Sulfone-type crosslinks in sulfonation of macronet polystyrene backbone

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(Received 5 March 1992; revised 10 December 1992)

Post-polymerization crosslinking of polystyrene solutions followed by sulfonation has been studied for the preparation and characterization of macronet crosslinked sulfonated polystyrene. A bifunctional benzene derivative (1,4-dichloromethyl-2,5-dimethyl benzene) was used as the crosslinking agent for the main crosslinking reaction. Extensive sulfone-type bridging was found to occur during sulfonation. In addition, the ion-exchange resins that were achieved by this process show increased network density at high sulfonating agent molar ratios. Determination of the porosity and the degree of swelling of the polymers in water was also performed in order to demonstrate the effects of the nominal sulfonating agent concentration on network properties.

(Keywords: Friedel–Crafts crosslinking; sulfone-type crosslinks; 1,4-dichloromethyl-2,5-dimethylbenzene; ion-exchange resins; chlorosulfuric acid; macronet polystyrene)

INTRODUCTION

Polystyrene networks are conventionally obtained by copolymerization of styrene and bifunctional reactive monomers. The copolymerization of styrene and divinylbenzene (S–DVB) is the most common reaction of this type. However, an uncontrolled and inhomogeneous structure occurs, caused by differences in reactivity between the two monomers[1].

Alternatively, three-dimensional polymer networks are formed via Friedel–Crafts type reactions with the styrene units of polystyrene, according to a post-polymerization process. These reactions lead to statistically controlled crosslinking and the products obtained exhibit higher swelling ratios in good and poor solvents for the same degree of crosslinking with the standard S–DVB networks[2]. This new class of materials is known as macronet due to the presence of bulky groups between the polymer chains. Friedel–Crafts methods for polystyrene (PS) modification are based on reactions of chloromethylated and alkoxy derivatives of aromatic compounds such as benzene, xylene and mesitylene with polystyrene in the presence of $AlCl_3$, $SnCl_4$, $ZnCl_2$, $SbCl_5$, H_2SO_4, $HClO_4$, etc. as catalysts. In fact, 1,4-dichloromethyl-2,5-dimethylbenzene (DCMDMB) has been proved to be a suitable crosslinking agent under reaction conditions[3–6].

With regard to crosslinking, the solution reaction has been extensively studied[7–9], although suspension techniques have also been described in organic phase[5], aqueous phase[6] and polar phase, that is, able to promote sulfonation[10]. The solution technique remains interesting and is preferred when specific particle size distribution is required, which cannot be obtained by suspension. This characteristic is considered important as far as mass diffusion-controlled processes are concerned.

Sulfonation of polystyrene

Ionic groups can be introduced to network structures and of these, crosslinked sulfonated PS is important since its ion-exchange behaviour and swelling ability make it appropriate for various applications. Soil conditioning, metal-ion and solvent separations, organic and biotechnological syntheses are fields where sulfonated PS can be used.

Although sulfonation is usually achieved in the form of pre-swollen particles, macronet polymers can easily be sulfonated due to their extended internal volume. With this modification, the polymers become efficient water absorbents and swell strongly in polar media. All common sulfonating reagents can be employed for the introduction of the sulfonic group into crosslinked polystyrene. Recent studies mention the use of sulfuric acid, mostly at high temperatures and concentrations[11,12], chlorosulfonic (chlorosulfuric) acid[13–15], fuming sulfuric acid, and sulfur trioxide solutions[16,17] at various reaction conditions. In fact, sulfonation is associated with sulfone-type bond formation, according to the conditions of the reactions and the sulfonating agent employed. When sulfone bridging is not desirable it is possible to add inhibitors such as acetic anhydride[11], silver sulfate[12] or triethylphosphate[17], in order to control its formation.

