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43. Reaction of Hydrolyzed Copoly(Glycidylmethacrylate-Ethylenedimethacrylate with Propane Sultone in the Presence of Phase Transfer Catalyst

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Summary

It has been found that the three-phase heterogeneous reaction of propane sultone with hydrolyzed macroporous glycidylmethacrylate copolymers in an aqueous alkaline medium proceeds to a higher degree in presence of phase transfer catalyst. The best results were obtained using tetra(n-butyl)ammonium hydroxide. An important finding is the increase in the degree of transformation of the reaction in flow arrangement compared with the batch procedure. The influence of phase transfer catalyst is also more effective. The reaction is discussed with respect to the properties of the products, i.e. of the overall and surface contents of groups introduced into the reaction, of the specific surface area and specific pore volume of sulfopropylated copolymers.

Introduction

In our preceding paper (RIBEIRO et al. 1980) we have described the preparation of methacrylate strongly acid cation exchangers by a reaction between the hydrolyzed copolymer glycidylmethacrylate - ethylenedimethacrylate (GMA-EDMA) with propane sultone (PST) in concentrated NaOH, i.e. in a system composed of two liquid phases and one solid phase. This heterogeneity is also the likely cause of the relatively low degree of substitution (about 1 mmol/g). Although, however, the capacity of the product is roughly five times lower than that of the standard polystyrene cation exchangers, it was found that the catalytic activity of both types in the re-esterification of ethyl acetate with propanol is roughly the same (SETÍNEK et al. 1981). A electron microprobe has revealed that the majority content of sulfo groups is localized closely to the surface and that the distribution of the groups in the cross-section of the particle exhibits a pronounced gradient. This

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study has had as its objective to find the way for raising the capacity and for obtaining particles without any substitution gradient.

Experimental

The synthesis of GMA-EDMA and their hydrolysis have been described elsewhere (ŠVEC et al. 1975, HRUDKOVÁ et al. 1977). The reaction with PST was carried out in a mixture containing PST:GMA:NaOH 1:7,6:6 with stirring in a flask at 35°C for 24 h. NaOH was added as a 7 mol/l aqueous solution. In some cases, tetra(n-butyl)ammonium hydroxide (TBAH) was added to the mixture in an amount of 0.047 mol/mol PST. In the through-flow arrangement the liquid components of the mixture were recycled through a column filled with the polymer under otherwise identical conditions. After that the products were thoroughly washed.

The total content of sulfo groups was determined using NaCl (RIBEIRO et al. 1980), the "surface" groups were determined similarly, but with TBAH or N-(α-carbethoxypentadecyl)-trimethylammonium bromide (KTMB) or tri-n-octylmethylammonium chloride (TOMAC). The sulfur distribution on the section of the particle was determined by electron microprobe JEOL-JXA 50 A.

Results and Discussion

PST reacts with hydrolyzed GMA-EDMA in the presence of a concentrated NaOH solution only to a low conversion. In the case of the reaction of both hydroxyls of the side chains, the theoretical value which can be ultimately reached in the modification of polyglycerolmethacrylate (hydrolyzed polyglycidyl methacrylate) amounts up to as much as 4.5 mmol SO_3H/g. The same theoretical value for copolymers is lower, reaching only 1.6 mmol/g for GMA-EDMA (15:85) wt.%). Assuming substitution of one hydroxyl group only, this value is 3.3 or 0.9 mmol/g (Fig.1).

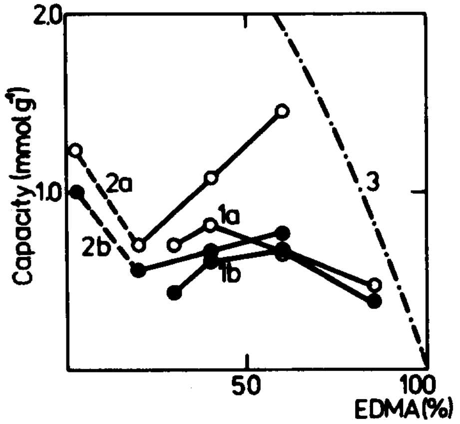

Fig.1. Effect of crosslinking of GMA-EDMA on content of sulfo groups
Method: 1 Batch, 2 Column; sulfogroup content: a total, b surface; 3 theoretical sulfogroup content

Since heterogeneity of the system can also be a cause of the relatively low reaction conversions (in addition to other factors), phase-transfer catalyst (PTC) was used for ensuring contact between the reacting components. Addition of tetra(n-butyl)ammonium hydroxide (TBAH) in the batch procedure raises the content of the groups by 6% (TABLE I) compared with a similar reaction without PTC. After transformation of the system into the through-flow arrangement, the effect of PTC is reflected, under otherwise identical conditions, in an increase in the content of the groups by almost 10%, which is an increase by as much as 16.5% compared with the uncatalyzed batch reaction. The utilization of other compounds as PTC, e.g. tetra(n-butyl)ammonium iodide (TBAI) or dibenzo-18-crown-6 (DB-18-C-6) was unsuccessful, because other solvent systems (dioxan, nitrobenzene) had to be used.

