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Microcapillary Oxidation-Reduction Polymers

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Synopsis

"Replica gel" polymers, characterized by their extremely high specific surface area, have not previously been prepared in "redox" form. Some illustrative syntheses are described, and the capability of these materials to oxidize acetic acid and to epoxidize oleic acid and cyclohexene is demonstrated.

INTRODUCTION

There is described in earlier publications[1–3] a basic method for securing a microcapillary structure in a polymeric, organic particulate substance. The technique employs anhydrous silica gel as a parent "matrix" within which is accomplished the polymerization of a fluid monomer or prepolymer. Subsequent to this polymerization, the silica gel matrix is selectively dissolved away and in this manner removed from the newly formed organic polymer. As a result of these operations, there is produced a new, microcapillary containing substance of high specific surface area, and with its own associated chemical characteristics and adsorptive properties. This new material has capillary and void space inverted, in relation to the parent silica gel matrix, and the name "replica gel"® is applied to these materials.

The present paper describes the preparation of oxidation-reduction polymer from "replica gel" polymer and its use, for example, to oxidize acetic acid to peracetic acid, and to epoxidize oleic acid and cyclohexene. The potential advantage of redox resins in "replica gel" form is that the resin produced is highly porous, containing microcapillaries giving it a much larger specific surface area than the conventional spherical beads.

The precursor "replica gel" was a copolymer of styrene and ethyl acrylate, crosslinked with divinylbenzene. The method of preparation followed generally that of Ferris and Lyman[4] for the comparison polymer in bead form, and that of Wagner[3] for the "replica-gel" polymer. The reactive group utilized is the carboxyl group provided by incorporation of the ethyl acrylate mer-unit and the subsequent hydrolysis of this. Additionally, the polymer was sulfonated, the sulfonic acid groups thus introduced acting as *in situ* catalysts for the oxidation of the carboxyl groups.[5] The carboxyl groups were oxidized to percarboxylic acid with aqueous hydrogen peroxide.

EXPERIMENTAL

Synthesis

The comparison resin in bead form was prepared according to Farris and Lyman[4] and Helfferich and Luten.[5] A mixture of approximately 52 weight parts styrene, 33 ethyl styrene, 9 divinylbenzene, and 25 ethyl acrylate was suspension polymerized in 200 weight parts of water containing 1.75 weight parts of 400 cps methyl cellulose and 0.75 weight parts benzoyl peroxide. Temperature was maintained at 75–80°C for 3 hr, following which time the resin was cooled, filtered, washed, and dried at 110°C for 16 hr.

The "replica-gel" polymer was prepared with the same monomer components in the same proportions, but imbibed by silica gel (Davison Chemical Co., Grade 59), according to Wagner.[3] The monomer/silica gel weight ratio was 1.20, corresponding to the pore volume of 1.15 cm^3/g for this silica gel. Following imbibition, the saturated silica gel particles were heated for 3 hr at 75–80°C. The silica fraction was then dissolved out in 24% hydrofluoric acid, and following water washing, the "replica gel" dried for 16 hr at 110°C.

The procedure of Ferris and Lyman[4] was followed for sulfonation. A mixture of 50 weight parts of polymer and 235 weight parts of ethylene dichloride was contacted for 30 min, then cooled to 10°C. Chlorosulfonic acid, 82 weight parts, was then added gradually over a period of 15 min, a temperature of 25°C being maintained during the addition. The mixture was then heated for 4 hr at 40–45°C with agitation. The mixture was then cooled to 10°C, and 82 parts of water was added over a period of 30 min. The ethylene dichloride was then removed by vacuum distillation, and 100 additional parts of water was added. A three-day period of contact was then allowed to ensure completion of hydrolysis.

Both resins were then conditioned by repeated ion exchange cycles, alternating 10% NaOH and 10% HCl. Following this, the resins were oxidized by placing in 30% hydrogen peroxide and heating at 45°C for 24 hr. Upon completion of this oxidation, the polymers were light orange in color.

Oxidation of Acetic Acid

The oxidized resins were used to oxidize acetic acid to peracetic acid. This was done by placing 3.0 g oxidized polymer in each of three 250-ml flasks, adding 10 ml glacial acetic acid to the first, 10 ml glacial acetic and 10 ml methyl alcohol to the second, and 10 ml glacial acetic acid and 20 ml methyl alcohol to the third. A contact time of 21 hr, at ambient temperatures, was allowed. The oxidation capacities of the resins were measured by reaction with excess aqueous potassium iodide for 20 min at 60°C. The solutions were then titrated with standardized thiosuofate solution, using starch indicator. Peracetic acid was also determined by reaction

TABLE I
Oxidation of Acetic Acid

Resin type	Oxidation capacity, meq/g water-filled resin	Acid concn, vol-%	Yield, %
Spherical bead	0.30	33	100
	0.30	50	100
	0.30	100	100
"Replica gel"	0.71	33	93
	0.71	50	80
	0.71	100	55

with aqueous KI and titration with thiosulfate. Table I shows the results obtained.

In some subsequent experiments, it was found that values for oxidation capacity and oxidation yield, as determined in Table I, increased with increase in reaction time allowed. Weight per cents of dry resin, based on the "water filled" resin, were typically on the order of 55% and 72% for the "replica gel" and spherical bead types, respectively. On a dry-weight basis and more extended reaction times, somewhat higher oxidative capacities and yields have been observed.

Epoxidation Reactions

Further experiments were conducted to determine whether the oxidized resin could be used to epoxidize oleic acid and cyclohexene. After the resin had been oxidized, it was converted to the sodium form by washing with 1*M* NaCl at 10°C. It was thereafter allowed to react with the chosen substrate, for 19 hr at ambient temperatures, in a 10% anhydrous ethyl ether solution.

In determining the epoxide formed, HCl was used to convert this to the halohydrin, the excess acid being then back-titrated. Since ether was used as the solvent here, the method described by Dobinson et al.[6] was used. Blanks were run on the unoxidized ether solution of substrate, ether solution of acid, and ethanol. Results are shown in Table II.

In order to further characterize the resins (before oxidation), the exchange capacity for each type of acid (sulfonic and carboxylic) was determined. For the spherical bead resin, this was found to be 2.20 and

TABLE II
Epoxidation of Oleic Acid and Cyclohexene

	Epoxidation, meq/g dry resin	
Resin type	Oleic Acid	Cyclohexene
Spherical bead	0.69	0.09
"Replica gel"	0.40	0.04

0.50 meq/g dry resin for sulfonic and carboxylic acid, respectively. For the "replica gel" resin, the corresponding figures were 4.4 and 1.0, respectively.

RESULTS AND DISCUSSION

From Table I, it is seen that the oxidation capacity of the "replica gel" is more than double that of the spherical bead form. This may be the result of the greater accessibility to the interior of the polymer particles afforded by the microcapillary structure. It is noted also that the oxidative efficiency of the "replica gel" for acetic acid increases as dilution of the acetic acid is made with methyl alcohol. On the other hand, the spherical bead form shows no such effect. A possible explanation for this may be a higher degree of swelling of the "replica gel" by methyl alcohol or, alternatively, an increase in diffusion of reacting and product species when the methyl alcohol solvent is present.

Table II shows an unexpectedly low epoxidation yield for both the oleic acid and the cyclohexene. The data do, however, demonstrate the feasibility of carrying out such epoxidations using redox polymers, and additional work along these lines is planned.

References

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