Although every sulfonating reagent allows sulfone bridging, HSO_3Cl apparently gives the most. This is consistent with the known ability of HSO_3Cl to form sulfonyl chlorides with aromatic substrate and the fact that these seem to form sulfones rather readily[18]. The formation of pyrosulfonic acid ($Ph\text{-}SO_2OSO_3H$) as intermediate has been proposed for sulfur trioxides ability in sulfone-crosslinking, a mechanism that also explains in part the action of sulfone-inhibitors[19].

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0032–3861/93/183905–06

However, similar interpretations proposed for HSO_3Cl have been only casually accepted. Nevertheless, it is reported that sulfone formation is a rather sensitive parameter, depending on polymer structure[20], the sulfonating agent concentration, the purity of the reagents[21], etc. These facts, which concern factors affecting sulfone formation related to the particular structure of Friedel–Crafts crosslinked polystyrene, have stimulated interest in the study of sulfonation of macronet polystyrene backbone using chlorosulfonic acid.

EXPERIMENTAL

Crosslinking of polystyrene

Crosslinking of PS was performed in solution. In a typical experiment, linear PS (Dow Chemical Hellas; $M_n = 1.18 \times 10^5$; 7.5 g) was dissolved in 1,2-dichloroethane (DCE, Merck analytical grade; 22.5 ml) at 45°C with simultaneous stirring to form a 33% w/v solution. The reaction was performed in a three-necked flask under a nitrogen blanket at 90 rev min^{-1} up to gel-point. The crosslinking agent (DCMDMB) was prepared according to the technique proposed by Peppas and Valkanas[22]. Afterwards, it was recrystallized from ethanol and washed with cool diethylether (0°C) in order to obtain a highly pure crystalline white powder.

The appropriate amount of DCMDMB was dissolved in DCE and was kept at 50°C for 10 min under nitrogen purging. Then concentrated H_2SO_4 was added to the reaction vessel (0.15 ml g_{PS}^{-1}). Gel-points appeared between 4 min and 15 min with respect to the nominal crosslinking ratio and the reaction mixture remained at the same temperature for 6 h.

Afterwards, the crosslinked polymer was first divided into pieces (1–5 mm diameter) to facilitate the penetration of solvents. Washing was performed with a 0.1 N KOH solution and afterwards with a 0.1 N HCl solution, where the PS particles were kept for 4 h successively. In this way, the networks were free of H_2SO_4 traces that could cause sulfonation while drying. Finally, the PS particles were washed with methanol and dried at 105°C for 24 h.

Sulfonation reaction

The dried samples of crosslinked PS were pulverized in a hammermill and fractions with a diameter of 0.40–1.04 mm were selected for sulfonation. Samples (0.5 g) of crosslinked PS were placed in a 100 ml Erlenmeyer flask, dispersed in DCE (20 ml). Chlorosulfonic acid was added to the swollen particles, as 1:1 v/v solution in DCE under mild stirring, while the temperature remained at 50 ± 1°C for 3 h.

When the reaction was complete, the samples were transferred to a G-3 glass filter and were washed with cool water (0°C) under vacuum to remove the residual HSO_3Cl and the solvent (exothermic). Subsequently, they were kept in 4 N KOH solution for 15 min, then in 4 N HCl for another 15 min, to ensure that the hydrogen form is regenerated and finally washed thoroughly with a 0.1 N HCl solution. The resins were dried at 105°C for 24 h.

Characterization of products

The kinetics of the crosslinking reaction was followed by determination of the HCl liberated from the reaction mixture. In fact, nitrogen was passed over the polymer solution at a rate of 25 ml min^{-1} to remove the HCl evolved. A vessel containing distilled water (~40 ml) was used to scrub the hydrogen chloride. Its content was titrated for chlorine ions with a standardized $AgNO_3$ solution in the presence of K_2CrO_4 as an indicator. In addition, 4% w/v $NaHCO_3$ (1.5 ml) solution was added to each aliquot to adjust the pH.

