



Preparation and characterization of high loading porous crosslinked poly(vinyl alcohol) resins

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Abstract

Porous crosslinked poly(vinyl alcohol) resin beads have been prepared by a two-step pathway involving a pre-crosslinking reaction followed by a reverse suspension crosslinking reaction with epichlorohydrin as crosslinker. The reaction conditions have been optimized for the two steps in order to obtain resins with various pores sizes. The crosslinking density of these resins was calculated from their swelling properties by a modified Flory equation. High loading of hydroxyl groups is one of the important characteristics of these resins (attaining ca. 17 mmol/g). The porosity, pore volume, pore structure and the swelling behavior in water of these resins have been studied.

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1. Introduction

Versatile polystyrene-based resins have been used as solid-phase catalysts, polymer supports for organic synthesis, absorption and separation of chemicals. [1,2]. Polystyrene resins are rather hydrophobic and thus some of their applications in aqueous media are limited. Hydrophilic polymers should have a better swellability in water. Poly(vinyl alcohol) (PVA), a hydrophilic and low cost polymer, would be a good candidate in making such solid supports. PVA can be made in hydrogel form after appropriate physical or chemical crosslinking. Examples include electron beam or γ -ray irradiation [3] and freeze-thaw treatment of PVA solutions [4]. Chemical crosslinking has been achieved by the use of crosslinking reagents such as boric acid, dialdehydes and epichlorohydrin [5–7]. Applications of PVA hydrogels have been proposed, particularly in the biomedical field [8–10] because of their inherent low toxicity, good biocompatibility and desirable physical properties such as elastic properties and good swelling in water. Only a few efforts have been made to prepare crosslinked PVA beads. Porous PVA beads have

been prepared by freeze-thaw cycles and used to immobilize lipoprotein lipase [11], but the mechanical properties of these beads were poor and they could be dissolved in water above 70 °C. Porous PVA beads were also obtained from the copolymer of vinyl acetate and triallyl isocyanurate after methanolysis of the crosslinked copolymer [12]. These beads were insoluble in water and difficult to further functionalize because of the different functional groups on the beads. It is still a challenge to obtain crosslinked PVA resin beads with well-defined porous structures and acceptable mechanical properties.

We report here a two-step process for the preparation of porous PVA beads crosslinked with epichlorohydrin. The porous structure, the swelling behavior and the high loading of functional groups make these resins potentially useful as polymeric scavengers and supports in solid-phase organic synthesis.

2. Experimental section

2.1. Materials

Poly(vinyl alcohol) (PVA, 98% hydrolyzed, $M_n = 14,900$, $M_w/M_n = 1.77$), epichlorohydrin (EP, 99%), and

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sorbitan monooleate (Span 80) were purchased from Aldrich. Paraffin oil was purchased from American Chemicals. Acetic anhydride (99%, from Pfaltz & Beauer) was distilled before use. Other chemicals were all purchased from Aldrich and used without further purification.

2.2. Preparation of crosslinked PVA beads

In a typical procedure, 40 g of 15% PVA aqueous solution and 4 g of powdered sodium hydroxide were mechanically stirred in a 500 ml round bottom flask for 1 h at 50 °C in a thermostated oil bath. Afterwards, 6 ml epichlorohydrin was introduced into the mixture for a pre-crosslinking, which was carried out in water at 50 °C with a gentle stirring. It is important to control the temperature, time and stirring speed to avoid excessive crosslinking of the PVA solution. The stirring was stopped after pre-crosslinking and 250 ml paraffin oil was added to the viscous mixture, which was first stirred with a relatively high speed for about 1 min followed by the addition of 0.4 ml of Span 80. PVA beads were formed during this reverse suspension crosslinking reaction carried out at 50 °C for 24 h with appropriate mechanical stirring. At the end of the reaction, the PVA beads were washed by a mixture of toluene and petroleum ether (1:1, 3 × 200 ml) and by methanol (100 ml) to extract the oil from the beads. They were subsequently washed by large amounts of deionized water (5 × 1000 ml). The beads were extracted in a Soxhlet extractor successively by the use of acetone, ethanol and water each for 24 h. Finally, the PVA beads were filtered and freeze-dried for 48 h. With the same method, other PVA beads with different degrees of crosslinking were prepared by adding various amounts of the crosslinker, with a good control of the stirring speed and reaction temperature. Five sets of bead samples were obtained, and they were designated as PVA-5, PVA-6, PVA-7, PVA-8 and PVA-10, respectively, where the number following the PVA indicates the volume (ml) of crosslinker (EP) used in the reaction. All beads were sieved into different ranges of mesh sizes: 20–30 (580–850 μm), 30–40 (340–580 μm), 40–60 (250–340 μm), 60–100 (150–250 μm). The beads larger than mesh size 20 were not used for the characterization.

