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Preparation of bifunctional macronet polymers having both strongly and weakly acidic groups in one step. Gel–solution transition of a transformable hydrogel

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The hydrolysis, sulfonation and crosslinking modification of a poly(styrene-*co*-acrylonitrile) copolymer in one step was studied. An extremely vigorous process has been developed for the preparation of a series of hydrophilic gels bearing strongly and weakly acidic groups on the same polymer backbone. The products were characterized using infra-red spectra, scanning electron microscopy, elemental analysis and titrimetric determination of the strongly and weakly acidic groups. Kinetic data and swelling measurements in aqueous media were also performed. A fully transformable hydrogel was obtained from a series of macronet products having different degrees of crosslinking. This irreversible gel–solution transition was recorded within 15 weeks, a fact that indicates that these polymers may have specific applications in fields where separation media are required, or as transformable soil conditioners.

(Keywords: bifunctional ion exchangers; macronets; transformable hydrogel; swelling; post-polymerization crosslinking; gel–solution transition)

INTRODUCTION

Highly swollen hydrogels find many applications in fields of analytical chemistry, medicine and biotechnology[1–6]. Much attention has been directed recently at crosslinked, three-dimensional hydrophilic polymers that undergo changes in response to stimuli such as temperature, pH, ionic composition of the external solution, light, etc.[7–9]. Although volume changes are mainly studied, a wide number of phase transitions also occur. These changes may have a reversible or irreversible nature.

In addition, the possible presence of strongly and weakly acidic groups on the same polymeric substrate demonstrates that the swollen network presents a behaviour that is strongly affected by the pH of the external solution. A characteristic like this one is desired for some more specific applications. It has been proved that hydrophilic networks can be used satisfactorily as soil conditioners[10,11]. In this case their action comes mainly from their high water-holding capacity and secondarily from the availability of ion-exchange sites. The presence of carboxylic acid groups in the polymer indicates that, except for the release of residual moisture on soil, properties like aeration and resistance to erosion can be improved as well[12].

Although not yet widely used, post-polymerization crosslinking of polymers has two main advantages compared to the common copolymerization techniques. Normally, a uniform macronet structure can be achieved, owing to the statistical distribution of the crosslinks[13]. A macronet structure also indicates high swelling ability of the polymers in various media, for the same degree of crosslinking. The second important issue is that a post-polymerization process is applicable to polymer recycling, since it refers to already polymerized materials[14].

Hydrolysis of acrylonitrile is a well known reaction that can be performed in the presence of protonic acid like hydrogen chloride or sulfuric acid[15,16]. In addition, sulfonation of macronet polystyrene is a rather easily applied procedure[17,18]. In this case, sulfuric acid is a common medium for the introduction of sulfonic groups. Sulfuric acid is also used as Friedel–Crafts catalyst for a post-polymerization crosslinking and as a secondary crosslinking agent itself[19].

Thus, one may think that it is possible to obtain networks having both sulfonic and carboxylic groups in one step starting from poly(styrene-*co*-acrylonitrile) copolymer (SAN). The major problem here is that water, which is necessary for the hydrolysis of acrylonitrile, is undesirable for the other reactions, sulfonation

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and crosslinking, due to the deactivation of the relative agents.

Attempts in this direction have been successfully performed by Japanese companies[20,21] that refer to the formation of carboxylic groups as a result of the presence of sulfuric acid. On the other hand, it has been proposed that products having different degrees of crosslinking are achieved using bifunctional crosslinking agents and a compound of sulfur trioxide–trialkylphosphate[22].

In the present publication we describe an alternative technique to prepare highly swellable macronets with different degrees of crosslinking, having two ionic groups. Using a random SAN copolymer as raw material, we have prepared a series of networks of hydrolysed sulfonated styrene–acrylonitrile copolymer (HSSAN) via a post-polymerization modification. The principal crosslinking reaction was based on concentrated sulfuric acid's multiple role and on 1,4-dichloromethyl-2,5-dimethylbenzene (DCMDMB). DCMDMB is a bifunctional crosslinking agent that appears suitable in analogous systems[23–25].