The sulfonated products were initially measured gravimetrically for $-SO_3$ groups, according to the following method. After their previously mentioned purification, the polymers in the hydrogen form were weighed and their weight was related to that of the initial crosslinked polymer. Subsequently, they were also tested for ion-exchange behaviour. Quantities of dried resins (0.1–0.2 g) were placed in an Erlenmeyer flask and 0.5 N NaCl solution (40 ml) was added at 25°C for 3 h. The resins were filtered and the filtrate was titrated against a standardized KOH solution to determine the HCl liberated.

At the same time, the number average molecular weight between crosslinks was determined using swelling data in polar solvents. In fact, the samples were placed in a 2 N NaCl solution at 25°C for 24 h, filtered off, weighed, then washed with distilled water and dried at 105°C until a constant weight was achieved. The porosity of the sulfonated products was measured gravimetrically by solvent uptake experiments in cyclohexane. The solvent density was 0.778 g cm^{-3} and the samples remained in excess cyclohexane for 4 h.

Finally, the degree of swelling of the ionic resins in water was measured, using the same technique described for the electrolyte solution, with the exception that, in this particular case, the samples were left in distilled water for 3 h, a period that unpublished data from our group has established as adequate.

RESULTS AND DISCUSSION

Crosslinking of polystyrene

The bifunctional agent DCMDMB was selected for the crosslinking reaction since its ability in crosslinking PS has been proved under similar reaction conditions[3,4]. In addition, concentrated H_2SO_4 catalysis is rapid under these conditions and also permits variations in reaction techniques. Because of the significant role exerted by three-dimensional polymer networks in promoting swelling, a wide range of networks was prepared with a DCMDMB concentration to PS varying between 1% and 16% w/w.

The kinetics of the crosslinking reaction at 50°C for sulfuric acid at a concentration of 0.15 ml g_{PS}^{-1} is presented in *Figure 1*, for two typical density networks having 4% and 10% w/w DCMDMB concentrations, respectively. The arrows indicate gel-points. This graph shows the high rates at which these systems proceed. In fact, in short reaction times no induction period occurs and finally high-yield crosslinked products are achieved.

The results also indicate that the reaction system DCE–DCMDMB–H_2SO_4, where the catalyst concentration remains at 0.15 ml g_{PS}^{-1}, is advantageous when crosslinked sulfonated PS is desirable, since it behaves more efficiently than other similar crosslinking systems[4,8,9]. Nevertheless, it must be noted that in these previous studies the concentration of the catalyst ($SnCl_4$) is much lower than the one used here, since the aim was to produce crosslinked PS in one step from styrene. On the other hand, the results shown in *Figure 1* are close

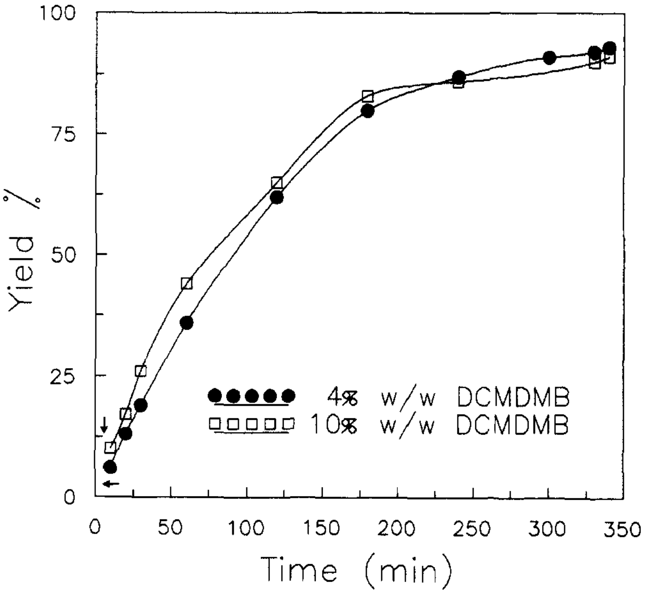


Figure 1 Kinetics of the crosslinking reaction at 50°C. Sulfuric acid concentration: 0.15 ml g_{PS}^{-1}

Table 1 Ion-exchange capacity of crosslinked PS using H_2SO_4 as catalyst

DCMDMB (% w/w)	I.e.c. (meq g^{-1})	SD ($n=3$)
1	0.26	0.15
4	0.16	–
16	0.11	0.03

to those obtained by employing a process[10] in which the H_2SO_4 concentration is significantly higher, since in this case the catalyst acts also as a suspension medium.

