

## Reactive Polymers

### XLII. Catalytic Activity of Macroporous Methacrylate Copolymers Containing Sulfopropyl Groups in Reesterification of Ethyl Acetate by 1-Propanol<sup>1</sup>

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The catalytic activity of macroporous methyl acrylate copolymers containing sulfopropyl groups has been tested with the use of gas phase and liquid phase reesterification of ethyl acetate by 1-propanol as the model reaction. The catalytic activity of these polymers has been evaluated with respect to their chemical composition, functional groups distribution, and the morphology of their porous structure. The results were compared with the catalytic activity of sulfonated macroporous styrene-divinylbenzene copolymers.

#### INTRODUCTION

We have recently reported on the synthesis and properties of macroporous copolymers containing sulfopropyl groups based on reactive glycidyl methacrylate-ethylenedimethacrylate copolymers (1, 2). The synthesis involved the reaction of hydroxyl groups of an acid-hydrolyzed glycidyl methacrylate copolymer with propane sultone in alkaline medium, which was used earlier in transformations of cellulose and starch. We have prepared a series of samples differing in the amount of crosslinking agent, conditions used in preparing suspension copolymers, as well as in the reaction with propane sultone. Some of the samples were also modified by partial neutralization with alkali metal ion.

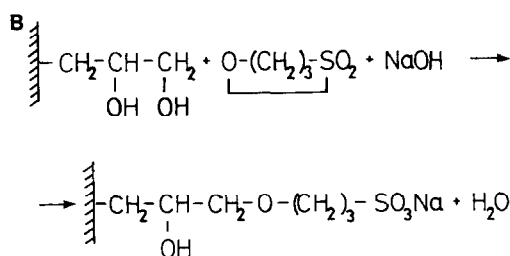
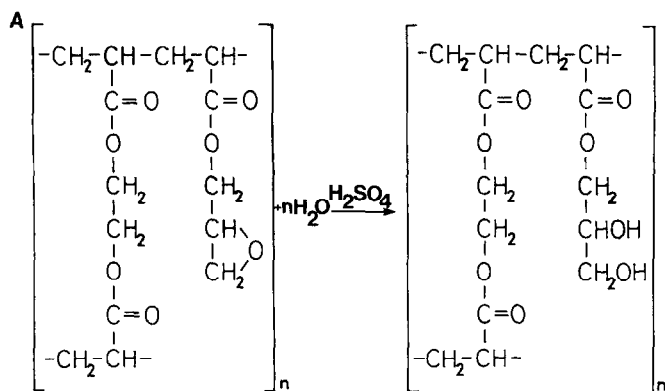
In the present work, we report on some catalytic properties of macroporous ion exchangers based on a hydrophilic glycidyl methacrylate copolymer (further designated as GM), particularly from the point of view of their chemical structure, distribution of active groups, and morphology of

their porous structure. With this aim, we used reesterification of ethyl acetate by 1-propanol as the model reaction. This reaction was already described in detail in earlier work (3-6) in which sulfonated macroporous styrene-divinylbenzene copolymers (further designated as MS) were used as catalysts.

#### EXPERIMENTAL

**Catalysts.** Macroporous glycidyl methacrylate-ethylenedimethacrylate copolymers with 30-85% (by mass) of the crosslinking agent were first acid hydrolyzed (1 mol/liter H<sub>2</sub>SO<sub>4</sub>, 90°C, 3 h) (reaction A) and after drying they were reacted with propane sultone in 22.7% (by mass) NaOH (GM : propane sultone : NaOH molar ratio = 1 : 8 : 5) at 35°C for 24 h (unless stated otherwise) (2) (reaction B). The modification reaction was mostly carried out batchwise in the following way: 0.85 g of ground NaOH was dissolved in 3 ml of water and then 1 g of hydrolyzed GM gel and 2 g of propane sultone (Fluka) were suspended in this solution. The mixture was maintained at 35°C for 10 h, filtered, the gel was washed with water and ethanol,

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and dried (70°C, 1.3 kPa). As indicated later, in some cases the reaction was carried out in a flow arrangement or in the presence of 6.7% (by mass) of the phase transfer catalyst, tetra(*n*-butyl)ammonium hydroxide.

