximum amination degree of 2 mmol/g when the ratio is equal to 1.4 : 1. The Hofmann degradation reaction of amide compounds is carried out in stages, as shown in the following expression. The degradation process contains a molecular rearrangement reaction and involves the formation of some intermediate products,[19] such as N-halo amide and isocyanate:

Process of Hofmann degradation of amide compound

$$\underset{\substack{\| \\ O}}{R-C-NH_2} + NaOCl \longrightarrow [\underset{\substack{\| \\ O}}{R-C-NCl}]^- \longrightarrow R-N{=}C{=}O \longrightarrow R-NH_2$$

In the Hofmann degradation reaction of PAM, there are some side reactions, such as chain scission of the hydrocarbon main chain, hydrolysis of the amido groups, and formation of alkyl urea.[20,21] When the amount of NaOCl is smaller, there is not enough NaOCl to transform the amido groups of PAM to

N-halo amide, causing a great number of acrylamino groups to be hydrolyzed and resulting in smaller amination degrees; with the added amount of NaOCl increasing, the amido groups of PAM are transformed continuously into N-halo amide, and the conversion of the grafted PAM into PVAM is
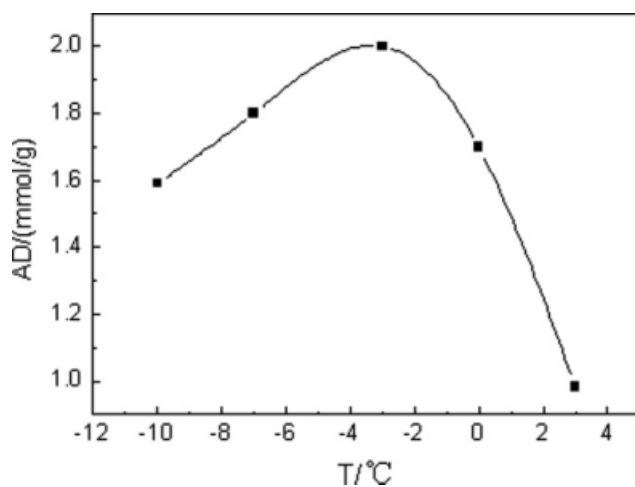
Figure 6 Effect of the reaction temperature (T) on the amination degree (AD) of PVAm–CPVA microspheres [conditions: $n(NaOCl)/n(AM) = 1.4 : 1$; reaction time $= 11$ h].

promoted, leading to the increase in the amination degree. However, when the added amount of NaOCl is too great and the molar ratio of NaOCl units to AM units is beyond 1.4 : 1, the previously described side reactions are probably intensified,[19] causing the decrease of the amination degree of the functional PVAm–CPVA microspheres. It is obvious that to obtain PVAm–CPVA microspheres with a high degree of amination, the amount of NaOCl that should be used is $n(NaOCl)/n(AM) = 1 : 4$, as shown in Figure 5.

Effect of the temperature

The Hofmann degradation reaction of the grafted PAM was performed at different temperatures, and the relationship curve of the amination degree in the same time period of 11 h and the reaction temperature is presented in Figure 6.

To depress the side reactions, lower reaction temperatures are suited for the Hofmann degradation reaction of PAM.[21] Figure 6 shows that when the reaction temperature is lower than $-10°C$, the amination degree in 11 h is lower because of the slow reaction rate. With the temperature rising, the amination degree increases and gets up to a maximum value of 2 mmol/g at $-3°C$, and then it decreases rapidly. A possible reason is that when the temperature is over $-3°C$, the rates of the side reactions, such as chain scission reactions and hydrolysis reactions of the amido groups, are too rapid, and this has a strong impact on the transform reaction of amido groups into primary amine groups, leading to the sharp drop of the amination degree. Therefore, to prepare PVAm–CPVA microspheres with a high amination degree, the reaction temperature should be $-3°C$.

Preliminary research on the functions of PVAm–CPVA microspheres

Isothermic adsorption of PVAm–CPVA toward Fe^{3+} ions

The adsorption isotherm of PVAm–CPVA microspheres for Fe^{3+} ions is shown in Figure 7. It is obvious that PVAm–CPVA microspheres have strong adsorption ability for Fe^{3+} ions, and the maximum adsorption capacity can reach 21 g/100 g. The grafted PVAm macromolecules, in which a mass of primary amine groups exists, have very strong coordination and chelating action for transition-metal ions, which leads to the high adsorption capacity. This sufficiently displays the chelating function of PVAm–CPVA microspheres for metal ions.

