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SHORT COMMUNICATION

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Monodisperse chloromethyl-functionalized macroporous polymer particles by seeded polymerization in aqueous media

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Abstract This study presents a method to produce monodisperse chloromethyl-functionalized macroporous poly(styrene-*co*-divinylbenzene) polymer particles by seeded polymerization in aqueous media. We observed that the molecular structure of polystyrene seed particles, the composition of the secondary monomer mixtures, and the type of solvents were very important factors that determine the morphology and porosity of the final particles. This study proposes that the molecular chemistry of polystyrene seed polymers, increasing molecular weight or crosslinking, is another factor that can control the porosity of the final particles. Also, the selection of a poor solvent was effective in forming the larger surface area. In this study, it was confirmed that the chloromethyl groups introduced on the surface of porous particles were quantified chemically and their effective incorporation had a close relationship with the surface area.

Keywords Chloromethyl-functionalized · Molecular structure · Porosity · Poor solvent · Surface area

Introduction

High performance packing materials using monodisperse porous polymer particles in a micron size range, have usually been prepared by a modified suspension polymerization process such as Vanderhoff's successive seeded and polymerization [1], Ugelstad's activated swelling and sequential polymerization [2, 3], and others [4, 5]. They swelled the second monomer mixtures comprised of styrene, divinylbenzene (DVB), and solvent into the monodisperse polymer particles, and polymerized the suspended polymer/monomers/solvent droplets. The monodispersity of the final particles is readily determined by means of the monodispersity of the seed particles, whereas the porosity is much dependent upon the experimental conditions, including molecular chemistry of seed polymers [6], solvent types [7], the second monomer compositions [8], and so on.

Employing the above-mentioned methods, it is possible to prepare various functionalized macroporous polymer particles of which applications can be expanded to the solid-phase synthesis and polymer-supported chemistry therewith [9–11]. The particle functionality can be achieved by either chemical treatment of porous particles or copolymerization of specific functional monomers; the latter is however more tempting than the former, which frequently involves the use of toxic chemicals.

In our previous work, we have found that urethane acrylate (UA) is an effective molecular chemistry controller of polymer particles in the preparation of macroporous poly(styrene-*co*-divinylbenzene) particles by seeded polymerization in aqueous media [12]. On the basis of the previous result in this study, we tried to prepare macroporous chloromethyl-functionalized polymer particles by using chloromethylstyrene (CMS) as a surface-functionalizable comonomer. In order to understand the importance of the chemical compositions, the present study investigates the effect of monomer compositions, the molecular chemistry of seed polymers, and solvent type on the pore formation of the final particles. Finally, the chloromethyl functional groups located on the surface of the porous particles are quantified chemically and characterized considering the total surface area of the particles.

Experimental

Materials

The inhibitors in styrene (St. Aldrich Chemical Co.) and DVB (55% grade, Aldrich) were removed by passing them through an aluminum oxide column (Aldrich). Chloromethylstyrene (0% *para*-isomer, Aldrich) was treated with 0.1% NaOH solution to remove the inhibitor before use. 2,2-azobis(isobutyronitrile), (AIBN, Junsei Chemical Co.) and benzoyl peroxide (BPO, Junsei) were recrystallized from methanol. The other materials were used as received; sodium lauryl sulfate (SLS, Junsei), polyvinylpyrrolidone (PVP K-30, $M_w = 4.0 \times 10^4$ gmol^{-1}, Aldrich), 1-chlorododecane (CD, Tokyo Chemical Industry), polyvinylalcohol (PVA, $M_w = 8.8 \times 10^4 \sim 9.2 \times 10^4$ gmol^{-1}, 87~89% hydrolyzed, Kuraray Chemicals Co.), toluene (Aldrich), and *n*-heptane (Aldrich). All aqueous solutions were prepared using distilled deionized (DDI) water.