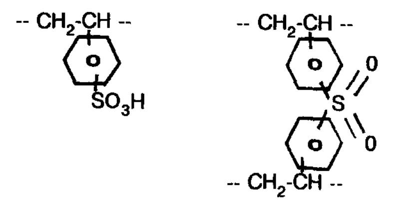
The sulfuric acid catalysis, however, also leads to introduction of sulfonic groups into polymer chains to a certain degree. This was estimated by titrating the acidic groups of the crosslinked polymer. The results of these measurements are shown in *Table 1*, where the ion-exchange capacity (i.e.c.) $H^+ \rightarrow Na^+$ of the crosslinked products is presented with respect to crosslinking agent concentration. The standard deviation of the values obtained is also recorded. It is shown that only a small amount of sulfonation products occurred, while their i.e.c. is higher in low network density polymers. Although the introduction of sulfonic groups in crosslinking reaction is low, the amount of equilibrium swelling of PS in organic solvents (DCE, toluene) was found to be small, a fact that is attributed to slightly sulfonated products.

Sulfonation and sulfone formation

The ion-exchange capacities ($H^+ \rightarrow Na^+$) of the polymers are given in *Table 2*, in relation to the molar ratio of chlorosulfuric acid to non-reacted styrene units. The volume of HSO_3Cl added to crosslinked PS (0.5 g) for DCMDMB concentrations of 1%, 4%, and 16% w/w is also presented. The data from *Table 2* indicate that i.e.c. remains at low levels for small amounts of sulfonating agent, increases to a maximum point when the molar ratio is approximately 2.5 and finally decreases again. The i.e.c. also depends on the degree of crosslinking. As expected, it is shown that i.e.c. decreases substantially when the concentration of the crosslinking agent increases from 1 to 16%.

In fact, the i.e.c. observed using chlorosulfonic acid is lower than that of products sulfonated using concentrated H_2SO_4 and fuming H_2SO_4[10]. This is due to the reduced ability shown by these reagents in sulfone formation. Nevertheless, the chlorosulfonic acid sulfonation is considered satisfactory, particularly when the molar ratio of HSO_3Cl is kept below 3. This decrease observed at high acid concentrations is also attributed to sulfone-type crosslink formation, a fact that was also proved by sulfonation yield measurements and calculations of molecular weight between crosslinks.

The differences at high molar ratios seem to decrease when network density is increasing. These differences become evident for samples E5–E8 in *Figure 2* which presents the weight change per cent of the sulfonated products related to the initial crosslinked polymer weight. The differences obtained at high ratios are caused by molecular weight differences of sulfonated styrene units (I) and sulfone-type crosslinks (II).



Sulfonated polystyrene **Sulfone crosslinks**

(I) **(II)**

Molecular structure

The number average molecular weight between crosslinks was determined using a modified Flory–Rehner equation[21]:

$$-[\ln(1-u_{2,s})+u_{2,s}+x_1u_{2,s}^2] = (V_1/vM_c)(1-2M_c/M_n)(u_{2,s}^{1/3}-u_{2,s}/2) \quad (1)$$

Table 2 Ion-exchange capacity $H^+ \rightarrow Na^+$ of sulfonated PS related to the molar ratio of HSO_3Cl to free styrene units

