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Cross-linking regulators in one-step synthesis of macronet ion-exchangers

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Hydrophillic macronet resins were prepared via a route which includes simultaneous sulphonation and cross-linking of styrene–acrylonitrile copolymer and polystyrene foam. Chlorosulphonic acid was employed as both the sulphonating reagent for the introduction of the sulphonic acid group on styrene units and the medium for the formation of sulphone-type cross-links. Controlled cross-linked structures were achieved by the parallel participation of acetic acid or acetic anhydride as sulphone cross-bridging regulators. The reaction yield, as well as the properties of the formed gels, were studied in respect to the cross-linking regulator concentration and the chlorosulphonic acid flow rate. Both strongly and weakly acidic ion-exchangers on the same substrate were achieved when styrene–acrylonitrile copolymer was used as a raw material. The synthesized macronet ion-exchangers were found to exhibit high swelling abilities and intermediate ion-exchange capacities while scanning electron microscopy (SEM) revealed their morphology.

1. Introduction

Polymeric networks of either hydrophobic or hydrophillic type are a class of materials with increasing interest in both the laboratory research and industrial practice. The introduction of polar groups on cross-linked polymers, the various type interactions with chemical species, the swelling in solvents, the enzyme and other active group immobilization, have led to the widespread use of such materials in biotechnological, medical, ion-exchange and soil-conditioning applications as well as in diapers technology [1–9].

Hydrophillic networks having ion-exchange capacity and swelling ability in water and other polar media, are usually synthesized by the introduction of an ionic functionality on preformed cross-linked structures. Styrene–divinylbenzene (S–DVB) copolymer ranks among the most broadly used backbones for ion-exchange resin synthesis. Cation-exchange resins containing sulphonic acid groups (–SO_3H) are normally prepared by aromatic sulphonation of S–DVB copolymer with sulphuric acid, sulphur trioxide or chlorosulphonic acid. The reaction is usually accomplished by the penetration of the sulphonating agent in preswollen S-DVB beads and thus, the reaction rate is diffusion controlled [10].

Much attention has been directed in recent years to swellable networks, formed by the sulphonation of polystyrene macronets, that were prepared through a post-polymerization Friedel–Crafts type reaction [11–16]. The statistical distribution of cross-links and the existence of bulky groups between the polymer chains result in a higher internal surface, an increased swelling ability and a more efficient penetration and interaction of molecules or groups with the composed ionic functional groups, in comparison with S–DVB networks [17, 18].

However, the most important advantage of a post-polymerization route is that with some small modification, it is applicable to recycling of commercial materials based on synthetic polymers. Several modification procedures of polystyrene (PS) have been reported to employ sulphuric acid (mostly at high concentrations and temperatures), chlorosulphonic acid, fuming sulphuric acid or oleum and sulphur trioxide as sulphonating agents [19–26]. In the case of styrene–acrylonitrile copolymer (SAN), sulphonation of the styrene units accompanied by acrylonitrile hydrolysis under the existing acidic conditions has been investigated using concentrated sulphuric acid [27].

A side reaction of major importance that proceeds during sulphonation involves the formation of sulphone [10]. Sulphone cross-bridging is usually undesirable because it results in the decrease of the sulphonic acid groups introduced on the PS backbone, while it increases the cross-linking density of the network, thus leading to a lower ion-exchange capacity and swelling ability of the final resin. Compared with the most widely used reagents, sulphone bridging is claimed to be mostly yielded by chlorosulphonic acid [28]. Acetic anhydride [19], silver sulphate [20] and

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triethylphosphate [26] have been mentioned to inhibit sulphone bridging during sulphonation of PS networks.

The possibility of employing such compounds as cross-linking regulators, for the formation of structures having controlled network density, was investigated in the present work, where synthesis in one step of hydrophillic macronets containing either strongly acidic groups ($-SO_3H$) based on PS foam, or both strongly and weakly acidic groups ($-SO_3H$, $-COOH$) based on styrene–acrylonitrile copolymer (SAN), is described. The novelty consisted in the absence of a common cross-linker and the employment of HSO_3Cl as both the sulphonating and the cross-linking agent, by the simultaneous usage of sulphone-bridging regulators. Preparation of macronet ion-exchangers having various cross-linking densities was accomplished by altering the cross-linking regulator concentration.