Preparation of PS seed particles

PS seed particles were prepared by dispersion polymerization. For the purpose of controlling the molecular structure of PS seed particles, UA was incorporated as described in the previous papers [13–15]. St, UA, AIBN, PVP, 2-methoxyethanol, and ethanol were weighed into 50 mL glass vials. After the vials were sealed in a nitrogen atmosphere, the polymerization was carried out at the rotation speed of 40 rpm at 70 °C for 24 h. The standard recipe of dispersion polymerization is given in Table 1.

Table 1 The standard recipe for the synthesis of seed polymer particles

Ingredient	Weight (g)
St	0.98
UA[a]	0.02$^{\text{variable}}$
PVP K-30	0.18
Aerosol-OT[b]	0.04
AIBN	0.01
2-Methoxyethanol	4.39
Ethanol	4.39

70 °C; 24 h; 10 wt% of monomer concentration based on total weight

[a] Abbreviation of urethane acrylate (UA) (2 wt% in this example)

[b] Costabilizer: Di-2 ethylhexyl ester of sodium sulfonsuccinic acid

Preparation of poly(St-*co*-CMS-*co*-DVB) macroporous particles

CMS-functionalized porous polymer particles were prepared by two-staged seeded polymerization in aqueous media [16, 17]. The swelling and polymerization were carried out in 4-necked glass reactor equipped with stirrer, reflux condenser, and a nitrogen gas inlet system. PS seed particles (0.5 g) were redispersed in 0.25% SLS solution (40 g) by applying 10 min sonication. The finely emulsified CD (0.5 g), which was prepared by ultrasonic homogenization in 0.25% SLS solution (10 g), was poured into the seed particle dispersion. The swelling was carried out for 10 h at 30 °C. After the complete diffusion of CD emulsion into the seed particles, 10 g of monomer mixture of St, DVB, CMS, solvent, and BPO (1 wt% based on total monomer) was emulsified and then poured into the CD-swollen seed particles. The swelling was continued for another 10 h at 30 °C. The swelling ratio of the monomer mixture to the PS seed particles was fixed at 20 folds by weight. Basically, the ratio of St to DVB was fixed at 1:1, and the amount of CMS was varied from 0 to 30 wt% based on total monomer mixture weight. Also, toluene and *n*-heptane were chosen as a good and poor solvent respectively, and added 40 wt% to the monomer mixture. After the complete disappearance of monomer mixture droplets, the monomer-swollen particles were stabilized with 5 wt% PVA solution. Then, the polymerization was carried out at 80 °C for 24 h. After the polymerization, the seed polymers and other impurities in the particles

Table 2 The characteristics of PS seed particle

Symbol [a]	D_n (μm)	PSD[b]	M_w ($gmol^{-1}$)	MWD[c]	N^d ($mol\ m^{-3}$)
UA0	2.87	1.01	5.3×10^4	2.69	–
UA2	2.96	1.01	10.1×10^4	3.17	–
UA3	2.83	1.01	–	–	87.1

[a] UAα: α corresponds to the concentration of UA (wt% based on total monomer weight)
[b] Particle size distribution, D_w/D_n [12, 13]
[c] Molecular weight distribution, M_w/M_n
[d] Effective number of chains in crosslinked network determined from the monomer transport rate [16, 17].

were eliminated by the Soxhlet extraction for 48 h in the methylene chloride solvent.

Characterizations

The swelling procedure was monitored with an optical microscope (OM, Nikon Microphot Fax). The morphology of porous particles was observed with a scanning electron microscope (SEM, JSM-6300, JEOL). To determine the particle diameter, about 100 individual particles were counted from SEM photographs and the average was taken. The specific surface area, mean pore size and pore volume of the porous particles were determined by Brunauer-Emmett-Teller (BET) measurements. The presence of the chloromethyl groups was confirmed from Fourier transform infrared (FTIR) spectra (Nicolet, Mahgna IR-550). Determination of effective chloromethyl groups in the particles was carried out based on the nucleophilic attack of the deprotonated glycine on the chloromethyl groups [18]. The dispersion of the particle in DDI water was reacted with 0.3 M glycine and 0.175 M NaOH. The reaction was carried out at 35 °C for 5 h. In order to evaluate and exclude the possible hydrolysis of chloromethyl groups by temperature, a blank without glycine/NaOH was also carried out. After the reaction, the reactant was centrifuged and the supernatant was reacted again with 0.05 M $AgNO_3$ aqueous solution. The chloride ions released were determined, as a function of the concentration of $AgNO_3$.

