

Synthesis and Characterization of a Cation-Exchange Resin Based on Vinylpyrrolidone-*co*-divinylbenzene: Effect of Nature and Amount of Diluent on Different Resin Properties

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ABSTRACT: Fundamental studies regarding the synthesis of a porous copolymer synthesized from 1-vinyl-2-pyrrolidone and divinylbenzene in the presence of different diluents were carried out. A series of porous copolymer resins was synthesized by suspension polymerization using the following diluents: dimethylphthalate (DMT), diethylphthalate, dibutylphthalate, and bis-2-ethyl hexylphthalate [dioctylphthalate (DOT)]. It was observed that the porosity of resin increases with increase in length of the methylene group in the phthalate ester of DMT to DOT. In another series of experiments the amount of solvent was increased from 30 to 60% while the crosslinkage was kept constant at

30% and the diluent used was DOT. It was observed that the porosity of resins increased as the fraction of solvent increased. However, surprisingly, the Na⁺ capacity did not show any appreciable change by varying the amount or nature of diluent, remaining approximately 4 meq/g. The resin remained mechanically strong despite higher porosity. The mechanical strength also did not show any significant change by varying the diluent or amount of diluent. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3917–3920, 2004

Key words: cation exchange; density; resins; crosslinking; suspension polymerization

INTRODUCTION

1-Vinyl-2-pyrrolidone-*co*-divinylbenzene (VP-*co*-DVB) polymers have been widely used for the chromatographic separation of aromatic acids, aldehydes, and phenols.^{1–3} It is also used as a tablet disintegrator in the pharmaceutical field. It has excellent properties, such as high swelling pressure with water, and it is therapeutically inactive and physiologically inert. This copolymer has desirable properties such as hydrophilicity, polarity, complexing ability, and compatibility.⁴ It can bind drug molecules, thus making it useful for drug absorption. It can also be used in textiles and azo dyes.⁵ The porosity plays an important role in the properties of resin. In microporous resins the swelling is highly dependent on composition of solution. Macroporous polymers, however, have higher capacities and are more selective than microporous resins. The macroporous resins have many advantages because porosity of the resin provides support against any radiolytic attack and osmotic shock, and thus this resin can be used in the nuclear industry.

There is a controversy⁴ about suspension polymerization of vinyl pyrrolidone with dimethacrylate^{6,7}

and divinylbenzene in aqueous media. Suspension polymerization of 1-vinyl-2-pyrrolidone and ethylene dimethacrylate in an aqueous medium has been reported to be difficult for preparation of regular spherical particles. This difficulty has been attributed to high polarity of amide groups, which are soluble not only in water but also in a range of organic solvents such as benzyl alcohol, carbon tetrachloride, and amyl acetate, for example. That is why, to make spherical particles, some investigators⁴ have used a stabilizer for the system. Highly crosslinked polyvinyl pyrrolidone has also been reported⁸ produced by proliferative polymerization. This polymer has been reported and used for removal of polyphenols from beverages, although the mechanical strength of the polymer is reported to be rather poor.

In the present work, VP-*co*-DVB copolymer after synthesis was modified into a cation-exchange resin by sulfonation. It is a superior ion-exchange resin. In this study we performed various experiments to determine the effects of varying both the amount and nature of diluent on different resin properties: porosity, capacity, and mechanical strength. The main feature of this investigation is that it can be used as a guide for the synthesis of resins of desired porosity, mechanical strength, and density, according to the requirements. A feature of the synthesized resin is that, despite its porous structure, the beads do not lose their shape and have sufficient mechanical strength

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TABLE I
Effect of Amount of Diluent on the Properties of VP-co-DVB Copolymer^a

Sample	Solvent fraction (Fs)	Pore volume (mL/g)	Average pore diameter (μ)	Density (g/mL)	Mechanical strength (kg)	Capacity, Na ⁺ (meq/g)
1	0.3	0.62	0.01	0.35	0.32	4.0
2	0.4	0.88	0.018	0.24	0.28	3.8
3	0.5	2.01	0.026	0.14	0.25	3.96
4	0.6	2.50	0.54	0.12	0.23	3.8

^a Crosslinking = 30%; diluent used: DOT.

and, further, this copolymer can be converted to a useful cation exchanger.

EXPERIMENTAL

1-Vinyl-2-pyrrolidone (97% purity) was supplied by Fluka Chemical (Buchs, Switzerland); divinyl benzene (60% purity) was purchased from Reidel-de Haën (Seelze, Germany). Benzoyl peroxide (BPO), obtained from Fluka, was used as initiator. Dimethylphthalate (BDH, Poole, UK), diethylphthalate (Riedel-de Haën), dibutylphthalate (Merck, Darmstadt, Germany), and bis-2-ethyl hexylphthalate (dioctylphthalate; Fluka) were used as diluents. Gum arabic and gelatin, obtained from Fluka Chemical, were used as suspending agents. Sulfuric acid (98%) was obtained from Merck.