2.3. Loading of hydroxyl groups on PVA beads

The average loading of hydroxyl groups on the PVA beads was determined by titration of the excess of acetic acid after acetylation of the resin with acetic anhydride [13]. 150 mg PVA beads were placed in a 100 ml flask, along with 1.0 ml of acetic anhydride and 5.0 ml of pyridine. The mixture was stirred at 60 °C for 12 h. At the end of the acetylation, 10 ml of water was added to the flask to convert excess acetic anhydride into the corresponding acetic acid, which was titrated at room temperature with a 0.501 M NaOH aqueous solution (a phenolphthalein solution was used as the indicator). Blank titration was performed in the

same way to avoid systematic errors. The loading of hydroxyl groups on the beads was taken as the average of three parallel experiments.

2.4. Infrared spectroscopy

The infrared spectra of PVA and the PVA beads were recorded on a Bomem MB-100 Fourier transform IR spectrometer at room temperature. KBr pellets were prepared mainly with beads of a 60 mesh size. Calcium carbonate was used as an internal reference [14,15].

2.5. Characterization of the PVA resins

True density. To estimate the true density of dried PVA beads, 0.3 g of PVA beads were first dried until a constant weight (W_0) was reached and then placed into a 10 ml volumetric flask of known weight at 21 °C. Into the flask was added 8 ml of cyclohexane and the mixture was kept at 21 °C for 24 h. The flask was then filled with cyclohexane to the mark and was weighed (W_1). The true density of PVA beads was calculated according to

$$d = W_0/[10 - (W_1 - W_0)/d_s] \quad (1)$$

where W_1 is the total weight of the resin and the solvent, and W_0 the weight of the dry resin, d_s the density of the solvent ($d_{\text{cyclohexane}} = 0.772 \text{ g/ml}$).

Degree of swelling. The swelling rate of the PVA beads in distilled water was determined by monitoring the weight gain of the resin in water. The PVA beads were dried and then placed into tubes with a sintered glass bottom. The tubes were immersed in distilled water for 48 h at 21 °C. The excess of water was removed by centrifugation at 2000 rpm during 1 min. The water content (W_Q) at equilibrium was calculated according to

$$W_Q(\%) = \frac{W_1 - W_0}{W_1} \times 100\% \quad (2)$$

and the degree of swelling (S_w) according to

$$S_w = \frac{W_1 - W_0}{W_0} \quad (3)$$

where W_1 and W_0 denote the weight of PVA beads with absorbed water and that of the dry PVA beads, respectively.

Pore volume and porosity. The pore volume of the PVA beads was studied by monitoring the weight gain of the resins [16]. The dried beads were placed into tubes with a porous glass bottom. The tubes were kept inside a flask filled with cyclohexane for 48 h at 21 °C. The excess cyclohexane was removed by centrifugation at 2000 rpm for 1 min. The volume of cyclohexane absorbed in the beads was used to estimate the porosity of beads. The porosity of the beads was indicated by

$$\phi = V_p/V_0 \quad (4)$$

where V_p is the pore volume in the beads and V_0 is the true

volume of beads:

$$V_0 = W_0/d \quad (5)$$

where W_0 is the weight of dry beads, and d (the true density of dried beads) was determined from Eq. (1).