Results and discussion

Control of molecular structure of PS seed particles

Chain transfer agents have been frequently employed to control the molecular weight of polymer particles during polymerization [6]. We were the first to report that the incorporation of UA in the polymerization of PS particles could also be applicable for controlling the molecular weight of the seed polymers [12, 16]. Furthermore, crosslinked PS particles could be obtained at a high concentration of UA, above 3.0 wt%. It was noticed that below 3.0 wt% UA concentration, the molecular weight of PS particles increased without forming a crosslinked network, while the particle size was independent of the UA concentration [16]. In this study, we used three PS particles prepared by changing the concentration of UA. The information about the PS seed particles is summarized in Table 2 and Fig. 1. Using those seed particles, we prepared macroporous poly(St-*co*-CMS-*co*-DVB) particles, and tried to understand their morphological changes and surface chemistry according to the chemical compositions.

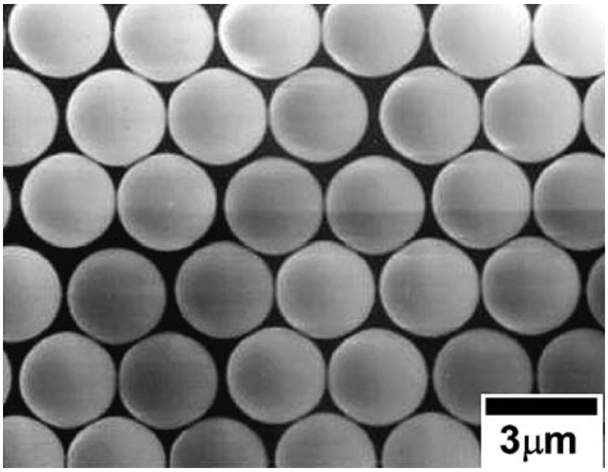

Fig. 1 A scanning electron microscopic image of the PS seed particles (UA3)

Effect of molecular chemistry of seed polymers on pore formation

Figure 2 shows the morphology of CMS-functionalized porous particles obtained after the Soxhlet extraction of the PS seed polymer of different molecular structures. All the particles displayed spherical shape and uniformity in size. It is evident from the SEM photographs that all the particles had a porous structure and became macroporous, as the molecular structure of PS seed polymers was bulky. Typical pore size distribution profiles for the porous particles are shown in Fig. 3. As