The copolymerization was carried out by the suspension polymerization technique. The aqueous phase was prepared by dissolving 1.5 g gum arabic, 1.5 g gelatin, and 3.0 g sodium chloride in 150 mL of demineralized water (DMW). The organic phase was prepared by dissolving 0.3 g of BPO in 30 mL of monomer and diluent. The amount of diluent was calculated by the following formula: $F_s = \text{amount of diluent} / (\text{amount of monomer} + \text{amount of diluent})$.

The organic phase was added slowly to the aqueous phase in a jacketed vessel. The reaction temperature was kept at room temperature for 0.5 h and stirring was carried out at about 800 rpm. The temperature was then increased to 80°C and kept constant for 22 h. Then the reaction mixture was refluxed for 2 h at 95–100°C. The copolymer was then removed from the reaction vessel and washed with hot DMW, followed by methanol through Buchner funnel suction until all the organics were removed.

Sulfonation of the copolymer

The VP-DVB copolymer was modified into a cation-exchange resin by sulfonation. A 10-g sample of VP-DVB copolymer was dried under vacuum at 100°C for 24 h to remove water, after which the resin was transferred to a reaction vessel. About 50 mL of sulfuric acid (90%) was poured into the reaction vessel and the

mixture was stirred for 3 h at 90°C. Then the resin was washed with DMW until it became neutral.

Characterization of copolymers

Porosity of the copolymer was measured by an Autopore 9220 porosimeter (MicroMetrics, Inc. Londonderry, NH). Density of the copolymer was measured by determining the volume and weight of the dry sample. Mechanical strength measurements were carried out using a similar procedure as that described earlier.⁵ The sodium ion (Na⁺) capacity of the cation exchange resin was determined by using the method described in the literature.⁹ The air dried sample was weighed in one gram portions each, one portion was dried under vacuum at room temperature for 24 h to determine the moisture contents while the other part was loaded onto a column of one cm diameter. The resin was impregnated with 200 mL of 1N NaOH and 50 mL of DMW. The effluent was collected in a 250 mL measuring flask. The concentration of NaOH in the effluent was determined by a standard analytical method. The amount of that of sodium ion settled on the resin is the Na ion capacity of the resin.

RESULTS AND DISCUSSION

During all the experiments carried out for the preparation of copolymers, spherical beads, ranging in size from 45 to 150 μm , were obtained. Interestingly, these beads, as shown in Tables I and II, have better mechanical properties than those of 4-vinylpyridine-co-divinylbenzene-based resin,¹⁰ even for the resin synthesized with a greater amount of solvent fraction. This shows that selection of a suitable suspension stabilizer is not of crucial importance in this case, compared to that reported for some systems, such as the one considered by Horak et al.⁴

Effect of amount of diluent

A series of experiments were carried out using varying fractions of solvent (i.e., $F_s = 0.3$ – 0.6), keeping the degree of crosslinking at 30%. The solvent used was

TABLE II
Effect of Variation of Diluent on the Properties of the VP-co-DVB Copolymer^a

Sample	Diluent used	Pore volume (mL/g)	Average pore diameter (μ)	Density (g/mL)	Capacity, Na ⁺ (meq/g)	Mechanical strength (kg)
1	DMT	0.62	0.0175	0.29	4.5	0.35
2	DET	0.82	0.0184	0.27	4.2	0.3
3	DBT	1.66	0.0284	0.19	4.2	0.28
4	DOT	2.01	0.0302	0.14	4.0	0.23

^a Fs = 0.5; crosslinking = 30%

DOT, and the obtained copolymers were characterized by determining the porosity, capacities, and so forth, results of which are given in Table I. It is observed that the porosity of resin increased with increase in fraction of solvent from 0.3 to 0.6. The pore size distribution curve shifted toward maximum pore diameter by increasing the amount of solvent (Fig. 1). The resin becomes porous and hence the density of the copolymers decreases accordingly. The mechanical strength of the copolymer decreased slightly with the increase in porosity of the resin, although the resin did not lose its mechanical strength. However, the sodium capacity for all polymers shows no appreciable change. These results are in good agreement with results reported for glycidyl methacrylate-co-ethylene glycol dimethacrylate (GMA-co-EGDM)¹¹ and 2-methyl-5-vinyl pyridine-co-DVB.¹²