Sample no.	DCMDMB (% w/w)	HSO_3Cl (ml added to 0.5 g of PS)	Molar ratio	I.e.c. (meq g^{-1})	SD ($n=3$)
C1	1	0.26	0.8	2.14	0.27
C2	1	0.32	1.0	2.28	0.18
C3	1	0.48	1.5	2.97	0.20
C4	1	0.64	2.0	4.24	0.04
C5	1	0.80	2.5	4.70	0.15
C6	1	0.95	3.0	4.51	0.18
C7	1	1.28	4.0	4.48	0.08
C8	1	1.60	5.0	4.52	0.17
D1	4	0.25	0.8	2.80	0.37
D2	4	0.31	1.0	3.60	0.15
D3	4	0.62	2.0	4.06	0.21
D4	4	0.78	2.5	4.30	0.04
D5	4	1.08	3.5	4.15	0.22
D6	4	1.40	4.5	4.10	0.23
D7	4	1.55	5.0	4.10	0.07
E1	16	0.20	0.7	2.00	0.13
E2	16	0.29	1.0	2.60	0.19
E3	16	0.49	1.7	3.05	0.17
E4	16	0.61	2.1	3.62	0.11
E5	16	0.75	2.6	3.91	0.28
E6	16	0.96	3.3	3.90	0.01
E7	16	1.25	4.3	3.90	0.09
E8	16	1.36	4.7	3.77	0.19

or inversely:

$$\frac{1}{M_c}=\frac{2}{M_n}-\frac{\ln(1-u_{2,s})+u_{2,s}+x_1u_{2,s}}{(V_1/v)(u_{2,s}^{1/3}-u_{2,s}/2)} \qquad (2)$$

where M_n is the number average molecular weight polystyrene ($M_n=1.18\times10^5$), V_1 is the molar volume of the solvent ($V_1=19\ \mathrm{ml\ mol^{-1}}$), x_1 is the Flory interaction

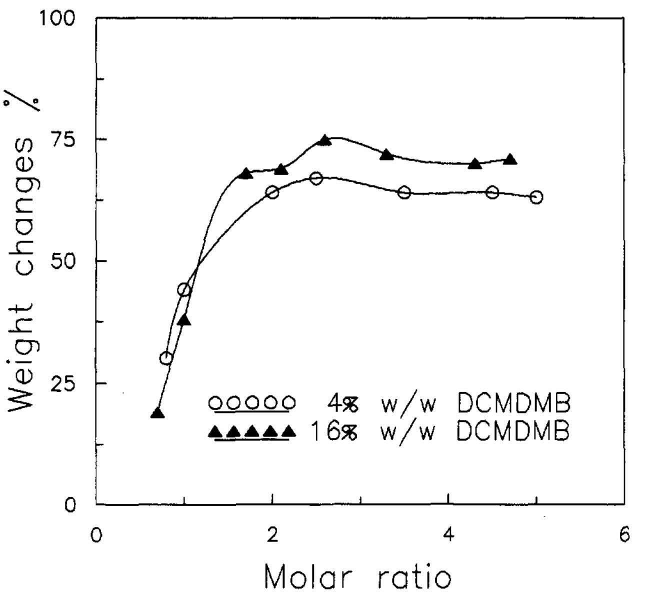


Figure 2 Percentage weight change of sulfonated PS with respect to the initial network weight *versus* the molar ratio of HSO_3Cl to styrene units

parameter for the NaCl-sulfonated PS system (x_1 approaches the value of 0.5^{15}), v is the specific volume of the polymer ($v=0.95\ \mathrm{cm^3\ g^{-1}}$), and $u_{2,s}$ is the equilibrium volume fraction of the polymer.

$u_{2,s}$ was calculated by the expression[24]:

$$\frac{1}{u_{2,s}}=\frac{1}{u_{2,\mathrm{app}}}-d_pP \qquad (3)$$

where $u_{2,\mathrm{app}}$ is the apparent volume fraction of the swollen network and d_p the density of the network (in this case it was assumed that, for the linear analogue experimentally determined, $d_p=1.05\ \mathrm{g\ cm^{-3}}$).