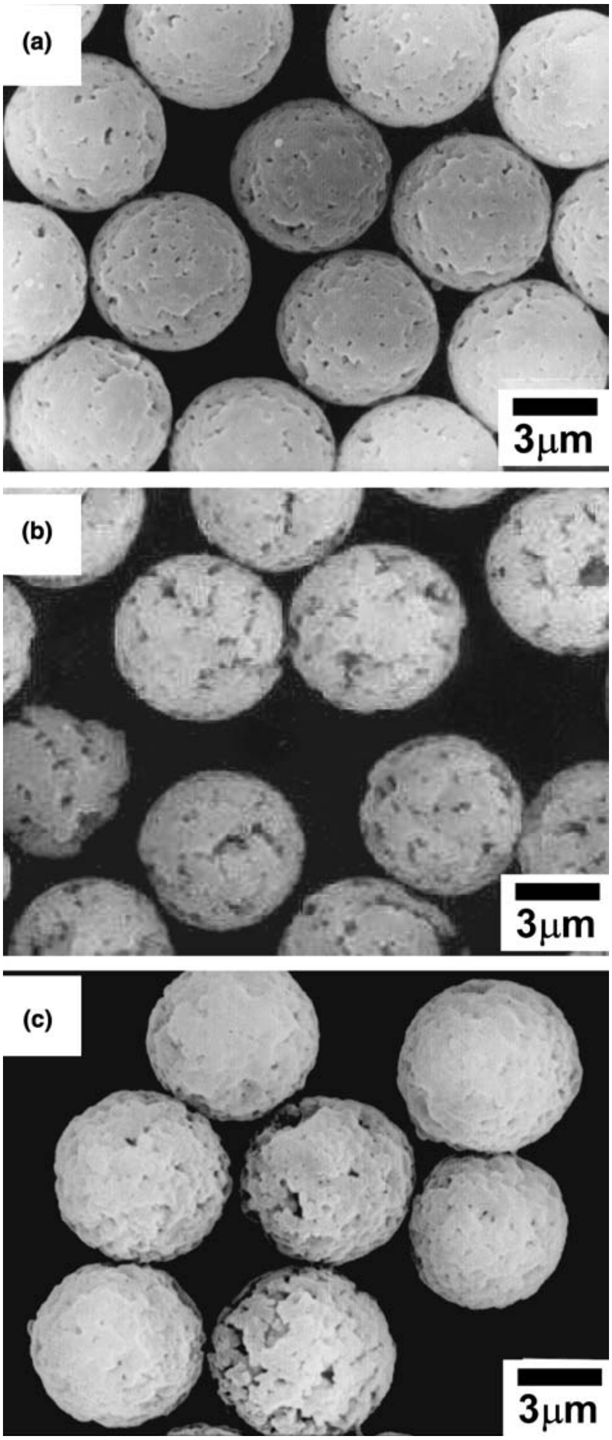

Fig. 2 Scanning electron microscopic images of the porous polymer particles prepared using the PS seed particles of different molecular structure; **a** UA0-10T, **b** UA2-10T, **c** UA3-10T

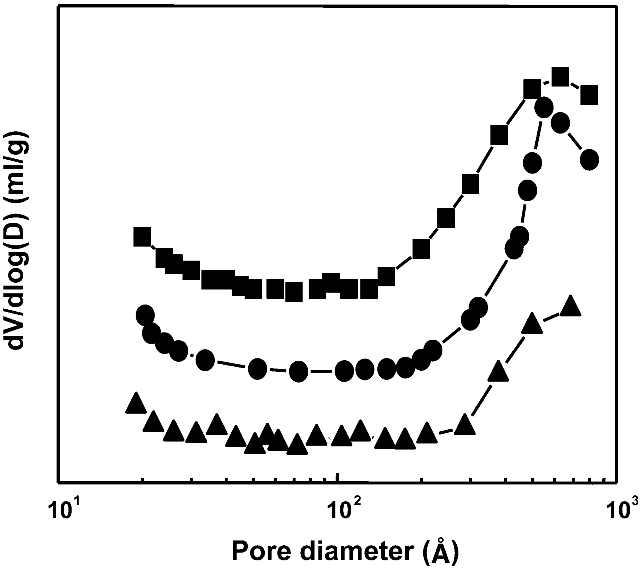

Fig. 3 Pore size distributions of the porous particles prepared using the PS seed particles of different molecular structure; UA0-10T (*filled square*), UA2-10T (*filled circle*), UA3-10T (*filled triangle*)

can be seen, there was a slight increase in mean pore diameter between UA0-10T and UA2-10T. The increase in mean pore diameter was particularly pronounced for the UA3-10T in which the PS seed polymers had a crosslinked network structure. This result indicates that the larger radius of gyration of the bulky PS seed polymers is responsible for the large pore formation [12]. The characteristics of porous particles are summarized in Table 3. The measured surface properties, pore size (D_p), pore volume (V_p), and specific surface area (A_p) could be characterized in the macroporous range.