TABLE I

Effect of PTC and of procedure used on reaction between hydrolyzed GMA-EDMA and PST

			Capacity, mmol/g			
PTC	Solvent	Method	Total	Surface	%[a]	Conversion,%[b]
No	H_2O	Batch	0.82	0.61	74.4	22.3
TBAH	H_2O	Batch	0.87	0.65	74.7	24.0
No	H_2O	Column	0.98	0.65	66.3	27.5
TBAH	H_2O	Column	1.08	0.67	62.0	31.1
TBAI	H_2O	Batch	0.72	0.61	84.7	19.4
TBAI	Dioxan	Batch	0.13	0.13	100.0	3.1
DB-18-C-6	Nitrobenzene	Batch	0.36	0.41	100.0	9.1

[a] Percentage of surface groups in total amount, [b] calculated according to BELYAKOVA et al. 1980
Conditions: Hydrolyzed GMA-EDMA (60 : 40 wt.%) 1 g, NaOH 0.85 g, H_2O 3 ml or PTC (10% solution in H_2O) 2 ml + H_2O 1 ml, PST 2 g, 24 h, temperature 35°C

The structure and morphology of polymer particles do not undergo important changes depending on the procedure used. For instance, the specific surface area according to thermal nitrogen desorption decrease from 66 to 44-52 m^2/g, the pore volume according to cyclohexane regain decreases from 1.16 to 0.79-0.91 ml/g; the pore radius changes from 35 to 30-40 nm, and the radius of the globules changes from 45 to 44 - 52 nm (calculated according to HRADIL 1978).

As has been already pointed out, in the modification without PTC the distribution of sulfo groups in the particle is not uniform and decreases very quickly with the distance from the surface towards the centre (Fig.2a). In the reaction taking place in the presence of PTC and in the column the distribution of the groups is more homogeneous (Fig.2d).

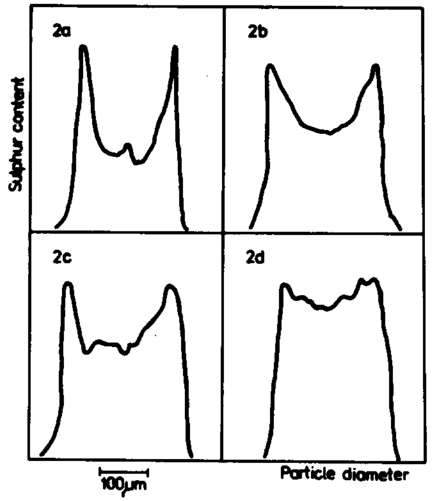

Fig. 2. Sulfur distribution in copolymer particle

Method: a,b Batch, c,d Column; a,c without catalyst, b,d TBAH

Apart from the distribution of sulfo groups on the section of the particle, the $-SO_3H$ groups can also be distinguished depending on their being situated inside the polymer mass or closely to the surface of the pores. In other words, depending on their ability to react with "bulky" compounds which cannot penetrate into the bulk of the polymer. As demonstrated by Fig.3, the capacity of the polymer depends on the size of the molecule of the reagent used in its determination and is always lower with a quaternary ammonium salt than with NaCl, with the exception of the case where the reaction with PST proceeded without PTC. The content of the groups on the pore surface is roughly 60-80% of the total capacity determined by NaCl splitting (TABLE II) and is markedly higher compared with styrene-divinylbenzene (ST-DVB) resins, where it reaches only roughly 25% (RAHMAN et al. 1977). The cause can be seen in the morphology of modified polymers and in the modification reaction.

TABLE II

Effect of composition of copolymer GMA-EDMA and of procedure used on reaction with PST

EDMA %	S_g[a], m^2/g	PTC	Method	Capacity, mmol/g total	surface	%[b]	Conversion %
30	42	No	Batch	0.71	0.43	60.6	16.2
40	66	No	Batch	0.81	0.61	74.3	22.3
60[c]	120	No	Batch	0.20	0.18	90.0	7.2
60[d]	120	No	Batch	0.52	0.47	90.4	20.1
60	120	No	Batch	0.64	0.66	100.0	25.4
85	304	No	Batch	0.47	0.38	80.9	48.0
2.5	0.1	TBAH	Column	1.26	1.02	81.0	21.9
20	19.5	TBAH	Column	0.71	0.56	78.9	14.2
40	55.5	TBAH	Column	1.08	0.67	62.0	31.1
60	120	TBAH	Column	1.47	0.80	54.4	68.5

[a] Specific surface area of basic copolymer, [b] percentage of surface groups in total amount, [c] reaction time 5 min, [d] reaction time 20 min.
Other conditions as in TABLE I.

The surface modification is preferred if the polymer is highly crosslinked, which for GMA-EDMA is always the case compared with the usual ST-DVB. In addition, the heterogeneous course of the reaction markedly reduces the possibility of interaction between the groups of the polymer and the reagent in the bulk. If, however, PTC is present in the system, the interaction between the reacting species is facilitated, and both the conversion of the reaction and the fraction of sulfo groups situated in the bulk of the porous polymer increases (cf.second part of TABLE II). An important role is also played by the size of the specific surface area. If the reaction proceeds in the noncatalyzed mode, the size of the accessible surface is decisive for the reaction yield. Since, however, the specific surface area is proportional to the amount of the crosslinking agent in the polymer (HORÁK et al. 1981), the fraction of glycidylmethacrylate, i.e. of one of the reacting components, decreases with increasing content, which has a negative effect on conversion. Thus, there exists an optimum of crosslinking at which the highest conversion is reached without addition of PTC, as well as an optimum at which the highest conversion is reached at the highest saturation of the surface layers only (TABLE II)(BELYAKOVA 1981).

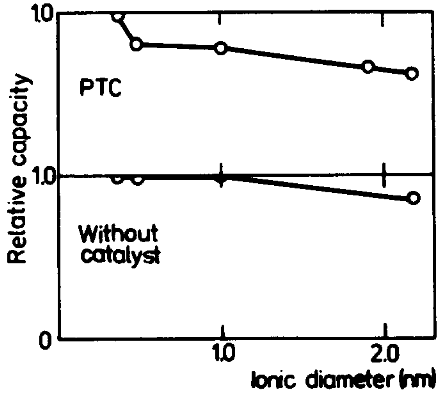

Fig.3. Dependence of fraction of determined sulfo groups on cation size used in determination

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