However, another interesting fact was observed as well. One of the products of the described process, which corresponds to zero nominal crosslinking agent concentration, has exhibited a transition between the gel to solution form under some specific conditions. Critical phenomena in hydrogels have attracted much interest, owing to their scientific importance and technological applications. Tanaka's group has performed pioneer work, by establishing theoretical background in this area[26–28]. The transition of slightly crosslinked hydrogels to polyelectrolyte solutions has been known for years[29]. Some quantitative results are provided here concerning the time that is needed for the transition, while an extended study of this phenomenon is in progress. In our case, due to the high swelling ability and the parallel presence of carboxylic groups, the transformable polymer combines properties of highly swollen hydrogels with properties of water-soluble soil aggregates agents. This '*in situ* transformable soil conditioner'[11] acts additionally to natural aggregating and water-retaining agents.

EXPERIMENTAL

The reaction

The styrene–acrylonitrile random copolymer (25% w/w acrylonitrile) supplied by Montedison was dried at 65°C for 4 h before use. The proportion of acrylonitrile was tested by elemental analysis (found 6.55 ± 0.05% N, which corresponds to the previously mentioned acrylonitrile content). The principal crosslinking agent (DCMDMB) was prepared and purified as described in the literature[30]. The employed solvent, 1,2-dichloroethane (DCE, analytical grade from Merck), remained in crosslinked sulfonated polystyrene for 24 hrs to ensure the absence of moisture.

The reaction was carried out with the dry solvent and reactants protected under a nitrogen blanket, in a 250 ml Erlenmeyer flask equipped with magnetic stirrer and gas inlet tube. The flask was immersed in a constant-temperature bath operating at 75 ± 1°C.

SAN (5 g) was dissolved in 20 ml of DCE under stirring. DCMDMB was added afterwards covering the range between 0 and 24 % w/w with regard to polymer weight. Then 51.5 ml of concentrated sulfuric acid (Merck, analytical grade) at the same temperature was added to the reaction vessel. Gel points appeared within some seconds and the mixture remained under the same conditions for 3 h.

Following preparation the products were introduced into 150 ml of 1 N KOH solution for 15 min (exothermic addition), washed repeatedly with a 0.25 N solution and finally with distilled water. The conditions of product treatment had to be strictly defined, since this stage could be important for hydrolysis of acrylonitrile units. The polymers in potassium form were dried at 65°C and the final product in swollen stage consisted of transparent yellowish hydrogels with respect to the nominal crosslinking agent concentration.

Characterization of products

I.r. spectra were recorded in KBr (Merck for i.r.) pellets with a Perkin-Elmer 841 spectrophotometer. The samples were washed three times with chloroform, precipitated in methanol and finally dried in a drying pistol at 90°C for one week in the presence of P_2O_5. Sulfonated polystyrene, crosslinked also with DCMDMB[19], was used as reference sample.

Elemental analysis was performed in a Fisons-Carlo Erba 1108 analyser for samples in sodium form purified as described previously. Scanning electron micrographs were taken with a JEOL JSM-35 microscope. The polymers here were in dry form, followed by critical point drying and finally sputtered with a coating of gold.

The kinetics of the crosslinking was followed by titration of the hydrogen chloride that evolves from the reaction of DCMDMB with the styrene units. Details of the applied procedure are described elsewhere[18].

The strongly acidic sulfonic group was determined according to the following batch method in low pH solutions. First, 0.1200–0.2600 g of small particle size polymers in the acid form were added to 60 ml of 0.5 N NaCl solution at 20°C for 4 h. Afterwards they were filtered off, washed with 5 ml of distilled water and the filtrate was titrated against a standard alkaline solution.

The total acidic groups of the products were determined by titrating swollen gels against a standard alkaline solution in high pH solutions. Here the presence of weakly acidic groups had to be taken into account. Polymer particles had to be smaller than 1 mm diameter in order to achieve the equilibrium point in short times. During the last stages of the titration, the equilibrium time was extended progressively to 30 min, caused by diffusion of the alkaline solution within polymer particles. Since carbon dioxide could influence the result of the determination in such an extended total time, the volumes of the solution were corrected by taking into consideration the consumption of a blank solution during the same period.