Effect of CMS content on pore formation

Since the pore formation of porous particles depends dominantly upon the degree of phase separation between the seed polymer and the highly crosslinked second polymer phase during polymerization, the characteristics of the second polymer phase have a strong influence on both morphology and porosity of the final particles. Figure 4 shows the porous particles prepared with varying the concentration of CMS in the second polymer composition (surface characteristics are listed in Table 3). An interesting observation was that the pore structure of the particles became collapsed from the CMS concentration of 20 wt% in the second polymer phase, which also can be confirm in the pore size distributions shown in Fig. 5. This trend can be understood considering the degree of phase separation

Table 3 Characterization of chloromethyl-functionalized porous polymer particles

Symbol[a]	St/DVB/CMS/solvent (w/w/w/w)	D_n (μm)	PSD[b]	A_p^c (m^2/g)	V_p^d (mL/g)	[Cl$^-$]^e (μmol/g pol)	[Cl$^-$]$^f_{effective}$
UA0-10T	25/25/10/40	5.01	1.01	12.89	0.05	24.82	0.610
UA2-10T	25/25/10/40	5.02	1.01	11.76	0.04	19.61	0.487
UA3-10T	25/25/10/40	5.04	1.01	8.55	0.03	12.73	0.316
UA0-0T	30/30/0/40	5.41	1.01	20.23	0.12	–	–
UA0-20T	20/20/20/40	5.04	1.02	5.42	0.01	6.39	0.141
UA0-30T	15/15/30/40	–	–	2.30	–	4.71	0.095
UA0-0H	30/30/-/40	6.15	1.02	65.14	0.28	–	–
UA0-10H	25/25/10/40	6.62	1.01	31.51	0.14	25.28	0.686
UA2-10H	25/25/10/40	6.08	1.01	23.00	0.10	22.16	0.641

80 °C; 24 h; 4.0 wt% of solid content based on total weight. The conversions of the second monomers in each samples were located in 90–95%, which was determined by a gravimetic method [13, 14]

[a] UAα-β; α and β correspond to UA concentration in seed particles and CMS concentration in the monomer mixture by weight %. T indicates toluene, and H indicates *n*-heptane, respectively

[b] Particle size distribution, D_w/D_n [12, 13]

[c] Specific surface area from BET measurement

[d] Pore volume

[e] Concentration of chloromethyl groups was detected by a conductometric titration [18]

[f] $[Cl^-]_{effective} = [Cl^-]_{detected}/[Cl^-]_{introduced}$

of poly(St-*co*-CMS-*co*-DVB) globules [19]. As the concentration of CMS increased, the submicron-sized agglomerates of poly(St-*co*-CMS-*co*-DVB) copolymer gels which are formed in the suspended droplets would be rather miscible with the mixture of the PS seed polymer and toluene. This is mainly attributed to the decrease in the crosslinking density (see the second monomer composition in Table 2). Therefore, at high concentration of CMS, above 30 wt%, the porous particle structure could not be observed. Instead, the particles displayed an odd structure (Fig. 4c). It means that the low crosslinking density of poly(St-*co*-CMS-*co*-DVB) submicron-sized gels resulted in their mixing with the PS seed polymer in the suspended droplets. Therefore, after the extraction of the PS seed polymers, the particles shrank and became spherically concave. Based on our experimental results, it is reasonable to say that in order to get CMS-functionalized porous particles, the CMS should be incorporated in an appropriate concentration, around 10 wt% in the second polymer compositions.

Effect of solvent type on pore formation

In the preparation of porous polymer particles, the solvency of solvents against polymer compositions has an important role in determining the pore structure and porosity of the final particles. This study considers two solvents; a good solvent (toluene) and a poor solvent (*n*-heptane). The poly(St-*co*-CMS-*co*-DVB) submicron-sized gels formed by polymerization in the poor solvent-containing suspended droplets would have more condensed and more entangled chains compared with those in the good solvent, which gives a large surface area and high pore volume. To investigate the effect of solvency of the solvents on the pore formation, a series of porous particles was also prepared with *n*-heptane and compared with cases of using toluene. The results are displayed in Fig. 6 and Table 3. In contrast to the use of toluene, when *n*-heptane was used as a poor solvent, the specific surface area and pore volume of the porous particles were remarkably increased. Also, as shown in Fig. 7, the pores were distributed in the range of 10~100 nm. This directly demonstrates that the presence of a poor solvent enhances the phase separation and structure heterogeneity, which leads to higher specific surface area and pore volume [6, 7, 19].

