

Cation Exchange Resin Cum Polymeric Indicator Based on Sulfonated Styrene/Methyl Acrylate Copolymers

D. Ratna, V. Dalvi, B. C. Chakraborty

Naval Materials Research Laboratory, Maharashtra 421 506, India

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ABSTRACT: Styrene (ST)/methyl acrylate (MA) copolymers, having various MA contents (0–50 wt %), were synthesized in the form of a crosslinked bead and characterized by FTIR, solid state nuclear magnetic resonance (NMR) spectroscopy and elemental analysis. The copolymers were sulfonated using concentrated sulfuric acid. The copolymers with a higher MA content (20 wt % or above) undergo sulfonation even at room temperature, and higher temperature was required for the completion of sulfonation in case of the samples having lower MA content. This has been explained in terms of the polarity and porosity of

the beads as has been analyzed by scanning electron microscope (SEM). The sulfonated copolymer beads show built-in acid–base indicator property: yellow color in an acid medium changes to intense pink color at the equivalence point. FTIR and NMR studies clearly indicate that intramolecular cyclization takes place during sulfonation. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1517–1522, 2007

Key words: ion exchange resin; copolymerization; infrared spectroscopy; nuclear magnetic resonance spectroscopy

INTRODUCTION

Crosslinked polymers with functional groups such as $-\text{SO}_3\text{H}$ and CO_2H are widely used as ion exchange resins (IERS).^{1–5} IERS are generally used in two forms; thin film and spherical beads. In thin-film form, they are used as membranes for fuel cell and electrolytes for electrochemical capacitor.^{1–4} IERS in the form of small spherical beads are mainly used for demineralization and purification of water. The commercial cation exchange resins are basically sulfonated styrene-divinyl benzene networks, developed by Kunin et al.⁶ The crosslinked beads are porous and the porosity can be further controlled by adding nonreactive compounds such as cyclohexanol and cyclohexanone, which are called diluents.^{7–9} Addition of maleic anhydride or methacrylates as a comonomer has been investigated in the literature to improve the performance of ST-based IERS.^{10,11} The reports on polymeric indicators are mostly guarded by patents^{12,13} and very little information is available in open literature.¹⁴ Such indicators have potential applications in fiber optic pH probe and as pH indicators.^{15,16} Attempt for the preparation of IER beads with an acid–base indicator property has been performed by incorporating an organic dye into the polymer matrix.¹⁷ In our laboratory, we have demonstrated the acid–base indicator property of the

sulfonated ST/acrylic acid copolymers,¹⁸ and successfully developed the IER in bead form using a styrene/methyl acrylate (ST-MA) system.¹⁹ Since MA is immiscible with water for synthesis of beads in suspension polymerization, it was selected instead of acrylic acid.

This article discusses the characterization of various compositions of ST/MA copolymers and their sulfonated products using FTIR, NMR, SEM, and elemental analysis techniques.

EXPERIMENTAL

Materials

Styrene (ST) (Fluka) and methyl acrylate (MA) (Fluka) were purified by washing twice with aqueous NaOH solution (5% w/v) to remove the inhibitors, and then washed with distilled water for several times. The monomers were then dried over anhydrous calcium chloride for 48 h. Divinyl benzene, used as a crosslinker, was obtained from Fluka and used without further purification. Sodium polyacrylate, stearic acid, and sodium sulfate were obtained from SISCO India, India, and were used as received. Azobisisobutyronitrile was purchased from Fluka, and recrystallized from ethanol before use. Sulfuric acid (98%) was supplied by Glaxo, India.

Synthesis of copolymer beads

The copolymer beads were prepared by the suspension-polymerization method. The details of synthesis

Correspondence to: B. C. Chakraborty (bikas@hotmail.com).