2. Experimental procedure

2.1. The reaction

Two different procedures were studied, in order to demonstrate the application range of the process. The first one was based on SAN and acetic anhydride as a cross-linking regulator, while in the second one PS foam and acetic acid as regulator were employed (Table I).

2.1.1. Styrene–acrylonitrile copolymer (SAN)

An SAN sample ($M_n = 100\,000$, AN content = 25 wt %) supplied by BASF, was used as a raw material. It was purified by dissolving in 1.2 dichloroethane (Merck, analytical grade), precipitation after the addition of methanol and vacuum drying. The reaction took place in a 100 ml Erlenmeyer flask under magnetic stirring and a dry nitrogen atmosphere. A water bath was used in order to retain the reaction mixture temperature at a 25 ± 1 °C level.

2.5 g SAN were dissolved in 7 ml DCE followed by the addition of the appropriate amount (0–2 ml) of the regulator (acetic anhydride, Merck analytical grade). Then 7.6 ml HSO_3Cl-DCE solution containing 50 vol% HSO_3Cl (Merck, analytical grade) were dropwise added within 1/2 min ($15.2\,\mathrm{ml\,min^{-1}}$) for the preparation of the first series of resins (M_1–M_8) and 8 min ($0.95\,\mathrm{ml\,min^{-1}}$) for the preparation of a second series (N_1–N_8). Gel formations appeared in a few seconds but the mixture remained under the same conditions for 24 h.

Following preparation, the products were introduced to 300 ml distilled water, washed with 7×30 ml water and filtered off. The quantity of distilled water had to be specified in detail, due to the possible contribution of this stage to the hydrolysis of the acrylonitrile units and due to the subsequent estimation of the water-soluble (non-cross-linked) product. After water evaporation, the filtrate was weighed in order to determine the quantity of the water-soluble product. This determination was corrected by taking into account the weight of blank samples that were performed without the presence of initial polymer. The removal of the residual HSO_3Cl was accomplished by consecutive holding of products for 1 h in a 1 M KOH solution excess, filtration and washing with deionized water. The resins were regenerated in the acid form by holding them in a 4 N HCl solution, washing three times with 10 ml 1 N HCl solution and finally drying in 105 °C.

2.1.2. PS foam

A commercial PS foam sample, supplied by Dow Chemical Company and purified according to the aforementioned SAN purification procedure, was used as a starting material. The reaction was carried out at 20 ± 1°C in a 100 ml Erlenmeyer flask equipped with magnetic stirrer under a nitrogen blanket.

In fact, 3 g PS foam were dissolved in 10 ml DCE and the appropriate amount of the regulator (acetic acid, Merck analytical grade) varied between 0 and 1 ml was added. Subsequently, a 15.2 ml HSO_3Cl–DCE solution (HSO_3Cl content = 25 vol%) was added. The continuous dropwise addition was completed within 8 min ($1.9\,\mathrm{ml\,min^{-1}}$). Gel points appeared in about 3 min and the products remained under the same conditions for 24 h.

Afterwards, the products were washed for 1 h with distilled water and filtered off, followed by holding for 1 h in a 1 M NaOH solution, filtration and washing with water. Regeneration of the products in the acid form was accomplished as described for the SAN-based resins.

2.2. Product characterization

The strongly acidic groups ($-SO_3H$) of the hydrolysed-sulphonated SAN (HSSAN) networks were determined as follows. 0.1–0.15 g resin were kept for 2 h in 40 ml 0.5 M NaCl solution, filtered off and washed with 5 ml of distilled water. The filtrate was titrated with a standard KOH solution.

In order to determine the total acidic groups ($-SO_3H$, $-COOH$) of HSSAN, 0.15–0.2 g product were swollen in 40 ml of distilled water and titrated against a standard KOH solution. Owing to the

TABLE I Preparation conditions of polystyrene and styrene–acrylonitrile copolymer in the presence of regulators

Sample	Raw material	Type of regulator	Flow rate ($\mathrm{cm^3 min^{-1}}$)	Regulator concentration ($\mathrm{mol\,l^{-1}}$)
M_1–M_8	SAN	$(CH_3CO)_2O$	15.2	0–3.03
N_1–N_8	SAN	$(CH_3CO)_2O$	0.95	0–3.03
O_1–O_{10}	PS foam	CH_3COOH	1.90	0–1.75

diffusion of the alkaline solution in the polymer particles and the presence of carbon dioxide, the equilibrium point was estimated from preliminary experiments to be achieved in 1/2 h.