The morphologies of the pores in the beads were observed by the use of a scanning electron microscope (JEOL, JSM-8400). The beads in small amounts were frozen in liquid nitrogen and freeze-dried for 48 h and no collapsing of the pores or of the network was observed.

3. Results and discussion

3.1. Pre-crosslinking

The synthetic scheme for the preparation of the PVA resins is shown in Fig. 1. EP was used as the crosslinker. If each EP molecule reacted with two hydroxyl groups on the PVA chains, it could be expected that (1) each EP molecule would yield one hydroxyl group while consuming two hydroxyl groups of PVA; (2) the functional groups on the crosslinked beads would remain unchanged after the reactions. However, it is known that there may be some side reactions. For example, some EP molecules may only react with one hydroxyl group or react with unreacted pendant epoxy groups. Since it is difficult to quantify such side reactions, it is reasonable to assume that amount of functional groups from such side reaction is also directly related to the amount of EP used in the crosslinking reaction.

We have found that it is impossible to obtain crosslinked beads with desired mechanical properties and spherical shape from a direct reverse suspension

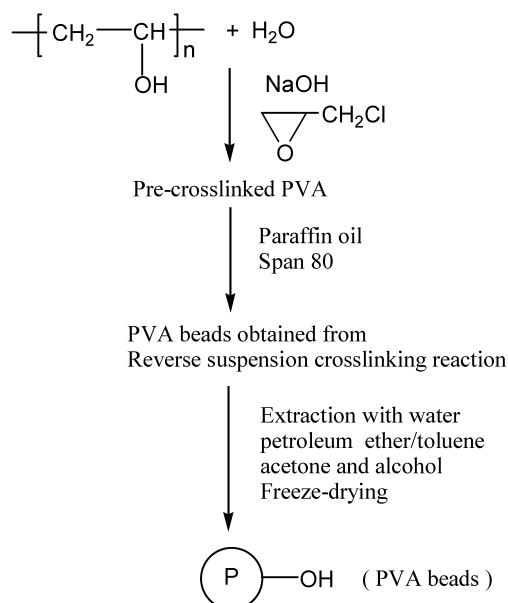


Fig. 1. Synthetic scheme for the preparation of PVA beads.

crosslinking reaction. The mixture needed to be pre-crosslinked since EP is somewhat oil-soluble. Therefore, a two-step process was employed. The concentrated mixture of PVA and sodium hydroxide is pre-crosslinked with EP first in water for a given time, and the aqueous mixture is then dispersed into paraffin oil for further crosslinking to take place. Since the crosslinking reaction in the second step also occurs in the aqueous phase of the water in oil mixture, the complete process is called a reverse suspension crosslinking reaction. In fact, pre-crosslinking is probably the most important step in controlling the property and morphology of the beads.

Since it was difficult to prepare concentrated PVA solutions above 15%, especially when the molecular weight of PVA is high, (e.g. >30,000), the concentration of PVA aqueous solution was kept at 15%. A PVA with lower degree of hydrolysis, e.g. a 85–90% hydrolyzed PVA, can be dissolved more easily in water. The 98% hydrolyzed PVA was chosen for this work, for the following reasons: (1) the fully hydrolyzed PVA has more OH groups and may react better with epichlorohydrin; (2) the beads made from fully hydrolyzed PVA should have a higher OH loading; and (3) the beads are free of acetate groups from unhydrolyzed monomeric units of vinyl acetate.