Isothermic adsorption of PVAm–CPVA toward CrO_4^{2-} ions

The adsorption isotherm of PVAm–CPVA microspheres for chromate ions (CrO_4^{2-}) is presented in Figure 8. PVAm–CPVA microspheres have very strong adsorption action for CrO_4^{2-} ions, and the maximum adsorption capacity actually reaches 101 g/100 g. This value is egregious, and such a high adsorption capacity has not been reported in the literature for various adsorption materials toward chromate ions. The dense primary amine groups of the grafted PVAm are protonated to a high degree in acidic or neutral solutions, so PVAm is a cationic polyelectrolyte. By electrostatic interactions, PVAm–CPVA microspheres can produce very strong adsorption action for anionic species, so an egregious adsorption capacity for CrO_4^{2-} ions is produced. This illustrates well the cationic character of PVAm–CPVA microspheres.
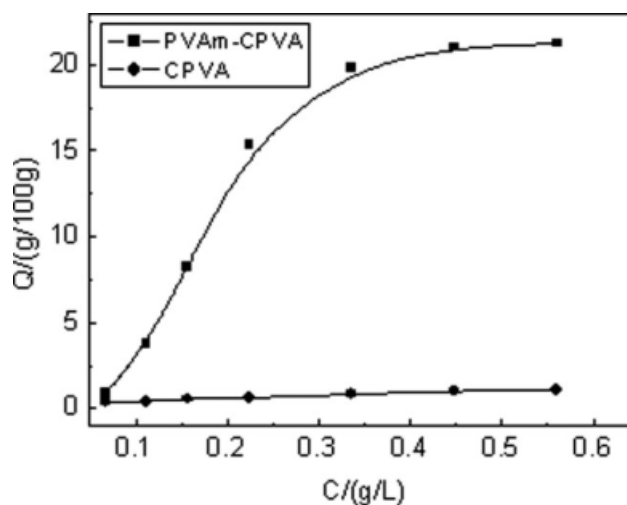

Figure 7 Adsorption isotherm of PVAm–CPVA microspheres for Fe^{3+} ions (C = concentration; Q = amount of adsorption; conditions: temperature = 30°C, pH = 4.0).
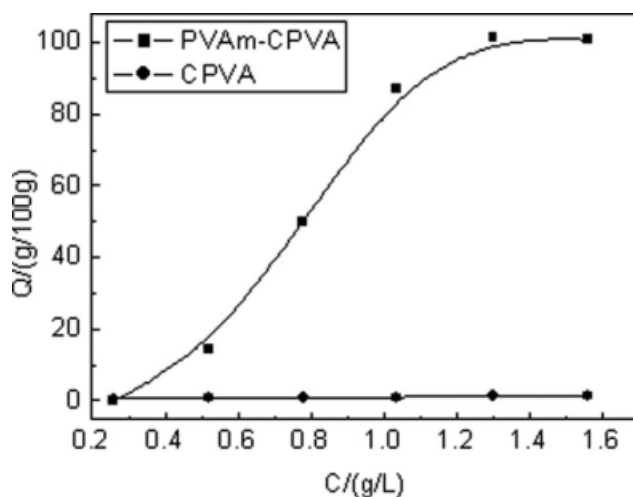
Figure 8 Adsorption isotherm of PVAm–CPVA microspheres for CrO_4^{2-} anions (C = concentration; Q = amount of adsorption; conditions: temperature = 30°C; pH = 4.0).

PVAm–CPVA microspheres have many functions, can produce multiple interactions toward different substances, such as chelation action for metal ions, electrostatic interactions for anionic species, and hydrogen-bond interactions for those hydrogen-bond acceptors or donors, and possess high reactivity toward many substances. In addition, in comparison with other amino-functional carrier materials, PVAm–CPVA microspheres have many advantages. For example, PVAm–CPVA microspheres have more plentiful primary amine groups resulting from the grafted PVAM macromolecule chains in comparison with other amine-modified carriers,[22] possess better biocompatibility because of the CPVA matrix in comparison with other amine-functionalized carriers,[23] and have finer mechanical properties resulting from the crosslinking of poly(vinyl alcohol) with divinyl benzene in comparison with other poly(vinyl alcohol)-based polymeric carrier materials.[24] Therefore, PVAm–CPVA microspheres are promising functional microsphere materials and will have widespread applications in many fields. Especially in bioscience and biomedicine, they have potential, and they can be effectively used for the immobilization, separation, and purification of biomacromolecules as well as drug release and clinical tests. In this work about the functions of PVAm–CPVA microspheres, only a rough and preliminary study has been conducted.

CONCLUSIONS

PVAm–CPVA microspheres were prepared successfully via a two-step process involving graft polymerization and Hofmann degradation. PVAm–CPVA microspheres are multifunctional microspheres, and they have potential in various scientific and technical fields. In the graft polymerization of AM on CPVA microspheres initiated by cerium salt, the acid concentration and the amount of Ce(IV) salt affect the grafting degree of PAM greatly. An overly high acid concentration will restrain the initiation step, and excessive Ce(IV) salt will accelerate the oxidation termination step, negatively affecting the graft polymerization of AM. Therefore, to obtain PAM–CPVA with a high grafting degree of PAM, the acid concentration and the amount of Ce(IV) salt should be selected to be appropriate. In the Hofmann degradation reaction of the grafted PAM of PAM–CPVA, the side reactions should be attached importance to. Lower reaction temperatures should be adopted to avoid side reactions, and −3°C is a suitable temperature. A suitable amount of NaOCl should also be used to obtain PVAm–CPVA microspheres with a high amination degree. The preliminary adsorption tests demonstrate that PVAm–CPVA microspheres are multifunctional and have strong chelation action toward metal ions such as Fe(III) ions and electrostatic interactions with oxyacid anions such as CrO_4^{2-} ions.

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