The content of sulfonic acid groups was determined alkalimetrically and checked also by elemental analysis of dried samples (80°C, 1.3 kPa, 72 h).

The specific surface of dried samples was determined by dynamic nitrogen desorption and the liquid regain (specific pore volume) in cyclohexane and in water was determined by the absorptivity of these compounds using centrifugation technique (7). The properties of the catalysts used are presented in Table 1.

The distribution of sulfonic acid groups in the catalyst beads was determined in the following way. The beads were cut into sections passing through the center and the sulfur surface concentration was determined by electron microprobe analysis (JEOL-JXA 50 A).

The catalytic activity of the polymers in the gas phase was examined in a glass flow reactor at 120°C. A mixture of liquid reactants was fed at the required rate into an evaporator through which an inert gas (nitrogen) was passed. The reaction mixture then passed through the reactor (the amount of the catalyst varied from 0.5 to 1 g). Liquid products were separated from the carrier gas by cooling to a temperature of -78°C and analyzed gas chromatographically. Conversions did not exceed 10% which made it possible to determine the values of initial reaction rates as ratios of conversions and contact times of the key component.

The catalytic activity of the polymers in the liquid phase was examined in a glass, ideally mixed flow reactor at 52°C. The proper function of the reactor was verified by the procedure reported by Bennett *et al.* (8). The samples for analysis were taken at the steady performance of the reactor. With respect to the differential character of the reactor, the values of initial reaction rates

TABLE I  
Properties and Catalytic Activity of GM Catalysts Used<sup>a</sup>

Designation of ion exchanger	Content of crosslinking agent (%)	P (%)	Content of SO <sub>3</sub> H groups (mol/kg)		Specific surface (m <sup>2</sup> /g)	Solvent regain (cm <sup>3</sup> /g)		Initial reaction rate of reesterification (mol h <sup>-1</sup> kg <sub>cat</sub> <sup>-1</sup> )	
			A	B		C	D	Gas phase <sup>b</sup>	Liquid phase <sup>c</sup>
Effect of crosslinking									
1	30	85	0.71	0.87	30.5	1.23	1.45	2.6	0.49
2	40	90	1.09	1.04	63.5	0.90	1.36	6.0	1.30
3	55	90	0.99	1.05	117.1	0.92	1.27	9.3	1.50
4	60	90	0.92	0.97	102.0	0.79	1.31	19.0	1.74
5	85	90	0.35	0.47	298.6	1.75	1.76	7.2	0.92
Effect of the extent of sulfopropylation									
6 <sup>d</sup>	60	90	0.20	0.20	122.6	0.97	1.39	2.7	0.38
7 <sup>e</sup>	60	90	0.60	0.60	99.3	0.94	1.42	6.0	1.62
Effect of the content of cyclohexanol used in copolymerization									
8	60	85	0.44	0.52	141.2	1.08	1.42	7.1	1.47
9	60	100	0.63	0.64	104.1	0.94	1.13	6.7	1.60
Effect of partial exchange of alkali metal ion									
10 <sup>f</sup>	60	90	0.76	—	—	—	—	8.8	1.40
11 <sup>g</sup>	60	90	0.57	—	—	—	—	4.4	0.89

<sup>a</sup> P, content of cyclohexanol in dodecanol in the preparation of the polymer; A, content of sulfonic acid groups determined by titration; B, content of sulfonic acid groups determined by elemental analysis; C, absorption of cyclohexane; D, absorption of water.

<sup>b</sup> Ethyl acetate : 1-propanol : nitrogen molar ratio = 1 : 1 : 2, temperature 90°C.

<sup>c</sup> Ethyl acetate : 1-propanol : dioxane molar ratio = 2 : 2 : 1, temperature 52°C.

<sup>d</sup> Reaction time of sulfopropylation, 5 min.

<sup>e</sup> Reaction time of sulfopropylation, 20 min.

<sup>f</sup> Twenty percent of protons of the sulfonic acid groups which are exchanged by potassium ion.

<sup>g</sup> Forty percent of protons of the sulfonic acid groups which are exchanged by potassium ion.

could be obtained again as ratios of conversions and flow rates of the key component.

Chromatographic analyses were made with the use of a chromatograph equipped with a flame-ionization detection and a 3400 × 4-mm column filled with 15% poly(ethylene glycol) 400 on Celite at 80°C with nitrogen as the carrier gas.