The apparent volume fraction of the polymer is expressed by:

$$u_{2,\mathrm{app}}=\frac{1}{1+Q} \qquad (4)$$

The swelling parameter, Q, derives from:

$$Q=\frac{(W-W_p)d_p}{W_pd} \qquad (5)$$

where W_p and W are the weights of dry and swollen samples, respectively, and d is the density of the solvent (here $d=1.084\ \mathrm{g\ cm^{-3}}$). The term:

$$q_s=Q+1 \qquad (6)$$

is the equilibrium swelling degree of the polymer. The theoretical molecular weight between the crosslinks $M_{c,t}$ was calculated using the equation[24]:

$$M_{c,t}=2M_0/X \qquad (7)$$

Table 3 Molecular weight between crosslinks and porosity of crosslinked sulfonated PS samples

Sample no.	$u_{2,\mathrm{app}}$	SD ($n=3$)	P ($\mathrm{cm^3\ g^{-1}}$)	$u_{2,s}$	M_c	$M_{c,t}$	$M_{c,t}/M_c$
C1	0.238	0.020	0.178	0.249	–	41600	–
C2	0.211	0.012	0.237	0.223	–	41600	–
C3	0.203	0.010	0.196	0.212	–	41600	–
C4	0.183	0.007	0.206	0.191	–	41600	–
C5	0.137	0.005	0.209	0.141	7500	41600	5.5
C6	0.149	0.007	0.156	0.153	6100	41600	6.8
C7	0.150	0.001	0.206	0.155	5900	41600	7.0
C8	0.162	0.010	0.157	0.166	4900	41600	8.5
D1	0.212	0.026	0.103	0.217	–	10400	–
D2	0.197	0.011	0.105	0.201	–	10400	–
D3	0.175	–	0.095	0.178	–	10400	–
D4	0.176	0.013	0.101	0.179	4000	10400	2.6
D5	0.188	0.024	0.119	0.193	3200	10400	3.2
D6	0.196	0.001	0.089	0.200	2900	10400	3.6
D7	0.196	0.008	0.106	0.200	2900	10400	3.6
E1	0.434	0.025	0.106	0.456	–	2600	–
E2	0.382	0.012	0.091	0.396	–	2600	–
E3	0.381	0.020	0.060	0.390	–	2600	–
E4	0.361	0.006	0.114	0.377	–	2600	–
E5	0.341	0.025	0.077	0.351	500	2600	5.2
E6	0.349	0.009	0.084	0.360	500	2600	5.2
E7	0.344	0.027	0.075	0.354	500	2600	5.2
E8	0.347	0.009	0.067	0.356	500	2600	5.2

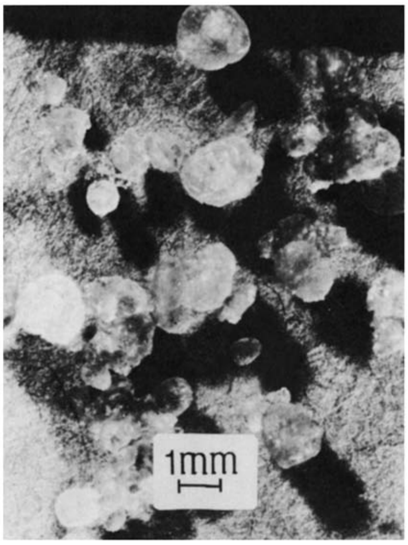


Figure 3 Crosslinked sulfonated PS with 1% w/w DCMDMB, swollen in water

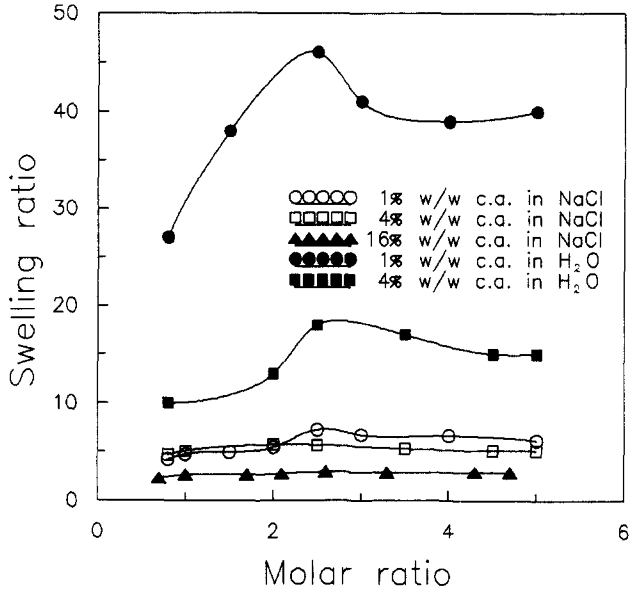


Figure 4 Degree of swelling of sulfonated PS in polar media *versus* the sulfonation molar ratio