Characterization of chloromethyl groups

The chloromethyl groups may be transferred to other derivatives by hydrolysis and/or crosslinking reaction during polymerization in aqueous media. Therefore, analytical quantification of the chloromethyl groups is critical to the assessment of the usefulness of our synthetic approach. Figure 8 shows the FT-IR spectra for the chloromethyl functionalized porous particles. As can be seen, the characteristic peaks of C–Cl stretching and bending vibration could be detected at 1,470 and 1,251 cm^{-1}, respectively. This means that the chloromethyl groups were present in/on the porous particles. In order to quantify the amount of chloromethyl groups on the particle surface, the concentration of chloromethyl groups present on the surface was also estimated using the conductometric titration method [18]. The values obtained were listed in Table 3. An interesting result was that when the effective concentration of chloromethyl groups, which is defined as $[Cl^-]_{effective} = [Cl^-]_{detected}/[Cl^-]_{introduced}$, was considered, the concentration of chloromethyl groups was detected largely depending on the surface area. With only

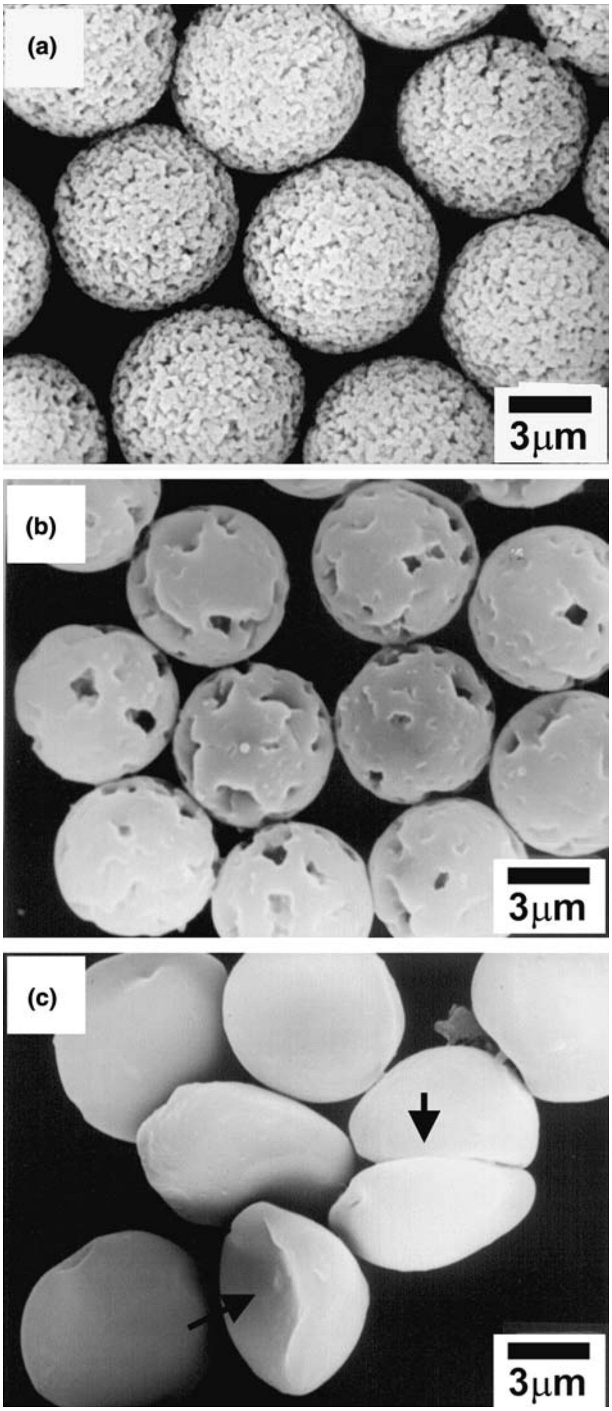

Fig. 4 Scanning electron microscopic images of porous particles prepared by varying the concentration of CMS in the second monomer mixture; **a** UA0-0T, **b** UA0-20T, **c** UA0-30T