The crosslinked PVA beads in the spherical form were found to be swellable in water and have the desired mechanical strength. Pre-crosslinking conditions for these samples were listed in Table 1 and the bead size distribution is shown in Fig. 2. Fig. 2 shows that smaller beads could be obtained more easily when the degree of crosslinking is higher. With a larger amount of the crosslinker, the pre-crosslinked PVA solution can be more easily dispersed into smaller droplets in the suspension media. The reaction time required for pre-crosslinking was also shorter when more crosslinker was added (Table 1). The amount of crosslinkers (EP) found in the crosslinked resins remained relatively constant when varying amounts of EP were used in the pre-crosslinking reaction. Table 1 shows that the time used for pre-crosslinking varied according to the amount of EP used. It is known that the crosslinker EP can react with the OH groups very fast, particularly in an alkaline medium while heating. When increased amount of EP is used, the time for pre-crosslinking reaction should be decreased accordingly

Table 1
Pre-crosslinking conditions for preparing PVA beads

Beads	PVA/EP weight ratio in feed	Time (min)	Bead size (mesh) ^a
PVA-5	1:0.99	14 ± 0.2	20–60
PVA-6	1:1.18	13 ± 0.2	20–60
PVA-7	1:1.38	12 ± 0.2	20–80
PVA-8	1:1.58	11 ± 0.1	20–100
PVA-10	1:1.97	9 ± 0.1	20–100

Preparation conditions: [PVA] = 15%; volume of the solution = 40 ml; temperature = 50 ± 3 °C; stirring rate = 110 ± 10 rpm.

^a The beads of mesh size larger than 20 were sieved out and excluded for further experiment and characterization.

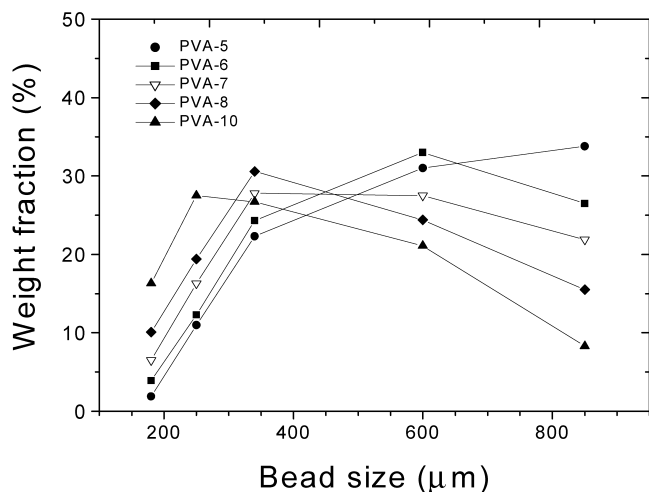


Fig. 2. Bead size distribution of PVA beads. PVA/EP weight ratios in the feed: PVA-5, 1:0.99; PVA-6, 1:1.18; PVA-7, 1:1.38; PVA-8, 1:1.58; PVA-10, 1:1.97.

to obtain a mixture not yet too viscous to be dispersible in the oil phase.

3.2. IR spectrum

Infrared spectroscopy was employed to characterize the PVA beads. The infrared spectra for PVA, PVA/calcium carbonate, PVA beads/calcium carbonate are represented in Fig. 3(A)–(C), respectively. Some characteristic bands in the IR spectrum of calcium carbonate can be found at ca.

840 and 2500 cm^{-1} [17]. Since some of the bands overlap with those of PVA [18], the peak of calcium carbonate at about 2500 cm^{-1} and the area of the peak have been used as the internal reference. In Fig. 3(C), the band at $3000\text{--}3600\text{ cm}^{-1}$ of the hydroxyl groups shows a decrease in its intensity in comparison to that of PVA (Fig. 3(A) and (B)). This suggests that some hydroxyl groups have been consumed for the crosslinking reactions.

3.3. Porous structure

It is important to study the morphology of the crosslinked PVA beads. Table 2 shows the pore volume, pore size and porosity of the beads. In comparison with PVA-10, the pore volume of PVA-5 is almost ten times larger and its porosity is also nearly eight times higher. The large differences in the pore volume and porosity can also be seen in Fig. 4, which shows the scanning electron micrographs of the porous structure for selected PVA beads with varying crosslinking density. The size and shape of the pores of three different beads are strikingly different. It is clear that PVA-10 has regular pores with smaller pore sizes than that of PVA-6 and PVA-8, while the porous structure of PVA-6 is less uniform than the other two resins. Since the number of free hydroxyl groups in the resins does not have a significant effect on the structure of the dry beads [19,20], these differences may be attributed to the difference in the density of crosslinking of the different resins. The network can be preserved without collapsing in the dry form after freeze-drying the beads (first frozen in liquid nitrogen) for about 48 h.