The swelling ratios and the holding capacity in water were measured gravimetrically at 25°C. Gel samples having potassium ions as the final form of the ionic groups were incubated in distilled water using Gouch 3 glass filters. Filtering time was 3 min for all samples, owing to the rather difficult determination of the swelling equilibrium point as a result of the high swelling ratios. The density needed for swelling ratio calculations was

Table 1 Nominal crosslinking agent concentration and density (d_p) of the prepared multifunctional networks

Sample number	Crosslinking agent concentration (% w/w)	d_p (g cm^{-3})
G1	0.00	1.30
G2	0.75	1.31
G3	1.50	1.32
G4	3.00	1.34
G5	4.50	1.36
G6	6.00	1.36
G7	12.00	1.37
G8	24.00	1.40

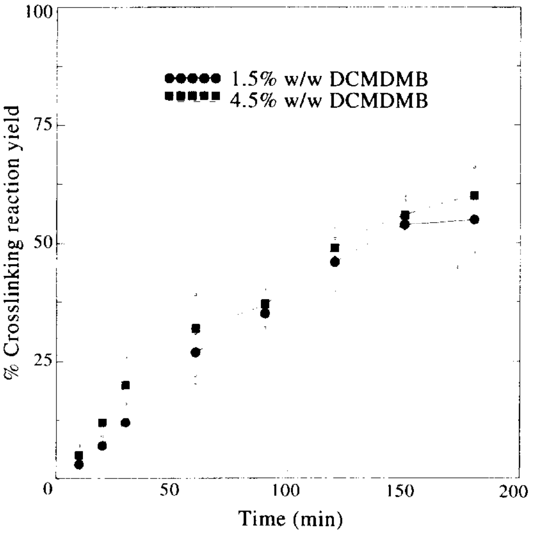


Figure 1 Crosslinking reaction kinetics at 75°C, for two different crosslinking agent concentrations

derived from the volume changes of organic solvents in the presence of preweighed polymer samples.

In order to monitor the gel–solution transition, the weight of the swollen gel was recorded at intervals, while a modified water-holding capacity that refers to the weight of the initial dry polymer was employed as a parameter.

RESULTS AND DISCUSSION

The efficiency of the described procedure and the swelling and ion-exchange properties of the obtained macronets were satisfactory. The nominal crosslinking agent concentration and the density of the products are summarized in *Table 1*. No initial crosslinking agent concentration corresponds to sample G1, while a crosslinked polymer was obtained. This topic will be discussed further in detail. The data in *Table 1* also show that the density of the products is increasing slightly *versus* the nominal crosslinking agent concentration, as a result of the introduction of crosslinks within polymer chains.

Figure 1 illustrates the kinetic behaviour of the principal crosslinking reaction for two different network density products. Crosslinker concentration is 1.5 and 4.5% w/w with respect to initial polymer weight. From *Figure 1* we may observe that the speed of the crosslinking reaction depends on the nominal crosslinking agent concentration, as expected.

A comparison of the applied reaction system with a similar system based on sulfuric acid catalysis of pure linear polystyrene at even lower catalyst concentration and lower temperature[18] shows significantly lower reaction yields in the case of SAN, during the same time. This fact is attributed to steric inhibition factors, due the presence of acrylonitrile and the products of its hydrolysis.

Two regions are interesting in i.r. spectra recording of the products: the region between 1500 and 1800 nm, where the absorption of –COOH groups is characteristic at 1700 nm; and the region between 2000 and 2300 nm, where the characteristic peak is attributed to –C≡N groups. *Figure 2* represents the spectrum of HSSAN having 4.5% crosslinker concentration (a) while crosslinked sulfonated polystyrene having 4% crosslinker concentration (b) is given as a reference sample. It is obvious that the peaks in the case of HSSAN are rather