TABLE I
DSC Data for PEO/clay/LIBF₄ Electrolyte

Sample	C%		H%	
	Theoretical	Experimental	Theoretical	Experimental
PS	92.3	91.26	7.69	8.569
PSMA10	88.65	88.09	7.617	8.477
PSMA20	85	85.21	8.315	8.246
PSMA30	81.35	83.75	7.474	8.219
PSMA40	77.70	80.96	7.402	7.892
PSMA50	74.05	76.79	7.325	8.008

and characterization of bead have been presented elsewhere.¹⁹ For the synthesization of different compositions of the copolymers, the feed ratio was used according to the method of Fineman and Ross,²⁰ taking $r_1 = 0.76$ and $r_2 = 0.15$.

Sulfonation of beads

The copolymer beads were sulfonated using concentrated sulfuric acid. Bead to acid ratio was kept as 1 : 3 (by weight). The reaction was allowed to occur for 6 h at different temperatures (50, 60, and 70°C). After carrying out the sulfonation reaction for a desired time, the sulfonated beads were recovered by pouring of the acid mixture containing the suspended beads in melted ice. The sulfonated beads were then washed several times with distilled water to make them completely free from sulfuric acid.

Analysis and measurements

Elemental analysis was carried out on an elemental analyzer, Thermofinnigan Flash EA 1112 series. The total cation exchange capacities of the sulfonated copolymers including sulfonic and carboxylic acid groups were determined by equilibrating a known weight of the beads with a standard NaOH solution for 12 h. A definite amount of treated alkali was pipetted out without the beads and back titrated with a standard oxalic acid solution.²¹ The IEC for sulfonic acid (IEC_{SO_3H}) alone was determined by equilibrating a known weight of the beads with an aqueous NaCl solution of 0.1M for 12 h and titrating directly the generated acid as a result of exchange with a standard NaOH solution. IEC_{COOH} is determined by subtracting the IEC_{SO_3H} from the total ion exchange capacity (IEC_{total}).

A low-voltage scanning electron microscope (SEM) (JEOL, JSM-840) was used to examine the porosity of the bead samples. Few beads were mounted on an aluminum stub using a conductive (silver) paint and were sputter coated with gold prior to the fractographic examination. Scanning electron photomicrographs were obtained under conventional secondary electron imaging conditions with an accelerating voltage of 20 kV.

UV-vis-NIR spectrophotometer CARY 500 was used to study the color change property of the beads. The beads were kept in between two glass slides and exposed to UV and the absorbance was recorded. The IER beads synthesized in the acid form was analyzed. Then the beads were neutralized with alkali and the same analysis was carried out for the beads in an alkaline medium.

The FTIR spectra of dried beads (before and after sulfonation) were recorded in a PerkinElmer spectrophotometer (Model No 1600) in KBr pellets. For FTIR, samples were prepared by powdering the beads in liquid nitrogen and mixing with KBr to make pellets.

Solid state ¹³C NMR spectra were recorded on Bruker 500 MHz spectrometer. The bead samples were soaked in liquid nitrogen and crushed into the form of a fine powder and the dried powder is used for the solid state NMR analysis.

RESULTS AND DISCUSSIONS

ST-MA copolymers (containing 0–50% of MA by weight) were synthesized in the form of a crosslinked bead by a suspension polymerization. The elemental analysis results for the copolymer beads are shown in Table I. The experimental values for the percent of carbon and hydrogen are very close to the theoretical values calculated for a particular composition. The FTIR spectra for the copolymers containing 0, 10, and 50% MA are shown in Figure 1. All the copolymers showed a sharp peak at 1730 cm⁻¹ due to ester group, and the peak intensity increases with increasing of MA concentration.

To study the MA content effect on the sulfonation, the copolymers with different compositions were sulfonated at various temperatures (30, 50, 60, and 70°C). The sulfonation time was kept 6 h for all the cases. The formation of the —SO₃H groups as strong acid exchange capacity (IEC_{-SO_3H}) was determined by using a sodium chloride solution as described earlier.

