REACTIVE POLYMERIC CARRIERS OBTAINED BY SUSPENSION POLYMERIZATION OF HYDROXYETHYL METHACRYLATE SULPHONATES

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Dedicated to Academician O. Wichterle on the occasion of his 70th birthday.

Reaction of monomeric 2-hydroxyethyl methacrylate with sulphochlorides, such as *e.g.* toluenesulphonyl chloride, gives rise to asymmetrical ethylene esters which can be polymerized to beads possessing alkylating properties. In this procedure, a single precursor can be used to prepare a large variety of polymeric sorbents, catalysts, and the like.

In recent skilful procedures used in the preparation of solid functional polymers a question always arises to what extent the synthesis ought to proceed in the monomeric form. If the polymerization is carried out as one of the initial stages, then too many consecutive polymeranalogous reactions may render the eventual sorbent less homogeneous, because in addition to the required groups it contains also residues of unreacted groups and products of side reactions of all the reaction stages. On the other hand, polymerization of a functional monomer with final functional groups is more labour-consuming, as for each monomer polymerization conditions must be found and optimized. This is so because such physical properties as shape, mechanical strength, porosity, swelling *etc.* are very important for the product, and are strongly affected by small changes in the polymerization conditions.

As has been shown earlier[1], 2-methacryloyloxyethyl benzene-(toluene-) sulphonates possess a good alkylating ability even in their polymeric form, thus making possible the preparation of various functional polymers. At present, after their polymerization has been effected in a useful physical form as reported in this paper, these polymers represent a reasonable compromise: polymerization in the penultimate stage determines the physical shape and properties, while by means of the ultimate, single polymeranalogous reaction the required functional groups are introduced quite smoothly.

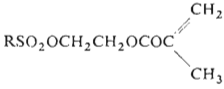
Alkylation is commonly used for this purpose. In this respect these polymers rank among the usual matrices, such as chloromethylated polystyrene, polymers

of glycidylmethacrylate, *etc.* In the chemistry of low-molecular weight compounds esters of sulphonic acids, along with alkyl halides, are the alkylating agents most commonly in use. In polymer chemistry sulphonates have not yet been investigated with such attention.

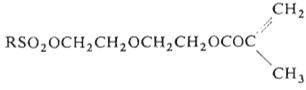
ω-Methacryloyloxyalkyl Sulphonates

The typical monomer – 2-methacryloyloxyethyl *p*-toluenesulphonate – was prepared by Dijkstra and Smith[2] by reacting 2-hydroxyethyl methacrylate with toluenesulphonyl chloride in pyridine. The same authors showed that by a reaction with thiourea this compound yields a monomer which is able to polymerize. In our preceding paper[1] we investigated the reactivity of this sulphonate in the polymeric form, with a positive result; however, in order to apply this sulphonate in practice, some more problems had to be solved.

We started by improving the synthesis of the monomer. An earlier procedure[3] was adapted, in which a two-phase system was used with pulverized hydroxide instead of the usual pyridine. This allows commercial stabilized 2-hydroxyethyl methacrylate to be used as the starting material, because during isolation the phenolic stabilizer passes into the aqueous phase as phenoxide. Ethyl ether is suitably employed as the organic phase, if the monomer is to be prepared in the pure state. In this case, spontaneous polymerization may take place during evaporation of the ether, even at room temperature, due to traces of peroxides in the latter. For this reason, it is recommended to add a small amount of stabilizer (0·02% octylpyrocatechol) before the evaporation. If, however, the following polymerization is to be carried out in a solvent, there is no need to isolate the monomer as such. In this case toluene is chosen as the organic phase. A solution is obtained which contains neither the stabilizer nor any of the two hydrolytic products (arylsulphonic and methacrylic acids): all these compounds remain in the aqueous phase. The only important impurity is a symmetrical methacrylate ester, such as ethylene dimethacrylate (*VII*) which is added anyway as the crosslinking agent in the following polymerization stage.



I, R = CH_3
II, C_6H_5
III, R = $CH_3C_6H_4$



IV, R = CH_3
V, R = C_6H_5
VI, R = $CH_3C_6H_5$

The procedure just described was used in the preparation of six mutually related compounds, *I* – *VI*. The details are given in the Experimental.