In the case of the sulphonated PS (PSS) networks, 0.1–0.2 g product were dipped in a 1 M NaCl solution for 1 h followed by filtration and washing with 5 ml distilled water. The ion-exchange capacity was measured by titrating the filtrate with a standard NaOH solution.

The swelling ratio in water was gravimetrically determined for both the HSSAN and PSS products. The resins were first achieved in the sodium form. Subsequently, dry preweighed sodium-formed gels were placed in a water bath for 4 h at 25 °C. The swollen gels were filtered in order to remove the residual water and finally reweighed.

Scanning electron micrographs (SEM) were depicted using a Jeol JSM-35 microscope. The predried samples were sputtered with a coating of gold and critical point drying was carried out in the presence of carbon dioxide. Finally, micrographs were taken for acid-formed resins.

3. Results and discussion

Rieche and Fischer [29] suggested that sulphone is formed by the interaction of unreacted benzene with benzenesulphonic acid. However, in 1955 Rueggeberg *et al.* [30] proposed a mechanism concerning the formation of pyrosulphonic acid as an intermediate product during sulphonation of aromatic hydrocarbons with sulphur trioxide. According to this mechanism, they investigated the ability of some compounds to diminish sulphone formation considerably. Besides the formation of pyrosulphonic acid as an intermediate, it has been proposed that sulphone cross-linking can be attributed to the formation of sulphonyl chlorides that tend to form sulphones readily [28]. Here, in the case of the styrene units–chlorosulphonic acid system, sulphone formation can be detected by an increase in the degree of cross-linking.

Sulphone cross-bridging is, in general, a rather sensitive reaction, affected by various factors, including the purity of the reagents, the concentration of the sulphonating medium, the feeding rate, and so on. In the present work, sulphone formation is controlled by altering the concentration of the cross-linking regulator. The decrease of the network density induces elevated degrees of swelling in water and aqueous solutions.

The reaction yield, expressed as cross-linked product mass per initial polymer mass, is illustrated in Fig. 1, as a function of the cross-linking regulator concentration. It can be clearly seen that for both the PS and SAN modifications the increase of the cross-linking regulator concentration results in the decreasing production of the cross-linked derivative. It is also noticed in the case of SAN that the HSO_3Cl flow rate has a less significant influence on the yield of the cross-linking reaction. The increase of the flow rate from 0.95 ml min^{-1} (series N) to 15.2 ml min^{-1} (series M) leads to a slight increase of the yield. This observation is confirmed likewise in Table II, where in contrast the water-soluble (uncross-linked) by-product yield is shown to be favoured when a lower HSO_3Cl solution feeding rate is applied (series N). The presented water-soluble product determinations were precorrected against blank samples, containing no starting polymer.

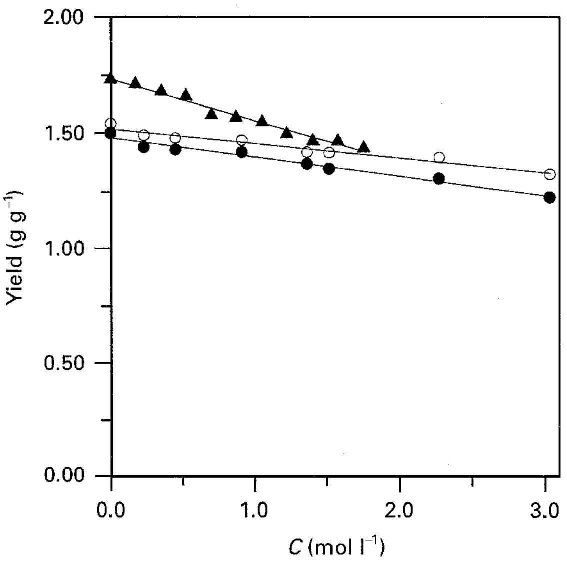

Figure 1 The reaction yield expressed as cross-linked product mass per initial polymer mass, as a function of the cross-linking regulator concentration. (○) series M, (●) series N, (▲) series O.