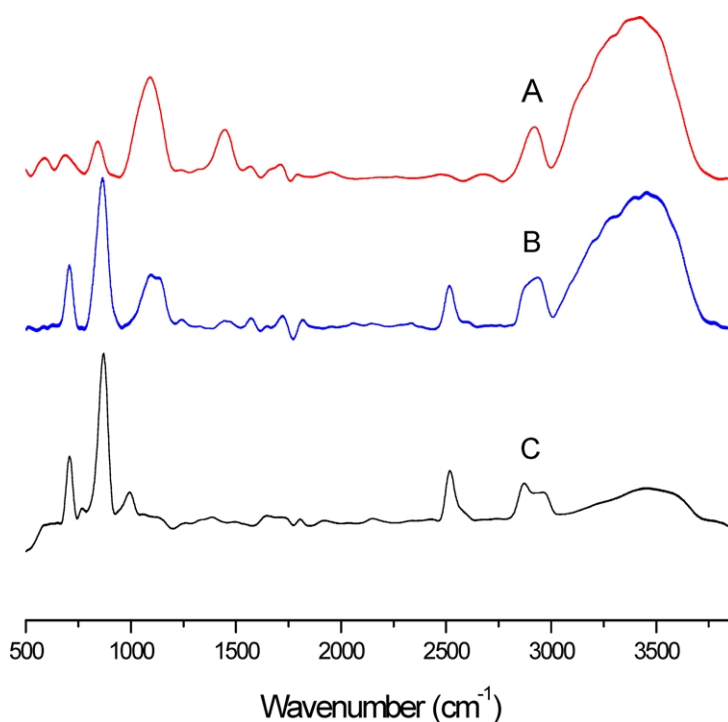


Fig. 3. FT IR spectra of PVA and PVA beads: (A) pure PVA (KBr/PVA = 100:8); (B) PVA and calcium carbonate (KBr/PVA/CaCO₃ = 100:8:5); (C) PVA beads (PVA-6, bead size: 250–340 μm) and calcium carbonate (KBr/PVA beads/CaCO₃ = 100:8:5).

Table 2
Pore parameters of the PVA beads

Beads	Pore volume of pores (V_p) (ml/g)	Porosity (ϕ)	Pore size (μm) ^a
PVA-5	4.69	4.69	1–15
PVA-6	3.49	3.36	1–10
PVA-7	2.34	2.19	1–5
PVA-8	1.24	1.42	1–5
PVA-10	0.45	0.60	1–2

Volume of pores and porosity were average values of the beads of different sizes.

^a The pore size of the beads was estimated from their SEM images.

3.4. Loading of hydroxyl groups

To determine the loading of hydroxyl groups on the PVA beads, the resins were acetylated by reacting with an excess of acetic anhydride, which was then converted to acetic acid and titrated with a base. Some of the results are listed in Table 3, in which each value corresponds to an average of three assessments. The loading decreased with increasing amount of EP. This is expected since one EP consumes two hydroxyl groups of PVA and generates a new one at the same time during crosslinking. Therefore, the amount of EP used reduces the number of hydroxyl groups in the resin. It is to be noted that the loading determined is dependent on the accessibility of the OH groups during acetylation. Table 3 also shows that the bead size does not have a significant effect on the loading of the beads within experiment error.

3.5. Swelling behavior and crosslinking density

Crosslinked polymeric networks can be conveniently characterized by the crosslinking density ρ [21], which is inversely related to the average molecular weight per crosslinking unit M_c , according to

$$\rho = (v M_c)^{-1} \quad (6)$$

where v is the specific volume of the polymer.