#### RESULTS AND DISCUSSION

GM catalysts used were characterized by basic chemical and texture parameters which are presented in Table 1. In order to understand the reasons for the variations of

activity for different resins it is important to know the detailed distribution and concentration of acidic sites. This depends on the method of preparation. From this point of view, the reaction of the polymer with propane sultone is of main importance since it proceeds in a medium consisting of three phases. Therefore, the catalytically active sulfonic acid groups are located preferentially in the surface layers of the polymer particles where the reactive sites are most likely fully saturated. In addition to sulfonic acid groups the macroporous polymer contains also carboxylic groups (up to 0.39 mol/kg) which are formed by parallel hy-

drolysis of methacrylate esters. Due to their low acidity, these groups seem to be inactive in the reaction studied.

The preferential occupation of the surface of polymer particles by sulfonic acid groups was proved by measurements with the electron-microprobe (Fig. 1). The same result was obtained regardless of the degree of polymer crosslinking and thus also irrespective of the specific surface of these particles. The relative depth of the border layers with higher sulfonic acid group concentration in the catalyst particle with respect to its diameter is essentially identical for all the samples differing in copolymer crosslinking. Individual measurements differed only by a small difference between the ratio of the concentration of sulfonic acid groups in the border parts of the particle and in its center. From this it follows that under conditions of the introduction of sulfonic acid groups into a heterogeneous system, the modification of the internal parts of the particles cannot be achieved even after 24 h, although these particles possess porous structure. In the case of the samples sulfopropylated to the lesser degree (samples 6 and 7, Table 1), the distri-

bution of sulfonic acid groups in particles was analogous, except that in internal parts the concentration of sulfonic acid groups was lower compared to the fully sulfopropylated samples.

Figure 1 illustrates also the measurement made with the sample partially neutralized with potassium ions. From the shape of line b it follows that potassium ions are distributed in the particle volume proportionally to sulfonic acid group distribution, which supports our presumption that during partial neutralization with univalent alkali metal ions in aqueous medium, the neutralizing ions are distributed uniformly over all the acid functional groups. Measurements of ion concentrations for the samples partially neutralized by higher valent transition metals have shown, however, that the concentration of these ions with respect to that of sulfonic acid groups decreases in the center of particles, i.e., these ions, due to their valency and size, are not distributed uniformly and occupy preferentially the more accessible acid groups located nearer to the particle surface. This effect is especially pronounced in the case of ferric ions.

These results illustrate differences between GM and MS ion exchangers, since with the latter polymers we observed a decrease in the concentration of sulfonic acid groups toward the particle center to much less an extent and that only for the most crosslinked samples. This indicates that the sulfonating agent (sulfuric acid) penetrated to the interior of particles of MS polymers via their porous structure. The great decrease in sulfonic acid group concentration in the direction toward the center of polymer particles has been observed only for the gel type of styrene-divinylbenzene ion exchangers.

By using an EDAX instrument connected to the JEOL electron microprobe, we have measured the relative concentrations of sulfonic acid groups and potassium ions in whole sections of several particles of catalyst 11. The results are presented in Table 2 and show that integral values correspond to

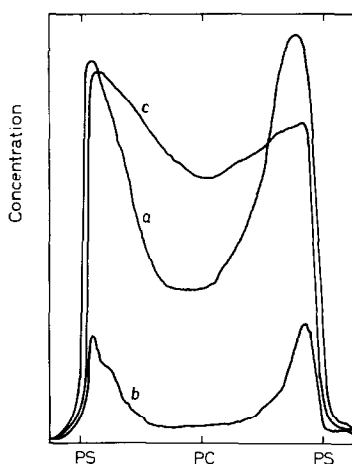


FIG. 1. Concentration of sulfur and potassium in cross-section of catalyst particle. Curve (a), sulfur concentration in catalyst 11; (b) potassium concentration in catalyst 11; (c) sulfur concentration in catalyst 17. PS, particle surface; PC, particle center.

TABLE 2

Mutual Content of Sulfur and Potassium in Section of Polymer Particle

GM ion exchanger (Table I)	Potassium % mol.	Sulfur % mol.
10	21.6	78.4
11	42.3	57.7

the expected molar amounts of potassium ion which was introduced by partial neutralization, although its distribution in the particle mass is controlled by the nonuniform distribution of sulfonic acid groups.