where M_0 is the initial molecular weight of the repeating unit and X is the molar ratio of the crosslinking agent to styrene units.

The results obtained are summarized in *Table 3* and are generally in accordance with the corresponding i.e.c. measurements. Only the amounts of equilibrium swelling are presented, for molar ratios lower than 2.5, since in this area we consider the polymer–solvent interaction as insufficient, caused by a deficient sulfonation of the polymer backbone. From the data in *Table 3* it is also derived that increased network density is obtained when chlorosulfonic acid is being used, compared to other sulfonating agents[10] for the same nominal degree of crosslinking.

The M_c measurements were related to $M_{c,t}$ calculations, assuming that the crosslinking reaction is completed. The ratio obtained is also recorded in *Table 3*, to give a quantity to express the crosslinking. In fact, an increased network density is obtained for large amounts of sulfonating agent. This, related to the data in *Table 2* and *Figure 2*, leads to the conclusion that high sulfonation molar ratios favour sulfone formation. This result becomes more important when one considers that other sulfonating agents (H_2SO_4, SO_3, etc.) require considerably higher molar ratios[12,16] in order to achieve a high-yield product on the same substrate.

In addition, from the porosity data in *Table 3* we concluded that the resins are gel-type and not macroporous, since the porosity remains at low levels. The porosity of the samples also decreases with crosslinking density in the range 1–16% w/w of the products examined. The appearance of the resins can also be used to determine the porosity condition[26]. *Figure 3* shows a photograph of the resins swollen in water. The polymers appear transparent, a property which is related to light scattering into the swollen particles and can characterize the resins as gel-type.

It is known that macronet polymers swell significantly in organic solvents and their ionic derivatives behave in the same way in polar media. The degree of swelling, q_s, of the hydrophillic resin in distilled water and in a concentrated aqueous solution (2 N NaCl solution) is presented in *Figure 4*, in relation to the HSO_3Cl-styrene units molar ratio. It is shown that the electrolyte effect in reducing swelling is more important in slightly crosslinked samples, while in denser networks the differences between water and aqueous solution become insignificant. In the absence of electrolyte, the amount of swelling in water is greatly increased and for samples C4–C8 it becomes extremely high. Finally, differences in high concentrations of sulfonating agent are also obtained.

CONCLUSIONS

Following a two-step procedure, strong acid ion-exchange resins have been prepared beginning with linear polystyrene. The applied crosslinking system based on DCMDMB and high-concentration sulfuric acid catalysis gives a rapid crosslinking reaction and a low introduction of sulfonic groups to the PS backbone. The sulfonating agent HSO_3Cl is indicative of increased network density, compared to H_2SO_4 and SO_3. The hydrophilic resins obtained have the ability to swell considerably in water, are of gel-type and have intermediate ion-exchange capacities.

Using molecular weight calculations, mass balance measurements and ion-exchange capacity determination, excessive crosslinking is demonstrated in high concentrations of sulfonating agent and is attributed to sulfone-type crosslink formation. The differences caused by sulfone bridging are more pronounced for slightly crosslinked polymers while they seem to be decreased in denser networks.

ACKNOWLEDGEMENTS

This work was supported by a research grant from Polysar SA, Leominster, MA, USA. The authors wish to thank Professor N. Hadjichristidis of the National University of Athens, Dr E. Kakoulides of the NTU and Dr V. Papadimitriou-Piki for helpful discussions and technical assistance.

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