Effect of nature of diluent

A series of experiments were carried out by varying the nature of diluent, but keeping the amount of diluent constant (i.e., Fs = 0.5). The percentage crosslinkage (i.e., the amount of divinyl benzene) was kept at 30% in all the experiments. The diluents for this series used were dimethylphthalate, diethylphthalate, dibutylphthalate, and dioctylphthalate, having solubility parameter values¹³ of 10.7, 10, 9.3, and 7.9 (cal/cm³)^{1/2}, respectively. These values suggest that DMT acts as a solvating diluent and DET is a

moderately solvating diluent, whereas both DBT and DOT are nonsolvating diluents. It was observed that the pore volume (porosity) increased from 0.62 to 2.01 mL/g by changing solvents, having different lengths of alkyl groups, that is, from DMT to DOT (shown in Table I). The pore size distribution curve shifted toward larger pores as the number of methylene groups increased from one to eight (DMT to DOT). The pore size distribution curve shifted toward maximum pore diameter by changing the diluent from DMT to DOT (Fig. 1). We observed and previously reported¹¹ the same trend in the case of GMA-co-EGDM and in the 4-vinyl pyridine-co-divinylbenzene system.¹⁰ However, contrary to the above, in the present work, the mechanical strength does not show any appreciable change.

Because of its better mechanical properties, this resin can be used for many chromatographic applications. The porous structure, coupled with better mechanical strength, gives suitability and stability to this resin against any radiolytic or thermal attack in the application. The sodium capacity showed no appreciable change with change in the nature of diluent. The capacity remained in the range of 4 to 4.5 meq/g, which is almost similar to the one obtained in *N*-vinylcarbazol-divinylbenzene copolymer.¹⁴

CONCLUSIONS

1-Vinyl-2-pyrrolidone-co-divinylbenzene copolymer was successfully modified into an ion-exchange resin.

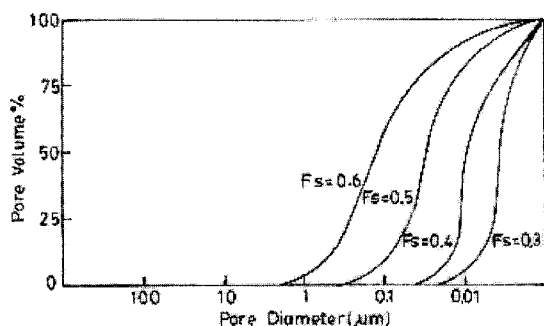


Figure 1 Pore size distribution curves showing effect of amount of diluent. DVB = 30%; diluent used: DOT.

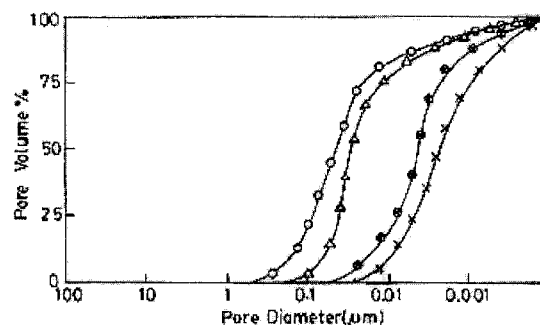


Figure 2 Pore size distribution curves of 1-vinyl-2-pyrrolidone-DVB copolymer (DVB = 30%; Fs = 0.5) with various diluents: DMT (x); DET (⊗); DBT (Δ); DOT (□).

The Na⁺ ion capacity of this resin shows that this is a useful cation-exchange resin. Effects of the nature and amount of different diluents on VP-co-DVB copolymer were investigated. This study gives guidelines for the synthesis of resin of desired porosity, mechanical strength, and density, according to the requirements. An important feature of this study is that, unlike other copolymers (e.g., vinylpyridine-co-divinylbenzene, glycidyl methacrylate-co-ethylene glycol dimethacrylate, etc.), the VP-co-DVB copolymer does not lose its mechanical strength with increase in the porosity. These properties show that this resin can sustain against any radiological attack and osmotic shock. The porosity of 1-vinyl-2-pyrrolidone-divinyl benzene copolymer increases with increasing number of methylene groups in the phthalate ester series (i.e., dimethylphthalate, diethylphthalate, dibutylphthalate, and diocylphthalate). The porosity also increases by increasing the fraction of solvent. The Na⁺ capacity remains almost constant by variation of solvent fraction. Similarly, in this system the mechanical strength also does not show any significance change. The resin remains mechanically strong even with the higher

porosity of the resin. In light of their properties, these resins show better prospects for use in the nuclear industry and for many other applications.

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