Several attempts were made to modify the sulfopropylation procedure used for GM copolymers so as to achieve a more uniform distribution of sulfonic acid groups within the whole particle. This has been realized by carrying out the modification reaction in a flow reactor and especially by using the phase transfer catalyst, tetra(*n*-butyl)ammonium hydroxide. According to the results represented in Fig. 1 by curve c, the procedure just mentioned gives particles with a more uniform sulfonic acid group distribution, but the catalytic activity of these samples is not higher than that of

the samples with the nonuniform distribution (Table 1). The properties of the ion exchangers prepared by the above procedure are given in Table 3.

Titration of GM ion exchangers (Table 3) with tetra(*n*-butyl)ammonium cation allows one to determine only the sulfonic acid groups located on the ion exchanger surface, since this bulky titrating agent is not able to penetrate into the mass of polymer gel. The content of the so-determined surface groups is essentially constant for the series of GM ion exchangers 12–17 and does not depend on the preparative procedure, which comports with the measurements of sulfur concentration made for particle sections by the electron microprobe. This also shows that the surface layers of polymer particles are fully substituted by sulfonic acid groups.

From the difference between the mass of GM ion exchangers exposed to air and after drying (105°C, 5 kPa, 6 h) it can be concluded that under normal conditions they absorb about 5 mass% of water vapor, regardless of their crosslinking. Under similar conditions, MS ion exchangers absorb ca. 20 mass% of water vapor. Comparison of the swelling volume of GM and MS ion ex-

TABLE 3

Effect of Preparative Conditions of Properties of Ion Exchangers<sup>a</sup>

GM ion exchanger	Procedure used for substitution	Content of sulfonic acid groups (mol/kg)				Solvent regain (cm <sup>3</sup> /g)		Specific surface (m <sup>2</sup> /g)	Initial reaction date of reesterification (mol h <sup>-1</sup> kg <sub>cat</sub> <sup>-1</sup> )	
		A	B	C	D	E	F		Gas phase	Liquid phase
12	J-V	0.82	0.72	0.48	0.61	0.89	1.38	44.1	12.83	0.59
13	OH-V	0.94	0.87	0.56	0.68	0.81	1.23	43.0	13.14	0.72
14	OH-V	0.96	0.87	0.69	0.65	0.85	1.61	49.8	15.02	0.87
15	OH-V	0.90	0.82	0.65	0.61	0.79	1.39	52.2	15.37	0.84
16	OH-P	1.15	1.08	0.77	0.67	0.91	1.41	50.8	16.66	1.32
17	OH-P	1.05	0.98	0.72	0.65	0.81	1.40	47.5	17.01	1.28

<sup>a</sup> A, direct titration of the ion exchanger with NaOH; B, treatment of the ion exchanger with NaCl and back-titration of the formed HCl with NaOH; C, direct titration with Me<sub>4</sub>N<sup>+</sup>J<sup>-</sup>; D, direct titration with *n*-Bu<sub>4</sub>N<sup>+</sup>J<sup>-</sup>; E, amount of absorbed cyclohexane; F, amount of absorbed water. J, catalyst Bu<sub>4</sub>N<sup>+</sup>J<sup>-</sup>; OH, catalyst Bu<sub>4</sub>N<sup>+</sup>OH<sup>-</sup>; V, bench reaction; P, flow reaction.

changers is presented in Table 4 and shows that the swelling of MS ion exchangers decreases more steeply with crosslinking.

In our previous work (9) we reported kinetic data on the reesterification of ethyl acetate by 1-propanol on sulfopropylated GM catalysts containing 30, 60, and 80% of the crosslinking agent. It was found that for all the catalysts the above reaction can be described by one kinetic equation in the case of the liquid phase reesterification and by another one in the gas phase reaction. Both relations are identical with those describing the reaction carried out in the presence of MS ion exchangers as catalysts (5). With regard to these results, in the present work the catalytic activity of polymers was examined for individual samples on the basis of initial reaction rates which were determined under constant conditions specified in the notes to Table 1.