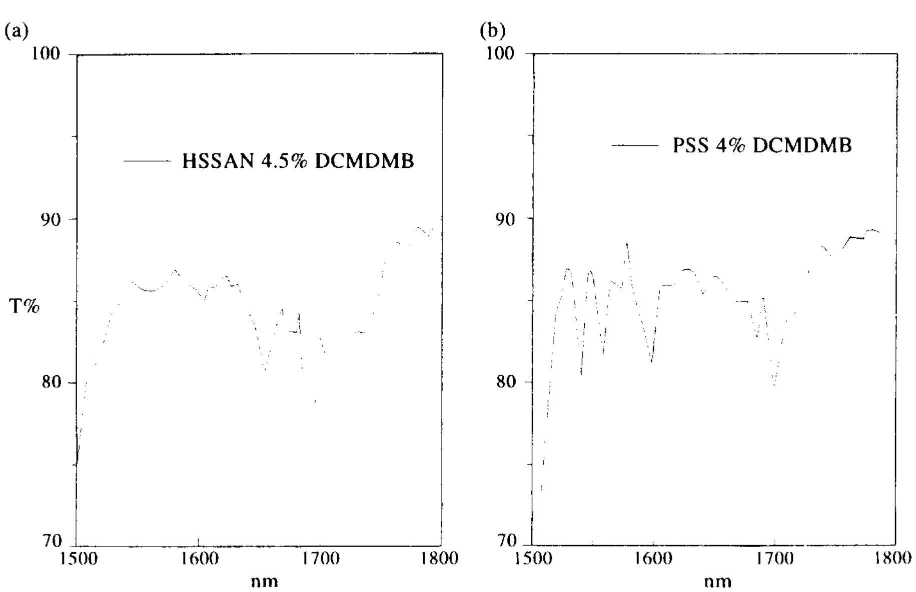


Figure 2 I.r. spectra of hydrolysed sulfonated styrene–acrylonitrile copolymer having 4.5% crosslinker concentration (a) and crosslinked sulfonated polystyrene having 4% crosslinker concentration (b) in the region 1500–1800 nm

wide, due to the absorption of other groups in the same area that also appear in the spectrum of pure sulfonated polystyrene. Thus, it is difficult to verify the presence of carboxylic groups according to the absorption at 1700 nm.

However, evidence about acrylonitrile hydrolysis was revealed from the study of the region between 2000 and 2300 nm. *Figure 3* illustrates the spectrum of linear SAN (a) and linear atactic polystyrene (b) in the same area. The characteristic peak at 2240 nm in case (a) is attributed to carbon–nitrogen bond tension of nitrile, in good agreement with literature[31]. As expected, no peak is observed in the case of pure linear polystyrene.

Figure 4 illustrates the spectrum of HSSAN having 1.5% (a) and 4.5% (b) crosslinker concentration, while the spectrum of pure macronet crosslinked sulfonated polystyrene having 4% crosslinker concentration is given as reference (spectrum c). No characteristic peak is observed at 2240 nm, a fact that demonstrates the absence of nitrile groups in every case and the existence of a hydrolysis reaction. Roizard *et al.*[32] have also observed the disappearance of the nitrile peak during acid or base hydrolysis of SAN. Generally, in i.r. spectroscopy the absence of a characteristic peak is more confident that an analogous presence, since factors like conjugation may exist.

Additional evidence concerning acrylonitrile hydrolysis is illustrated in *Figure 5*. Strongly and weakly acidic groups immobilized on a network backbone are presented as a function of the nominal crosslinking agent concentration. The total ion-exchange capacity and the equivalents of hydrogen ions of sulfonic group decrease as the degree of crosslinking increases, caused by steric inhibition factors. This result is assigned to the presence of methyl groups in DCMDMB that do not favour introduction of sulfonic groups.

Despite that fact, weakly acidic groups do not seem to be influenced by crosslinking agent concentration. It is of importance that the presence of weakly acidic groups demonstrates that hydrolysis of acrylonitrile proceeds satisfactorily according to the applied reaction. In addition, the total ion-exchange capacity covered the