Suspension Polymerization of ω-Methacryloyloxyalkyl Sulphonates

As suspension takes place in water, reactivity of the sulphonates becomes a disadvantage. Hydrolysis has an autocatalytic character due to the released strong arysulphonic acid; hence, if the process is left uncontrolled, the product may be completely spoiled by hydrolysis. One way for suppressing hydrolysis consists in the addition of an unusually large amount of initiator. In the presence of 2,2'-azobis-(isobutyronitrile) (10%) the polymerization is completed at 60°C within 10 min; if the suspension is immediately cooled, the hydrolysis cannot exceed some two per cent (*cf.* Experimental). This procedure would not be fully adequate if employed on a major scale, and a different one has therefore been suggested, based on the use of the dibenzoyl peroxide–dimethylaniline initiation system. This system causes initiation already at 30°C; hydrolysis at this temperature is sufficiently slow, especially if a small quantity of sodium bicarbonate is added, which buffers the acidity of the dispersing medium. At the same time, the presence of dimethylaniline as a base is guaranteed in this way, the respective salt being ineffective in the initiation system.

For the preparation of macroreticular beads, the polymerizing mixture of monomers is to be diluted with a suitable solvent. Toluene appeared to be adequate for this purpose, as it dissolves all monomers, neither dissolves the polymers nor causes them to swell, and does not mix with water. Ethylene dimethacrylate was successfully used as the crosslinking agent, poly(vinyl alcohol) was the stabilizer of the suspension.

Reaction of Beads of ω-Methacryloyloxyalkyl Sulphonates with Nucleophiles

The reaction partner may be chosen from all known nucleophilic compounds. In out first communication[1], typical examples were chosen from various types of compounds alkylated on the nitrogen, sulphur, oxygen and carbon atoms in various groups and positions, such as aliphatic and aromatic amines, thiourea, thiocyanide, cyanide, azide, alkoxide and carboxylate. These experiments were performed on thin films with the mere aim to demonstrate the extent of the alkylating ability of the polymer. In the meantime it was found that the reactions could take place in the bead form as well. As expected, the accessibility greatly depends on the degree of crosslinking and porosity, and it is just this accessibility by which physical properties given by the polymerization conditions in the preceding stage affect important utility properties of the sorbent, such as its maximal capacity and local concentration profiles of functional groups. Unfortunately, sorbents with the greatest accessibility and capacity possess low mechanical strength, so that a compromise must be looked for. In this respect, polymers of macroreticular character are especially useful.

As regards the individual structures *I*–*VI*, toluenesulphonate is known to be more reactive than benzenesulphonate, and the latter is more reactive the methanesulphonate. The longer chain in structures *IV*–*VI* acts as a spacer, which is parti-

cularly advantageous if bulky molecules are bound or used in the subsequent interaction.

An example of macroreticular materials prepared from these suspension polymers are sorbents containing histidine, histamine and other imidazole derivatives used in interactions with haemine and haemoproteins[4,5].

EXPERIMENTAL

Synthesis of ω-Methacryloyloxyalkyl Sulphonates (General procedure *A*)

Sodium hydroxide was ground to fine powder in a coffee mill. ω-Hydroxyalkyl methacrylate (0·25 mol) and purified sulphochloride in the molar ratio 1 : 1—1·05 were dissolved in ether, 250 ml, the solution was cooled and solid pulverized sodium hydroxide (0·6 mol) was added with stirring and cooling so as to maintain the temperature below 5°C. The best way for introducing the hydroxide is to use a closed system and a rubber tube; if not, the air moisture would make the powder sticky. After stirring for 1·5 h, the reaction mixture was shaken with icy water, the organic layer was separated and dried with sodium sulphate and magnesium sulphate. After that, *c.* 50 mg of octylpyrocatechol was added, and ether was evaporated *in vacuo* at room temperature. The results as listed in Table I are somewhat poorer for methanesulphonates for which procedure *C* is a better choice.

