SHORT COMMUNICATIONS

Pb²⁺-Specific Adsorption/Desorption onto Core-Corona Type Polymeric Nanospheres Bearing Special Anionic Azo-Chromophore

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Since polymeric particles with nanoscale in diameter have an extremely large surface area, they demonstrate a high adsorption property which is useful not only in technological systems¹ but also in biomedical fields.² The formation mechanisms,³ surface functionality,⁴ synthetic methods,⁵ and morphology⁶ of polymeric nanoparticles have therefore been widely studied. Polymeric nanospheres (NS) may have shown a high capacity to collect and separate metal ions, which has very important environmental as well as inorganic chemistry applications. However, selective collection and separation using functional polymeric NS have not yet been reported, although there has been studied the collection of various metal ions.⁷

In our previous work, monodispersed polymeric NS with core-corona structures were prepared by dispersion copolymerization of macromonomers with hydrophobic monomer such as styrene or methyl methacrylate in ethanol/water solvents (macromonomer method).^{4,8} In these studies, size control and surface modification of NS were easy. Functionalization of the corona layer on the surface was attained by using functional macromonomers.

In this paper, we extended the macromonomer method to prepare functional poly(vinylamine) grafted polystyrene (PVAm-g-PSt) NS having azo-chromophore (CHR) (Figure 1) on their surfaces and investigated the adsorption selective for metal ions in aqueous solution. If these NS can be used to detect metals selectively, this technique may have a variety of future applications.

Figure 1. Molecular structure of CHR and PVAm-g-PSt NS form.

EXPERIMENTAL

Materials

St was purified by distillation under reduced pressure, and 2,2'-azobis(isobutyronitrile) (AIBN), which was used as an initiator, was purified by recrystallization from ethanol and dried under vacuum prior to use. Poly(*N*-vinylacetamide) (PNVA) macromonomer⁸ (number-average molecular weight M_n = 5100, the polydispersity was 2.2) and CHR⁹ which has a Ca²⁺ binding group, were synthesized according to previously described methods.

Synthesis

Radical copolymerization was carried out as follows. The PNVA-g-PSt NS were prepared by dispersion copolymerization of PNVA macromonomer with styrene in ethanol/water (vol/vol = 4/1) solvents in the presence of AIBN (1 mol% of total monomers) under

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vacuum at 60 °C for 24 h. Then, PVAm-g-PSt NS were obtained by hydrolysis of purified PNVA-g-PSt NS.⁸ The condensation of PVAm-g-PSt NS with CHR was carried out in 0.05 mol L⁻¹ KH₂PO₄ aqueous solution using water soluble carbodiimide below 5 °C for 24 h.

RESULTS AND DISCUSSION

The elemental analysis of NS surfaces of PNVA-g-PSt, PVAm-g-PSt, and PVAm-g-PSt surface-modified by CHR was performed by electron spectroscopy for chemical analysis (ESCA; Shimadzu ESCA 1000). The degree of hydrolysis from –NHCOCH₃ of PNVA to –NH₂ of PVAm was estimated as about 60% (unit mol) from the reduction of oxygen peak area relative to nitrogen peak area. Molar composition of CHR in functional PVAm-g-PSt NS was estimated as about 14% from the ratio of sulfur peak area to nitrogen peak area. Hydrodynamic diameters (*D_h*) and its distribution for two type NS were estimated by laser light scattering (LLS; MALVEN2000) measurements. The *D_h* values were 503 nm and 540 nm for PNVA-g-PSt and PVAm-g-PSt NS, respectively. The *D_h* of PNVA-g-PSt NS was increased by hydrolysis into PVAm-g-PSt NS. This phenomenon may be due to the increased thickness of the corona layer due to electrostatic repulsion between the positively charged chains on the PVAm-g-PSt NS surfaces. The *D_h* distributions of the NS were not influenced by hydrolysis or surface modification. We roughly estimated the amount of the corona chain per particle as 2.4×10^5 since the surface area occupied by each macromonomer and the total surface area of the core could be calculated as 3.8 nm² and 9.1×10^5 nm² referring the previous paper.¹⁰ The immobilized amount of CHR on a NS can be estimated as $\sim 10^{-16}$ mmol by the previously reported calculation method¹⁰ from results of ESCA and LLS.

