

Studies of Porous Polymer Gels. I. One-Step Suspension Technique for Preparation of Moderately Crosslinked Methacrylic Acid Gels

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Synopsis

A new method of preparation of carboxyl cation exchangers directly from methacrylic acid and divinylbenzene is described. A suspension technique with a concentrated aqueous calcium chloride solution as the water phase was used. *n*-Octane and toluene were inert diluents of the monomers. The copolymers obtained have high ion-exchange capacity (9.6–10.6 mequ./g) and porous structure.

INTRODUCTION

Crosslinked polymers of acrylic and methacrylic acids in the form of small beads are prepared mainly from derivatives of the corresponding acids (esters, nitriles, etc.) by suspension copolymerization. Bifunctional monomers are used as crosslinking agents.¹ The resulting copolymers are then converted to acid form. There are only few reports on direct copolymerization of methacrylic acid (MA) and divinylbenzene (DVB) in aqueous suspension.²⁻⁴

The simple one-step method for copolymerization of MA and DVB should be more efficient and of lower cost than previous methods. Using this method one can easily modify the properties of the product.

EXPERIMENTAL

All chemicals except the monomers were of analytical grade and used without purification. MA was distilled in vacuum and further purified by fractional crystallization. DVB was a technical product containing 60.7% by weight of DVB isomers, the rest being ethylstyrenes. The DVB was purified by shaking with 1*N* aqueous sodium hydroxide and repeatedly with water, and then dried over anhydrous magnesium sulphate. The polymerizations were carried out using benzoyl peroxide as initiator (0.5% by weight of the organic phase) at 70°C under nitrogen for 12 hr. The ratio of organic phase to aqueous phase was 1:5. As aqueous phase a calcium chloride solution of the density 1.3 g/ml was used.

The product in the form of milky-white beads of diameter 0.3–1.0 mm was extracted with cold methanol and treated by repeated conversion to sodium (Na) and hydrogen (H) forms using 1*N* sodium hydroxide and 1*N* hydrochloric acid, respectively. Before the measurements the resins were converted into H form, and then washed with a large amount of deionized water.

The ion-exchange capacity was determined semidynamically using the method

similar to that described by Gustafson,⁵ the apparent density of the resins were determined using a mercury pycnometer,⁶ and the water regain by centrifugation.⁷ The dry weight of the sample in H form was determined after drying the gels at 60°C over phosphorus pentoxide in vacuum for at least 8 days.

RESULTS AND DISCUSSION

A complication and disadvantage of the suspension method in this case is the solubility of MA in water. Using aqueous solution of calcium chloride of a density from 1.25 to 1.40 g/ml as water phase the solubility of MA is greatly reduced. The concentration of MA and its homopolymer in the CaCl₂-water phase decreases during copolymerization, e.g., from about 45 mg/ml down to about 12 mg/ml.⁸

During copolymerization the suspension can be stabilized by a finely powdered inorganic compound such as barium sulfate, bentonite or hydroxyapatite. The stabilization occurs only under the condition that the copolymerization reaction in the suspended monomer phase is faster than the homopolymerization of MA dissolved in the water phase. In this way it is easy to stabilize monomer mixtures of MA and DVB in which DVB is in larger amount than about 10% by weight. Polymer of low degree of crosslinking containing less than 10% DVB can be prepared by adding to the mixture of MA and DVB a reactive monomer, which accelerates the polymerization in the suspended phase.⁹

Modified copolymers of MA and DVB can be prepared by adding water insoluble inert diluents to the monomer mixture prior to polymerization. Using a monomer mixture (100 parts by volume) containing 83.3% MA, 10% of DVB isomers, and 6.7% of ethylstyrenes, to which ten parts of aliphatic hydrocarbons are added, macroporous structures with radii of macropores about 30, 84, and 94–200 nm were obtained for *n*-heptane, kerosene, and liquid paraffine, respectively. By mercury porosimeter measurements it was found that such polymers contain a significant amount of small pores with radii below 3 nm.⁸ The composition of the monomer mixtures and the properties of the resins are listed in Table I.

The yield of polymerization, measured as the weight of resins in comparison with that of the monomer mixture, exceeded 97%. At the same time, the ion-exchange capacity of the resins (i.e., content of carboxyl groups active in neutralization) is in every case considerably lower than the values, calculated from the MA content in the starting mixtures. This is due to partial inaccessibility of the carboxyl groups. The apparent loss of MA during polymerization is measured as decreased resin capacity with increasing DVB content. Similar effects for copolymers of MA and DVB prepared in bulk have been observed.¹⁰

The low apparent density (i.e., the high porosity) of the resins obtained from MA, DVB, and monovinyl aromatic monomers is due to the inert diluents and unreacted MA present during the polymerization. The effect on apparent density and water regain from *n*-octane present in the monomer mixture is more pronounced than the effect of toluene.

Detail consideration of factors influencing the structure of MA-DVB copolymers will be published separately.¹¹

TABLE I
Compositions and Properties of Crosslinked Methacrylic Acid Gels Prepared Using One-Step Suspension Method

| Symbol of sample | Monomer blend composition | | | DVB ^a , % | Ion-exchange capacity ^b , mequ./g | Water regain ^b , g/g | Apparent density ^b , g/cm ³ |
|------------------|---------------------------|---|-----|----------------------|--|---------------------------------|---|
| | MA, % | toluene/ <i>n</i> -octane, parts/100 parts of monomers by volume | | | | | |
| S-53 | 91.8 | ... | ... | 5.0 | 10.6 | 1.06 | 1.16 |
| S-54 | 85.0 | ... | ... | 5.0 | 10.2 | 1.01 | 1.16 |
| ST-5052 | 85.0 | 5/... | ... | 5.0 | 10.1 | 1.10 | 1.16 |
| SO-5052 | 85.0 | .../5 | ... | 5.0 | 10.0 | 1.13 | 1.09 |
| ST-512 | 85.0 | 10/... | ... | 5.0 | 10.1 | 1.21 | 1.04 |
| SO-512 | 85.0 | .../10 | ... | 5.0 | 10.1 | 1.29 | 0.96 |
| S-1 | 85.0 | ... | ... | 9.1 | 9.7 | 0.65 | 1.38 |
| ST-101 | 85.0 | 5/... | ... | 9.1 | 9.8 | 0.69 | 1.36 |
| SO-101 | 85.0 | .../5 | ... | 9.1 | 9.6 | 0.71 | 1.33 |
| ST-111 | 85.0 | 10/... | ... | 9.1 | 9.7 | 0.79 | 1.28 |
| SO-111 | 85.0 | .../10 | ... | 9.1 | 9.8 | 0.83 | 1.27 |
| ST-1151 | 85.0 | 15/... | ... | 9.1 | 9.7 | 0.86 | 1.33 |
| SO-1151 | 85.0 | .../15 | ... | 9.1 | 9.7 | 1.04 | 1.02 |

^a Calculated for *m*- and *p*-DVB in a technical product.

^b Values for vacuum dried resins in hydrogen form.

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