TABLE II Water-soluble product (WSP) mass per initial polymer mass, in relation to the cross-linking regulator concentration

Sample	Regulator concentration (mol l^{-1})	WSP (g g^{-1})	Standard deviation ($n = 3$)
M_1	0	0.0539	0.0048
M_2	0.23	0.0737	0.0083
M_3	0.45	0.1191	0.0106
M_4	0.91	0.1974	0.0187
M_5	1.36	0.3499	0.0497
M_6	1.51	0.4727	0.0467
M_7	2.27	0.6040	0.0724
M_8	3.03	0.6381	0.0797
N_1	0	0.0749	0.0097
N_2	0.23	0.0976	0.0122
N_3	0.45	0.1359	0.0154
N_4	0.91	0.2565	0.0247
N_5	1.36	0.4837	0.0496
N_6	1.51	0.5784	0.0486
N_7	2.27	0.6991	0.0669
N_8	3.03	0.7178	0.0634

The ability of the cross-linking regulator to inhibit sulphone cross-bridging is demonstrated here by its observed tendency to favour the formation of uncross-linked product, for both the M and N preparation series as seen in Table II, and thus to diminish the production of the final macronet resin as illustrated in Fig. 1. The interpretation of the observed differences in series M and N is in good agreement with the literature [10, 24]. Normally, sulphone formation is favoured when the concentration of the sulphonating agent is high. High flow rates (series M)

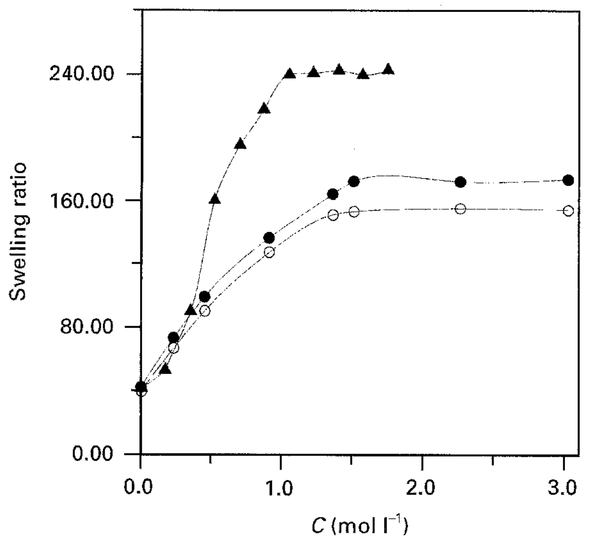

Figure 2 Swelling ratio of the PSS and HSSAN products in water, versus the cross-linking regulator concentration. (○) series M, (●) series N, (▲) series O.

result in elevated "instantaneous" concentration of the sulphonating medium and thus, to an increase of the cross-linking reaction yield and a subsequent decrease in the water-soluble product.

The swelling ratios of the PSS and HSSAN gels (Fig. 2) prove the efficiency of the preparative route to lead to resins with controlled network density by simply altering the cross-linking regulator quantity. By increasing the regulator concentration, sulphone bridging is reduced, and therefore gels having a lower cross-linking density and a higher swelling ability are derived. In the case of SAN, the lower swelling ratios of the products of series M indicate that the increase of the sulphonating agent flow rate promotes cross-linking, a fact which is in agreement with the previous observations concerning the yield of the reaction in cross-linked and water-soluble product.

A noteworthy point involves the remarkably higher swelling ratios (up to 243) of PSS products compared with those (up to 175) attained for the HSSAN resins. This can be attributed, in part, to the known ability of the SAN acrylonitrile units to promote cross-linking [27], which results in higher cross-linked structures that consequently exhibit lower water-swelling abilities than PSS gels. Although HSSAN contains –COOH groups, it should be expected that their presence reduces the degree of cross-linking, according to an action similar to that of acetic acid. However, hydrolysis reaction follows sulphonation, because the water excess that is required is present during the stage of purification.

A comparison of Figs 1, 2 and the data in Table II indicates that when the regulator concentration is extremely high, although the swelling ability of the products is not influenced efficiently, the amount of the water-soluble product becomes high and the reaction yield is reduced. In conclusion, regulator concentrations between 0.2 and 1 mol l^{-1} ensure satisfactory reaction yields and, in addition, desirable properties of the final products.