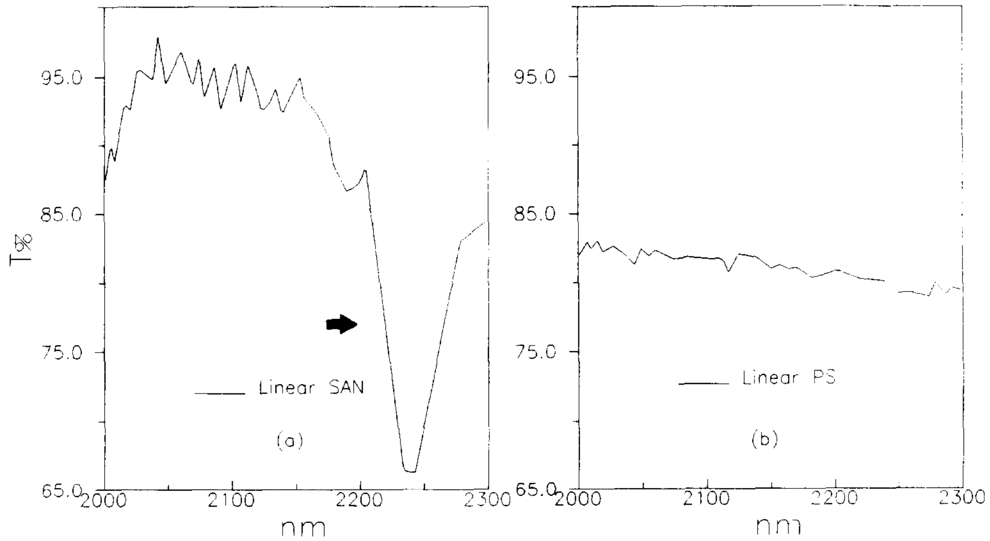


Figure 3 I.r. spectra of linear styrene–acrylonitrile copolymer (a) and linear polystyrene (b) in the same region 2000–2300 nm

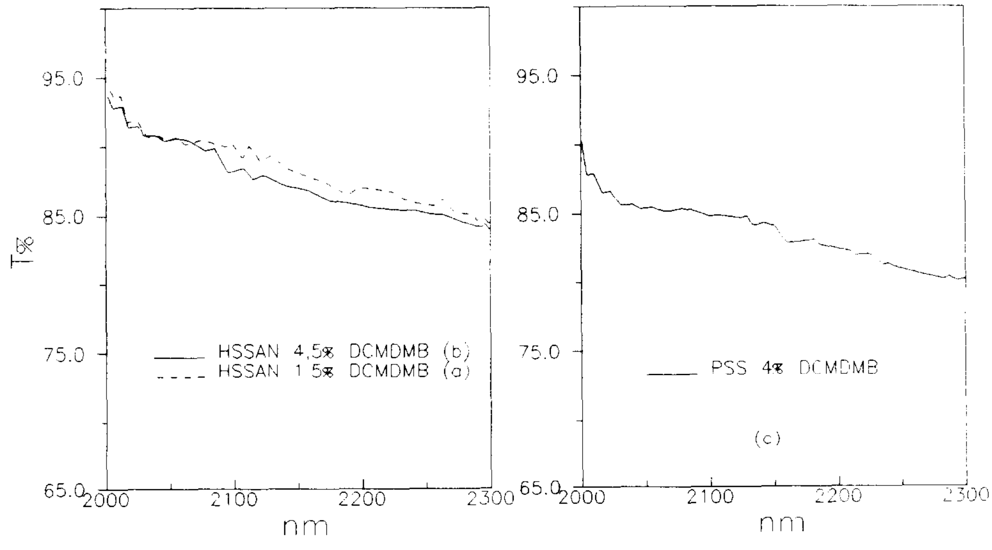


Figure 4 I.r. spectra of hydrolysed sulfonated styrene–acrylonitrile copolymer having 1.5% crosslinker concentration (a) or 4.5% crosslinker concentration (b) and crosslinked sulfonated polystyrene having 4% crosslinker concentration (c) in the region 2000–2300 nm

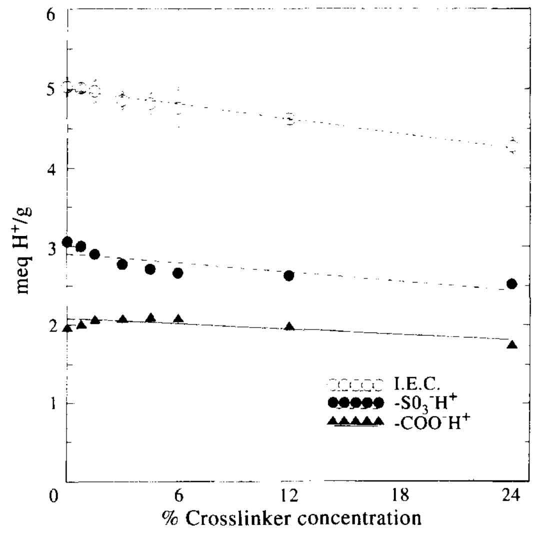
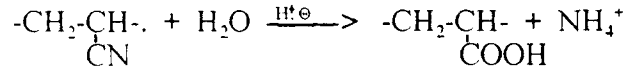


Figure 5 Total ion-exchange capacity, meq H^+ of the strongly acidic groups and meq H^+ of the weakly acidic groups, as a function of crosslinking agent concentration

range within 5.03–4.27 meq g^{-1}, designating a polymer that is competent for various applications.