Procedure *B*. Synthesis in Toluene Solution

2-Hydroxyethyl methacrylate, 200 g, and toluenesulphonyl chloride, 308 g, were dissolved in toluene, 600 ml, and treated with 150 g of sodium hydroxide, similarly to procedure A at 5 to 15°C. The washed and dried toluene solution, 811 g, was analyzed for the sulphur content and the saponification number (5·78% and 284·8, respectively, which corresponds to the concentrations 1·80 or 1·76 mmol/g, respectively, and to the yield 93·8%).

Procedure *C*. Synthesis of 2-Methacryloxyethyl Methane Sulphonate

2-Hydroxyethyl methacrylate 10 g and triethyl amine purified with phthalic anhydride, 9·7 g, were dissolved in 120 ml of absolute ether. Methanesulphonyl chloride was added to the solution in an amount of 9·7 g within 15 min at 0—5°C; after stirring for another 30 min, the reaction mixture was gradually washed with cold water, 2M-HCl, water, bicarbonate solution, and dried with magnesium sulphate. After that, the ether was evaporated in the presence of a stabilizer as sub procedure *A*. Yield of *I* was 90·5%.

Suspension Polymerization

Compact gel particles. The monomer and ethylenedimethacrylate (*VII*) or divinylbenzene (*VIII*, technical grade-60%) as the crosslinking agents were weighed (in respective amounts of about 40 and 4 g), deaerated *in vacuo* and stored under nitrogen. Water, also deaerated, was stirred at 500 rpm in a closed tank with an anchor stirrer, together with 0·1% of poly(vinyl alcohol) (m.w. 125 000; BDH chemicals). Water was preheated to 60°C. 2,2'-Azobis(isobutyronitrile), 4 g, was dissolved in the monomer mixture, and the latter was poured into the aqueous phase with stirring and heating to 60°C. After 10 min the mixture was quickly cooled from the outside,

the beads were filtered by suction, washed with water and ethanol, and dried *in vacuo*. The degree of hydrolysis was calculated using titration of an aliquot fraction from joined washing solutions; it is expressed as the mole fraction of the acid from the overall amount of sulphonate used in the polymerization (Table II).

Macroreticular beads. Deacrated water, 150 ml, containing poly(vinyl alcohol), 0·52 g, and sodium bicarbonate, 2 g was stirred in nitrogen atmosphere together with a solution of *III*, 60 g, and *VII*, 40 g, and dibenzoyl peroxide, 1·37 g, in toluene, 100 g. The vessel used was a 500 ml closed tank with an anchor stirrer, 500 rpm, 30°C. After that, freshly redistilled N,N-dimethylaniline, 0·8 ml, was added at once, and the stirring continued at 30°C for 6 h. The product was filtered by suction, washed and dried as indicated in the preceding procedure. The yield was 93·2 g macroreticular beads, sulphur content 6·22%, heptane regain 0·77 ml/g, methanol regain 1·25 ml/g, size 90—180 μm.

TABLE I

Preparation of ω-methacryloylcxyalkyl sulphonates in ether (procedure *A*)

Sulphonate	Yield %	% S		n_D^{20}
		found	calculated	
I	42	15·17	15·40	1·457[5]
II	94·1	11·96	11·86	1·512
III	94·9	11·44	11·28	1·511
IV	36	12·50	12·71	1·438
V	91·2	10·19	10·20	1·508
VI	90·7	10·08	9·76	1·507

TABLE II

Suspension polymerization (40 g of monomer, 4 g of initiator) to compact particles

Monomer	Crosslinking agent (g)	Water ml	PVA g	*T* °C	Time min	Hydrolysis %
II[a]	*VII* (4)	150	0·2	60	10	1·5
II[a]	*VII* (5·6)	320	0·47	85	10	7·3
II	*VII* (4)	240	0·32	65	20	2·1
III	*VII* (4)	270	0·32	60	20	2·3
III	*VIII* (4)	160	0·2	80	15	7·2
V[b]	*VII* (3·2)	320	0·4	70	25	4·2
V	*VIII* (4)	240	0·32	65	30	3·6
VI[c]	*VII* (4)	240	0·32	65	30	2·8

[a] 36·5 g of *II*, [b] Polymerization with 1·3 g of initiator. [c] 40·8 of *VI*.

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