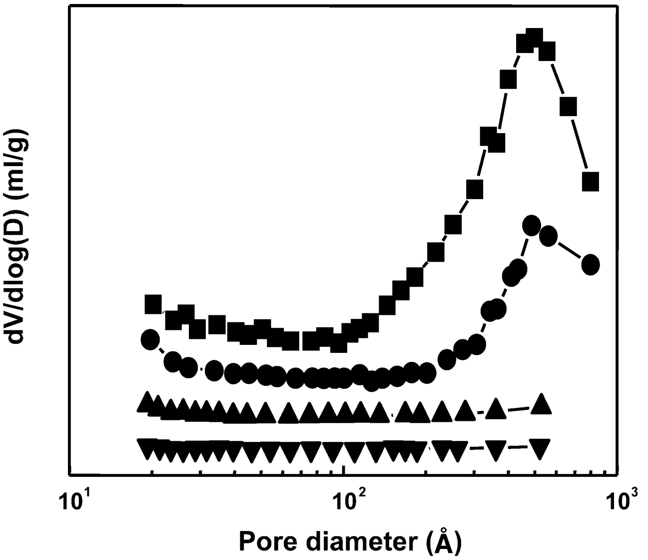

Fig. 5 Pore size distributions of the porous particles prepared by varying the concentration of CMS in the second monomer mixture; UA0-0T (*filled square*), UA0-10T (*filled circle*), UA0-20T (*filled upright triangle*), UA0-30T (*filled reversed triangle*)

increasing the copolymerization amount of CMS, a high $[Cl^-]_{effective}$ could not be expected, just as in the case of UA0-20T and UA0-30T. Consequently, in this study, it was found that to increase the actual concentration of chloromethyl groups on the particle surface, the particles should have a large surface area by forming a strong porous structure.

Conclusion

Chloromethyl-functionalized porous poly(St-*co*-CMS-*co*-DVB) particles were produced in a macroporous range by changing the molecular strucure of the PS seed polymers, the concentration of CMS, and the solvency of solvents. It was found that the enhanced porosity could be obtainable by using low molecular weight and linear seed polymers, copolymerizing relatively low concentration of CMS, around 10 wt%, and using a poor solvent such as *n*-heptane. An effective incorporation of chloromethyl groups on the surface could be especially achieved by enlarging the surface area of final porous particles. Since the chloromethyl groups located on the surface of porous particles can be easily transformed to another functional moiety by a simple chemical treatment, it is expected that those chloromethyl functionalized porous particles are applicable for