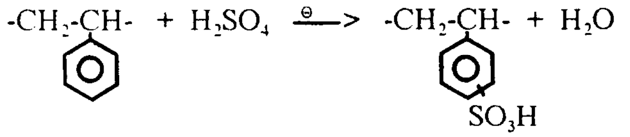
Amide formation is usually observed as an intermediate of nitrile hydrolysis to carboxylic groups. Although amides display some very weak acid character[33] they are not normally considered as ionic groups. Following elemental analysis, sample G1 was found to contain 0.36 ± 0.05% N. As a result of the other reaction yields, an accurate calculation of the theoretical nitrogen proportion in the final product is difficult, without assumptions. However, calculation of a polymer having solely amide groups and fully monosulfonated styrene units in sodium form, without the presence of sulfones, gives 3.63% N. This result indicated a possible amide formation in small extension.

In conclusion, i.r. spectra, titrimetric determination of strongly and weakly acidic groups and elemental analysis demonstrated that, although water remains at very low levels during the main process, due to the other parallel reaction requirements, hydrolysis of acrylonitrile units proceeds satisfactorily according to the following reaction:



$$\underset{CN}{-CH_2-CH-}. + H_2O \xrightarrow{H^+\ominus} \underset{COOH}{-CH_2-CH-} + NH_4^+$$

Water excess exists during the alkaline treatment stage, while during the crosslinking and sulfonation reaction stage, water comes as a product of the sulfonation of styrene units according to the following reaction:



Scanning electron micrographs allow visualization of the morphology differences. *Figure 6* illustrates the product appearance in dry form; the scale bar indicates 10 μm. Although some pores are revealed, all products were transparent in the swollen state, which characterizes low-porosity hydrogels. The porosity in these materials arises from the interstitial voids. There are a number of variables that influence the formation of pores, including the nature and the percentage of the crosslinking agent, the presence of various porogens, etc. In our case, gas formation during preparation is attributed mainly to hydrogen chloride as a product of the primary crosslinking reaction.

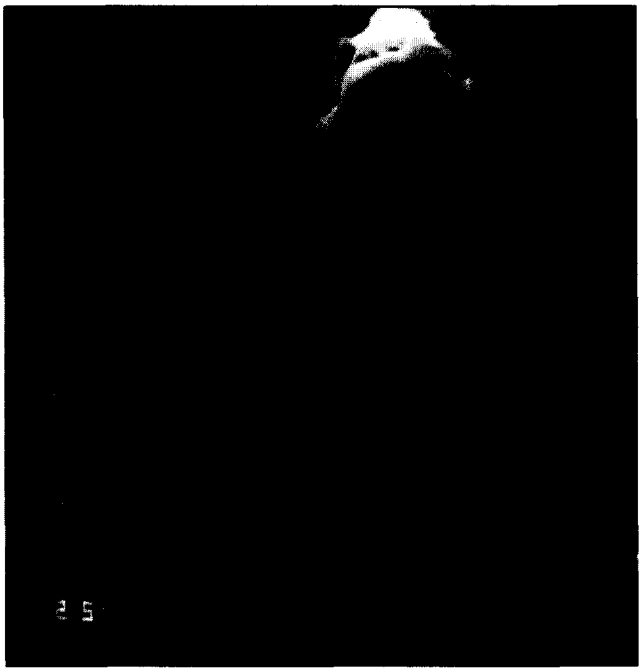


Figure 6 Scanning electron micrographs of HSSAN in dry form, having 12% w/w crosslinking agent concentration. Scale bar represents 10 μm