The morphology of the NS in the dry state was analyzed by transmission electron microscopy (TEM; Hitachi 7000A). The sphericity of all samples was excellent (insert image in Figure 1) and there were no marked changes in morphology as a result of hydrolysis or surface modification.

The adsorption behavior of Cu²⁺, Sr²⁺, and Pb²⁺ onto CHR of the NS surfaces in aqueous solution (metal ions: 5 µg, NS: 50 mg, solution volume: 3 mL, 20 °C) was studied. The adsorption efficiency of Cu²⁺ (324 nm), Sr²⁺ (716 nm), and Pb²⁺ (479 nm) was estimated as the percentage of metal ion concentration loss in the supernatant relative to the original concentration, as measured by UV-vis spectroscopy (JASCO V-550). The results of these adsorption tests are summarized in Table I. The adsorption efficiency of Cu²⁺ onto NS

Table I. Adsorption efficiency of various heavy metal ions on NS

NS Type	adsorption efficiency (%)		
	Cu ²⁺	Sr ²⁺	Pb ²⁺
PNVA-g-PSt	15.3	54.0	–
PVAm-g-PSt	79.4	–	24.5
Functional PVAm-g-PSt ^a	78.2	52.0	100

^aCa²⁺ did not bind to NS surfaces.

was enhanced by hydrolysis of the corona layer from –NHCOCH₃ to –NH₂, which may be attributed to the chelation ability of Cu²⁺ by amine groups. However, the adsorption efficiency of Cu²⁺ showed little change in spite of surface modifications using CHR. These results showed that CHR did not increase Cu²⁺ adsorption. On the other hand, the adsorption efficiency of Sr²⁺ onto the NS was reduced by hydrolysis, implying that Sr²⁺ has an affinity for the amide groups. The adsorption efficiency of Sr²⁺ onto the surface-modified PVAm-g-PSt NS was almost the same as that of the PNVA-g-PSt NS. Similarly with Cu²⁺ adsorption, CHR did not effectively increase the adsorption efficiency. The adsorption efficiency of Pb²⁺ onto the PNVA-g-PSt or PVAm-g-PSt NS was extremely low. However, surface modification effectively improved Pb²⁺ adsorption. That is, after the functional NS were added into Pb²⁺ aqueous solution, Pb²⁺ was not detected in the supernate, indicating perfect adsorption. This perfect adsorption was due to the condensation of CHR on the surface of PVAm-g-PSt NS (total mole of CHR; 10^{-5} – 10^{-4} mmol). Since molar amount of absorbed Pb²⁺ is 2.3×10^{-5} mmol, this system might be the one-to-one absorption. It was noted that Ca²⁺ did not show the binding behavior in the system, presumably due to the loss of –COOH group.

The absorption specificity of Pb²⁺ may not be attributed to the electrostatic interaction since the larger ionic diameter of Pb²⁺ (0.24 nm) than those of Cu²⁺ (0.14 nm) and Sr²⁺ (0.22 nm) should give the weaker interaction with anions.¹¹ Pb²⁺ ion has an appropriate size to fit CHR binding pocket (0.24 nm) having –OH, –N=N–, and –CONH– (Figure 1). The –CONH– group was converted from –COOH when being immobilized on NS, losing the Ca²⁺ binding property.⁹

Another important observation was that the functional PVAm-g-PSt NS showed perfect desorption (95%) in the presence of HCl at 40 °C and 3 times adsorption/desorption capacity for Pb²⁺, suggesting the possibility of repeated use (Figure 2). This suggests that NS surface-immobilizing CHR have application potentials, such as purification of Pb²⁺ polluted water.

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Figure 2. Schematic illustration of adsorption/desorption behavior.

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