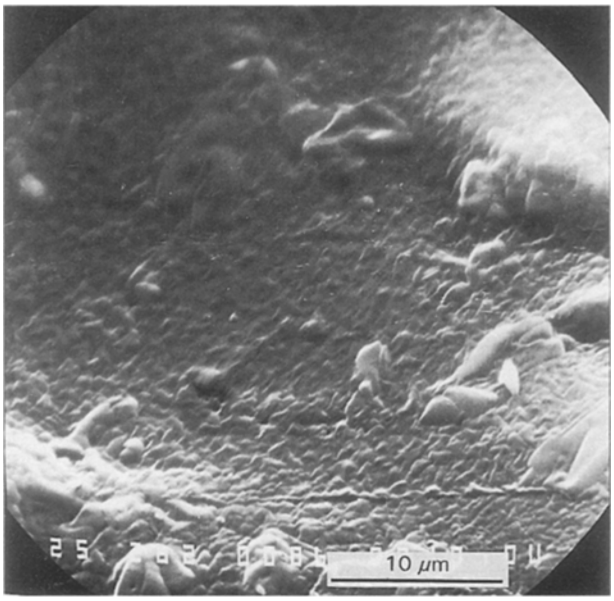

Figure 3 Scanning electron micrographs of HSSAN resin. Regulator concentration $C = 1.51$ mol/l^{-1}.

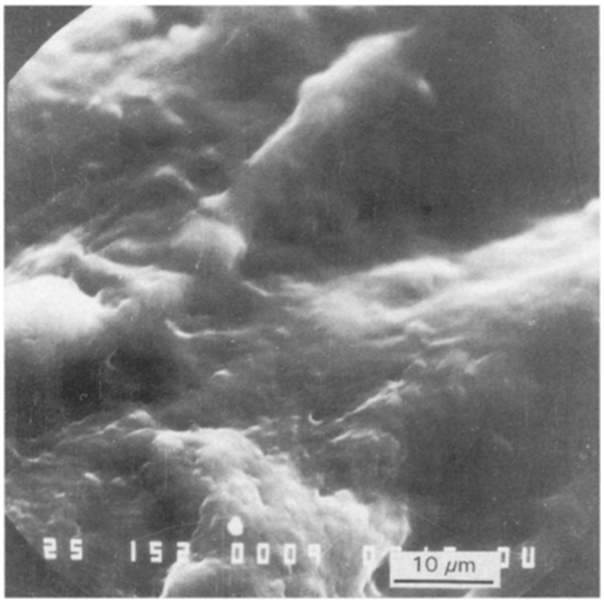

Figure 4 Scanning electron micrographs of PSS resin. Regulator concentration $C = 1.05$ mol/l^{-1}.

Scanning electron micrographs of prepared macronet ion-exchangers are presented in Figs 3 and 4. All products were transparent in the swollen state, a fact that can classify them as of gel-type, although some pores appear in the photographs. Pore appearance could be attributed to factors such as the bubble formation caused by agitation and evolution of gaseous products like hydrogen chloride which is formed during sulphonation.

The total ion-exchange capacities derive from the presence of strongly acidic groups in the case of the PSS resins and the existence of strongly and weakly (–COOH) acidic groups in the case of the HSSAN products (Fig. 5). The total ion-exchange capacities appear higher in the case of PS foam, but in both products are considered as intermediate, because the sulphonating medium remains at low levels. A distinct

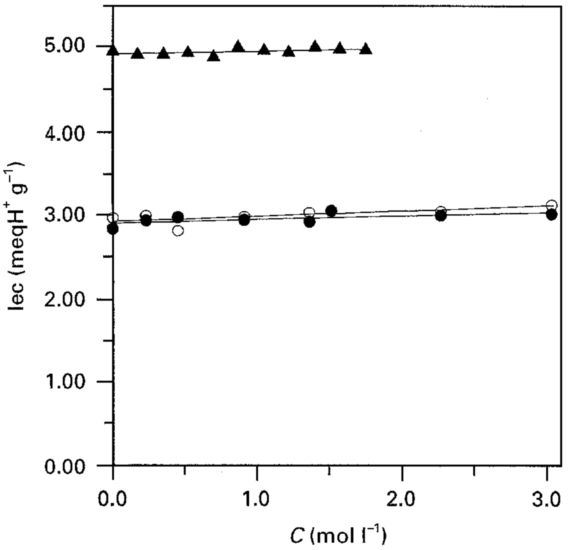

Figure 5 The total ion-exchange capacities (Iec) of the PSS and HSSAN products, versus the cross-linking regulator concentration. (○) series M, (●) series N, (▲) series O.