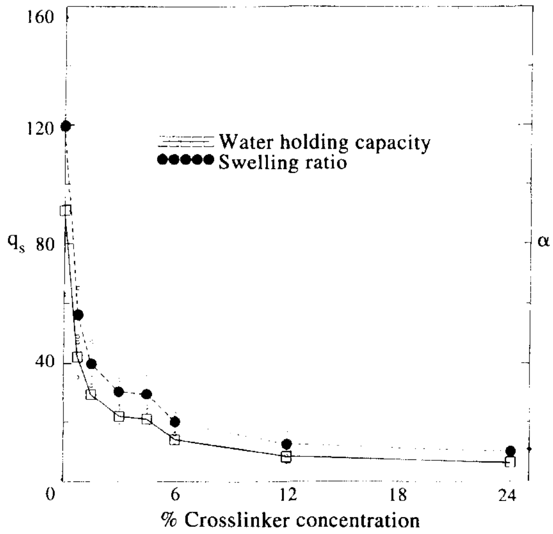


Figure 7 Swelling ratio (q_s) and water-holding capacity (α) as a function of crosslinking agent concentration

As mentioned previously a crosslinked swellable product was obtained even for sample G1 that corresponds to zero nominal DCMDMB concentration. The swelling characteristics of the products in water are given in *Figure 7*, where the swelling ratio (q_s, where $q_s = V_{swol}/V_p$) and water-holding capacity (α, where $\alpha = w_{solv}/w_p$) are presented as a function of DCMDMB concentration. Here V_{swol} and V_p are the volume of polymer in swollen and dry form, and w_{solv} and w_p are

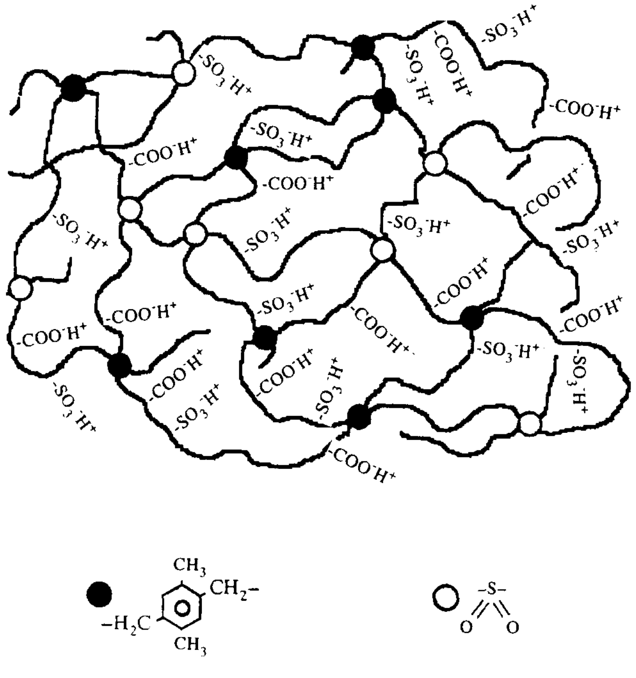


Figure 8 The structure of hydrolysed sulfonated styrene–acrylonitrile copolymer networks

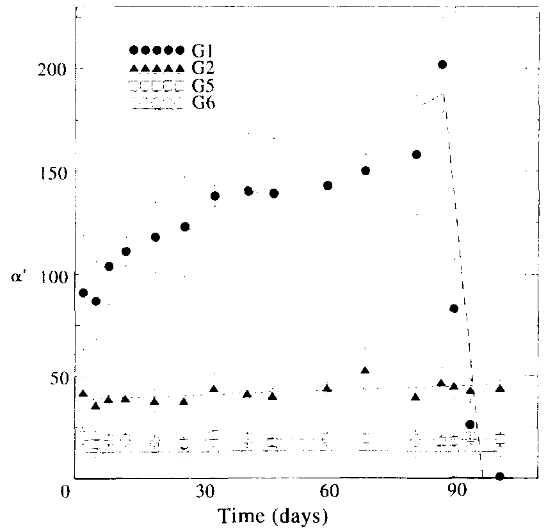


Figure 9 Modified water-holding capacity as a function of time for HSSAN samples having different degrees of crosslinking

the weights of the solvent and dry polymer respectively. Both q_s and α were found to decrease as a function of DCMDMB concentration as expected.