From the true density of the dry beads, the volume fraction of PVA in the swollen bead in water, V_s , and the volume fraction of PVA in solution before crosslinking, V_r ,

Table 3
Loading (mmol/g) of hydroxyl groups in PVA beads

Beads	Mesh size				Average loading (mmol/g)
	20–30	30–40	40–60	60–100	
PVA-5	17.8	17.8	17.3	17.6	17.6
PVA-6	17.2	17.4	17.1	17.4	17.3
PVA-7	16.7	17.0	16.9	17.2	17.0
PVA-8	15.1	15.5	15.3	15.9	15.4
PVA-10	13.6	14.3	14.0	14.5	14.1

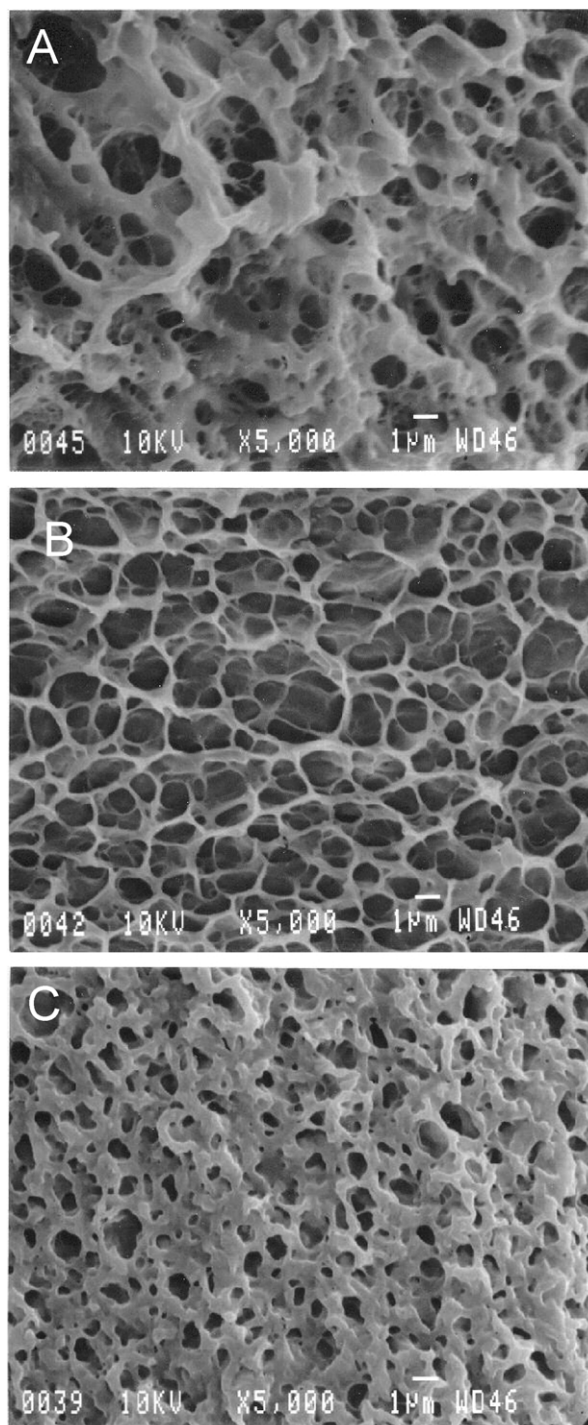


Fig. 4. Scanning electron micrographs of crosslinked PVA beads. (A) PVA-6, (B) PVA-8, (C) PVA-10.

can also be calculated: [22]

$$V_s = \frac{(1 - W_Q)d}{W_Q + (1 - W_Q)d} \quad V_r = \frac{W_p/d}{W_p/d + W_s} \quad (7)$$

where d is the density of the dry beads, W_p the weight of PVA added before crosslinking, W_s the weight of total water in PVA solution before crosslinking, and W_Q the water content at equilibrium. The density of water is taken as

1 g/mL. The average true density of the dry beads is around 1.2 g/cm³.