TABLE III Strongly and weakly acidic groups of the HSSAN products

Sample	SO_3H (meqH$^+$ g^{-1})	Standard deviation (n = 3)	COOH (meqH$^+$g^{-1})
M_1	2.16	0.03	0.81
M_2	2.40	0.03	0.60
M_3	2.33	0.04	0.49
M_4	2.47	0.08	0.52
M_5	2.56	0.06	0.48
M_6	2.74	0.08	0.32
M_7	2.76	0.06	0.27
M_8	2.92	0.09	0.22
N_1	2.07	0.06	0.77
N_2	2.51	0.07	0.43
N_3	2.60	0.04	0.38
N_4	2.59	0.05	0.36
N_5	2.69	0.08	0.24
N_6	2.79	0.03	0.27
N_7	2.73	0.06	0.28
N_8	2.79	0.07	0.24

determination of the strongly and weakly acidic groups of the SAN-based resins is quoted in Table III. The weakly acidic groups (–COOH) were estimated by subtracting the strongly acidic groups (–SO_3H) from the total ones. Here, the increase of the regulator concentration is shown to cause an increase in the introduction of SO_3H groups to SAN (Table III) and a negligible one in the case of PS (Fig. 5).

From the data presented in Table III, it is worth noting that the presence of the –COOH groups in the HSSAN resins is diminished by the increase of the regulator concentration. This may lead us to consider that the presence of acetic anhydride inhibits hydrolysis of the acrylonitrile groups. Nevertheless, the total ion-exchange capacities of the SAN-based products are not considerably influenced by the regulator concentration and the sulphonating agent flow rate, as seen in Fig. 5. This means that sulphone-type cross-linking has almost no effect on the total ion-exchange capacities, in contrast to preparative procedures in which cross-bridging is achieved by the action of common cross-linkers [21]. From a practical viewpoint, the existence of both strongly (effective pH range 1–14) and weakly (effective pH range 5–14) acidic groups on the same resin makes it exhibit different ion-exchange abilities, when a continuous flow method is applied instead of the batch method used here.

Finally, regarding the reaction itself, the use of a remarkably low HSO_3Cl/styrene molar ratio equal to 1.98 in the case of the PS reaction must be emphasized. In most of the known techniques applied for polystyrene sulphonation, the usually large sulphonating agent excess is removed from products by water treatment. The recovery of this excess from water is avoided because of its difficulty, thus resulting to the loss of a significant quantity of the sulphonating reagent. This disadvantage is considerably limited here by the employment of a low HSO_3Cl excess. The relative technological simplicity, the absence of a particular cross-linker, the one-step completion of the reaction and the use of it for the recycling of polystyrene-based commercial products like PS foam, should also be underlined. These factors, taken together with the high swelling ratios of the attained gels in water, may indicate the future application of such products in diapers technology, soil conditioning and other application fields.

4. Conclusions

The above described procedure involves the synthesis of hydrophillic macronet resins with controlled network density, by modifying PS and SAN linear polymers. Chlorosulphonic acid was employed as both the sulphonating reagent for the introduction of strongly acidic groups (–SO_3H) on styrene units and the cross-linker. HSO_3Cl cross-linking action derives from its long-known ability to form sulphone cross-bridges during styrene units sulphonation.

Sulphone inhibitors were used successfully, in order to regulate the extent of the cross-linking reaction. The sulphonating agent flow rate was found to have effect on the reaction yield and the properties of products. Cross-linking regulator concentration was proved to influence the yield of the reaction and the acrylonitrile hydrolysis, as well as to control the cross-linking density and, therefore, the swelling abilities of the macronets. Regulator concentration varying between 0.2 and 1 mol l^{-1} is recommended under the applied conditions, in order to achieve high reaction yields and swelling abilities in water. The gel-type resins exhibited intermediate total ion-exchange capacities, which appeared to be almost irrespective of the extent of the sulphone-type cross-linking.

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