Also, from *Figure 7* data, it is observed that, when swelling is expressed by the swelling ratio, higher values appear compared to the corresponding water-holding capacities. It is the density of the dry polymer that is responsible for these differences, since polymer density has to be taken into account in order to evaluate the volume fraction of the swollen polymer. This influence was expected since swelling ratio and holding capacity are connected by the following obvious equation:

$$q_s = (\alpha d_p / d_{solv}) + 1 \qquad (1)$$

where d_p and d_{solv} are the densities of polymer and solvent respectively. Here, the densities of the products are given in *Table 1*, while the density of the solvent was assumed as $1.00\,g\,cm^{-3}$ at 25°C.

A comparison of the swelling ratios of HSSAN to crosslinked sulfonated polystyrene[34] shows that samples having similar nominal crosslinking agent concentration show significantly lower swelling ability in the case of HSSAN. This fact indicates an extended degree of crosslinking. Although the number-average molecular weight of the linear analogue is different, we can conclude that a secondary crosslinking reaction is enhanced in HSSAN, due to the presence of acrylonitrile units. This secondary crosslinking reaction is attributed to sulfone bridging as a parallel reaction of the sulfonation that normally is common during the introduction of sulfonic groups on styrene units[18]. The vigorous gel formation of sample G1, that has no chloromethylated crosslinker, compared to pure polystyrene reinforces this issue.

According to these remarks, the structure illustrated in *Figure 8* should represent the product of the described process. Both strongly (effective pH range 1–14) and weakly acidic groups (effective pH range 5–14) that were found on the same substrate denote that the ion-exchange properties of the polymer in the acidic form are dissimilar when a batch method is applied, compared to a continuous flow method. It is interesting, for example, that flow rate is expected to influence definitely the equivalents of hydrogen cations released during an ion-exchange process.

The transition of the swollen polymers from hydrogel to solution form is described in *Figure 9*. Four swollen samples that correspond to different degrees of crosslinking were tested for 100 days in a distilled water environment. The modified water-holding capacity (α', where $\alpha' = w_{solv}/w_{p,in}$) that includes the weight of the initial polymer ($w_{p,in}$) is given as a function of time. This correction was necessary, since transition could be done even in the early stages; thus, a non-constant polymer weight could be taken into consideration.

Samples G2–G6 do not change during this period, owing to the increased degree of crosslinking. Despite that, a continuous increase is observed in modified water-holding capacity of sample G1 attributed to a slow decrease of the degree of crosslinking. This decrease is caused by osmotic pressure, which arises from the difference of ion concentration between the polymer immobilized ionic groups and the external solution[35,36]. Since distilled water is used as a swelling medium, the ionic composition is insignificant and a continuous breaking of polymer chains occurs.

Within 100 days sample G1 presents a critical behaviour, since a fully water-soluble polyelectrolyte is the final product of the procedure. Although such a phenomenon is expected for slightly crosslinked networks, the parallel presence of sulfonic and carboxylic groups has some evident advantages. Since carboxylic groups are proved to be excellent aggregating agents in agrochemical research, when applied on a water-soluble polymeric substrate[12], the polymer combines properties of swellable water-retaining agents and soil erosion protective media.

It has already been proved that the water retention rate of HSSAN macronets is rapid when polymer particles remain at low levels and that the polymer increases crop yields when applied on soil systems[11]. All these specific properties and the fact that many recycled SAN products can also be used as raw material indicate that the transformable polymer could have interesting applications in soil conditioning, diaper (nappy) technology and in areas where combined swellable, water-soluble and ion-exchange materials are required.

CONCLUSIONS

Strongly and weakly acidic ion-exchanger series were prepared as styrene–acrylonitrile copolymer derivatives. Crosslinking as a result of the action of 1,4-dichloromethyl-2,5-dimethylbenzene and a secondary crosslinking reaction were detected according to this route. The hydrolysis of acrylonitrile units proceeds satisfactorily in spite of crosslinking and sulfonation reaction requirements for absence of water. Highly swellable macronets were finally achieved, while the total ion-exchange capacity covered the range between 5.03–4.27 meq g^{-1} with respect to the nominal crosslinking agent concentration. The presence of acrylonitrile units seems to increase the degree of crosslinking compared to pure polystyrene modifications under similar reaction conditions. A gel–solution transition was recorded when gels without DCMDMB remained in a distilled water environment. The presence of carboxylic groups in the transformable product indicates that the polymer may have specific interest, since applications in both crosslinked and water-soluble form may arise.

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