The values of initial reaction rates (Table 1) confirm data reported in our previous work (9) which showed that the most active catalysts in the gas and liquid phase reaction are those containing 55–60% of the crosslinking agent. This differentiated GM ion exchangers from MS ion exchangers which exhibited the highest activity in the gas phase for the most crosslinked samples having high specific surface area (3), while in the liquid phase reaction their catalytic activity was independent of crosslinking (4). This latter finding was explained by the

compensation of the swelling effect by the effect of high specific surface in the case of the higher crosslinked catalysts.

We have also examined the effect of the content of cyclohexanol used as the component of porogene in the synthesis of macroporous GM copolymers. It was found that the highest activity is exhibited by the copolymer prepared in the presence of 90 mass% of cyclohexanol (Table 1).

Comparison of the results of the reesterification catalysed by macroporous GM and MS ion exchangers shows that the initial reaction rates determined for GM ion exchangers are higher than those expected on the basis of the total amount of their sulfonic acid groups. This phenomenon is most distinct in the gas phase catalysis where in some cases the initial reaction rates are the same for both types of ion exchangers (3), although the content of sulfonic acid groups in GM ion exchangers is lower than in MS ones. This indicates a high surface concentration of sulfonic acid groups in the case of GM polymers compared to MS polymers in which sulfonic acid groups are located within the whole mass of the copolymer.

The study of catalytic activity of GM ion exchangers prepared by incomplete sulfopropylation and by partial neutralization of fully sulfopropylated GM ion exchangers with alkali metal ion gave the results summarized also in Table 1. These data allow us to compare the relative activity of samples partially neutralized by potassium ion with those partially sulfopropylated both in the gas phase and liquid phase reesterification. In all cases the decrease in the amount of acid functional groups of the polymer leads to a decrease in its catalytic activity. In the case of partial neutralization it was assumed that the alkali metal ion is uniformly distributed on sulfonic acid groups, i.e., that there is an actual decrease in the concentration of acid functional groups in such regions of the polymer which participate in the catalytic reaction. Hence the reaction parameter decreases with decreasing

TABLE 4

Swelling of Selected GM and SM Ion Exchangers

Ion exchanger	Volume increase in swelled ion exchanger related to dry sample vol%				
	Water	0.1 N HCl	0.1 N NaOH	Dioxane	Cyclohexane
GM 1	25	21	23	7	5
GM 4	25	23	21	21	5
MS-25 <sup>a</sup>	28	24	40	20	10
MS-60 <sup>a</sup>	10	0	15	7	10

<sup>a</sup> Macroporous styrene-divinylbenzene ion exchangers; number denotes the content of crosslinking agent (divinylbenzene) in percent.

relative acid group concentration so that in liquid and gas phase it gives a straight line in logarithmic coordinates, the tangent of which equals three for the gas phase reaction and one for the liquid phase reesterification. This corresponds to reaction orders in the catalyst, expressed by kinetic equations reported in our previous work (9). The different course of decrease in the catalytic activity was observed only for the partially sulfopropylated samples. In the gas phase reaction the activity decrease with decreasing content of sulfonic acid groups in the polymer is slow and in logarithmic coordinates it is expressed by a slope much less than one. This relates obviously to the fact that sulfonation leads first to the occupation of the surface of polymer particle by sulfonic acid groups so that in the gas phase reaction, where swelling of the polymer is minimal, the decrease in the concentration of surface sulfonic acid groups is small. In the liquid phase reesterification, however, on going from fully sulfopropylated ion exchangers the activity decreases with decreasing content of the acid groups first slowly and only at a content lower than 80% of total amount is this decrease faster. This seems to result from the fact that in the liquid phase the swelling of polymer mass proceeds to a greater extent; the structure of polymer chains is more released, which improves the contact of the reactants with a greater volume of the particle mass, in which volume the sulfonic acid group concentration decreases strongly toward the particle center.

As far as partially sulfopropylated and neutralized samples of GM ion exchangers are concerned, all the results obtained and the conclusions made are identical with those obtained for the ion exchangers based on MS polymers. This indicates that the type of copolymer from which the strongly acidic ion exchanger is prepared does not play an important role, especially when the procedure used for its preparation, i.e., the introduction of functional groups on the already prepared crosslinked copolymer, is the same in both cases. It has been found that GM ion exchangers have a higher surface concentration of sulfonic acid groups, which only manifests itself in particular in the gas phase reactions.

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