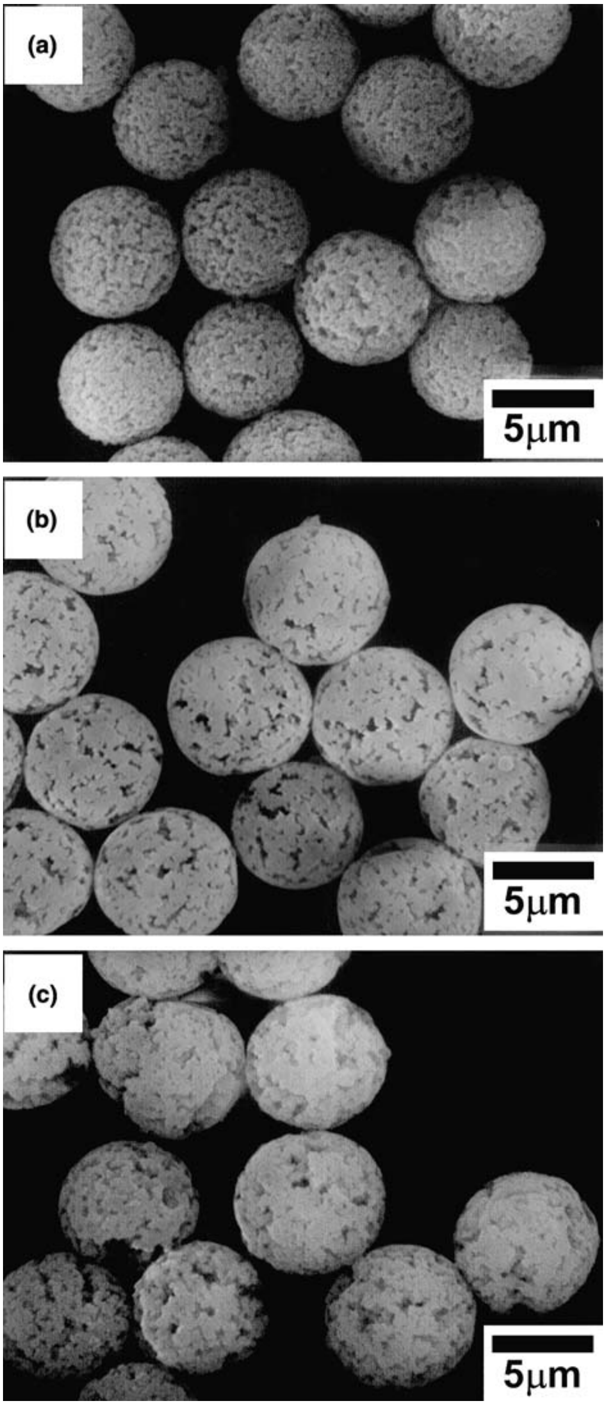

Fig. 6 Scanning electron microscopic images of the porous particles prepared using *n*-heptane as a poor solvent; **a** UA0-0H, **b** UA0-10H, **c** UA2-10H

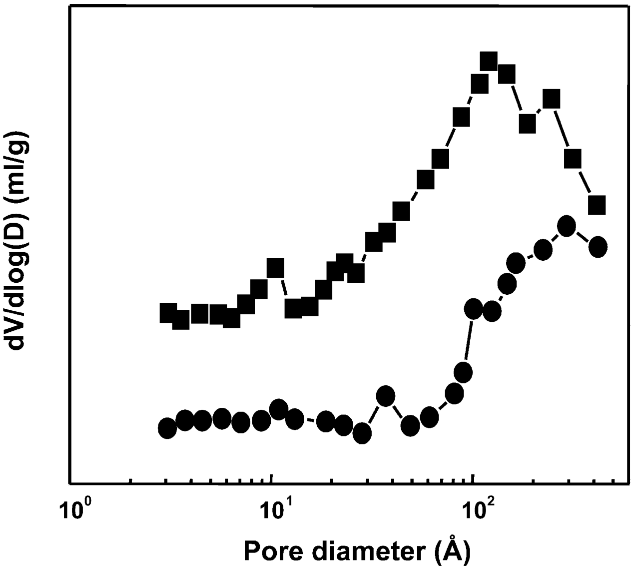

Fig. 7 Pore size distributions of the porous particles prepared by varying the concentration of *n*-hetpane in the second monomer mixture; UA0-0H (*filled square*),UA2-10H (*filled circle*)

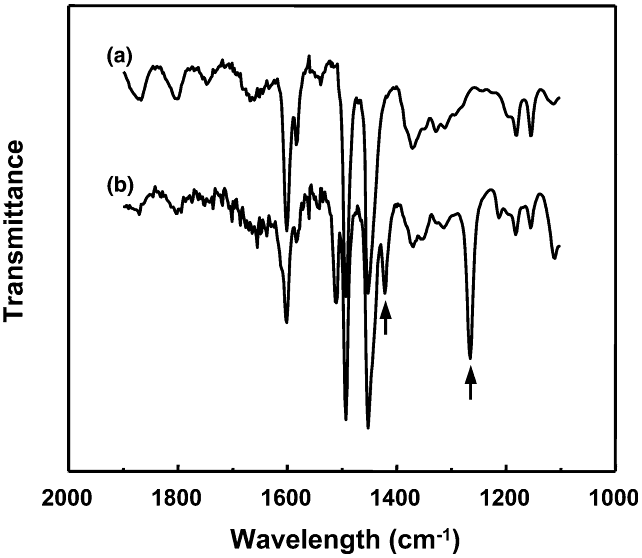

Fig. 8 FT-IR spectra of the porous particles; **a** UA0-0T, **b** UA0-10T

polymer-immobilized extractions, precursors for the synthesis of ion exchanger resins, and column packing materials.

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