A modified Flory equation can be used to calculate the crosslinking density ($1/M_c$) when crosslinkers were introduced between polymer chains while the polymer was dissolved: [23]

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{\frac{v}{V_1} [\ln(1 - V_s) + V_s + \chi_1(V_s)^2]}{V_r \left[\left(\frac{V_s}{V_r} \right)^{1/3} - \frac{1}{2} \left(\frac{V_s}{V_r} \right) \right]} \quad (8)$$

where v is the specific volume of polymer in the amorphous state (0.788 ml/g) and V_1 the molar volume of the solvent (18 ml/mol). The Flory polymer–solvent interaction parameter χ_1 takes a value of 0.494, while M_n of PVA is known. Eq. (8) can be used for crosslinked PVA gels. Since the crosslinked beads are similar to a gel, Eq. (8) can be also applied in this case. The calculations for such beads were made with the help of Eqs. (1)–(8), and the results are given in Table 4. Unlike a linear homopolymers of PVA, many of the OH groups of the resins have reacted during crosslinking. Therefore, the parameters used in the calculations are rather approximate, and the results obtained here are likely also approximate.

Although S_w and M_c differed greatly for the five resin samples, the W_Q value did not change much. It is natural that S_w will decrease when M_c decreases (i.e., ρ increases) since the PVA chains were held together more tightly. In addition, we have also noted that both S_w and M_c decreased sharply at the beginning followed by a more gradual decrease when the amount of crosslinker was more than 8 ml. The differences of S_w and M_c for the various samples may suggest that some of the crosslinker were dissolved in the oil phase in the suspension. It is possible that the crosslinker EP was not completely consumed in the step of pre-crosslinking, especially when the amount used was increased. It is clear that ρ should have a direct influence on the swelling behavior of the PVA beads. The number of free hydroxyl groups in PVA beads is more important in determining the swelling properties of these resins. It has been known that both free and bound water exist in most colloids swellable in water [24]. Since the amount of bound water in the beads is

Table 4
Swelling behavior of PVA beads and crosslinking density of PVA beads

Beads	W_Q (%)	S_w	True density (g/ml)	V_s	V_r	M_c	$\rho \times 10^{-4}$
PVA-5	94.9	17.7	1.19 ± 0.04	0.043	0.128	6310	2.01
PVA-6	92.3	12.3	1.20 ± 0.03	0.065	0.128	4710	2.69
PVA-7	89.6	9.27	1.19 ± 0.02	0.088	0.128	3150	4.03
PVA-8	86.8	7.13	1.21 ± 0.01	0.113	0.128	1430	8.88
PVA-10	84.2	6.04	1.21 ± 0.01	0.135	0.128	1160	10.1

W_Q and S_w changed with the beads size and they were calculated as an average value from the beads of different sizes. V_s and V_r were calculated from the average W_Q and the average true density of the beads (~1.2 g/ml).

closely related or even proportional to the number of hydroxyl groups, the high W_Q value (84.2%) for PVA-10 implies that these PVA beads have a fairly high loading of hydroxyl groups even though they have a relatively high crosslinked density and that only a small difference in loading of hydroxyl groups for these five samples is expected.

4. Conclusion

Porous crosslinked poly(vinyl alcohol) resin beads have been prepared by a two-step pathway involving pre-crosslinking with epichlorohydrin followed by a reverse suspension crosslinking reaction. Under optimized reaction conditions, these resins possess very high loading of hydroxyl groups even though they have a relatively high density of crosslinking. The difference in the crosslinking density of the resins does not cause significant difference in the average loading of hydroxyl groups. The resins are easily swellable in water and their pore size and volume and the porosity depend strongly on their crosslinking density. In general, a low crosslinking density results in resins with relatively large pore volume, high porosity and small bead size. The use of such resins, after proper chemical modification, as supports or scavengers in solid phase organic synthesis is promising and is a subject of investigation.

Acknowledgements

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