IEC_{-SO_3H} values as a function of temperature for various copolymers are presented in Figure 2. It was clear that sulfonation was not found to occur in cross-linked polystyrene ($IEC_{-SO_3H} = 0$) up to 70°C. On the other hand, the sulfonation takes place even at room

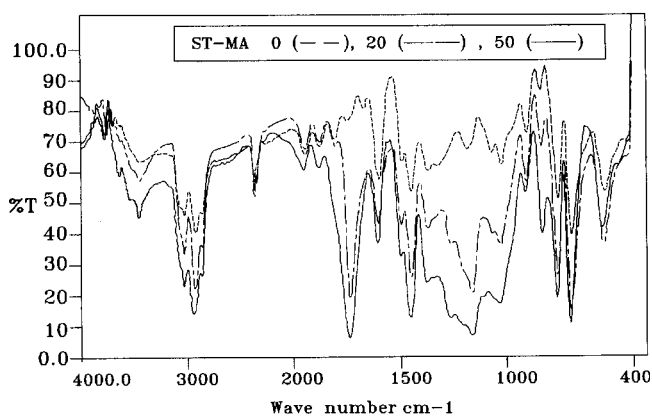


Figure 1 FTIR spectra of ST-MA copolymers with MA content 0% (.....), 20% (-----), and 50% (_____).

temperature (30°C) in the case of the copolymers having MA content 20% and above. The value of IEC_{-SO_3H} reaches almost to the theoretical value when the sulfonation is carried out at 60–70°C, indicating almost the completion of the sulfonation reaction. The higher the MA content, the lower was the temperature required for the completion of the sulfonation.

The presence of the ester groups, which undergoes hydrolysis to produce the carboxyl groups during sulfonation, are not likely to have any effect on sulfonation reaction as such, in the presence of sulfuric acid, which is a strong acid. The observation can be explained in terms of two mechanisms: increase in polarity and increase in porosity of the beads because of the incorporation of MA into the network structure of the beads. An increase in polarity of the beads facilitates the interaction with highly polar sulfuric acid and thereby enhances the extent of sulfonation. The porosity of the beads was studied by SEM analysis. The SEM photographs for the bead samples with a varying MA contents are shown in Figure 3. It shows that the extent of porosity increases with increase in MA content in the copolymer beads. The increase in porosity of the crosslinked beads by using diluents and comonomers has been reported.^{8,9} The higher porosity increases the diffusion of sulfuric acid into the

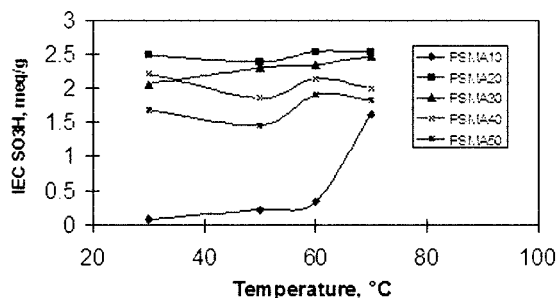
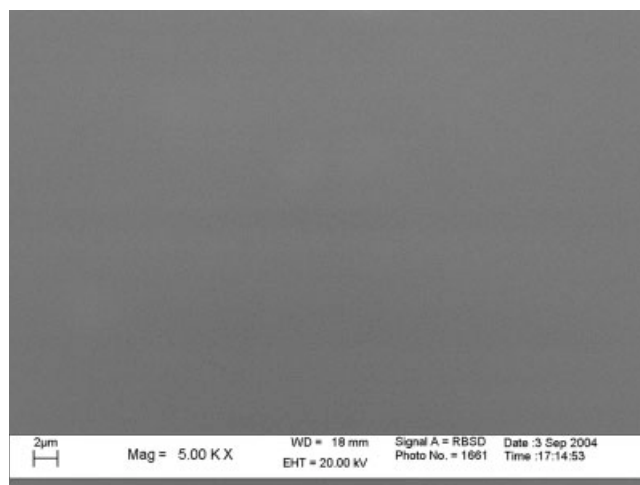
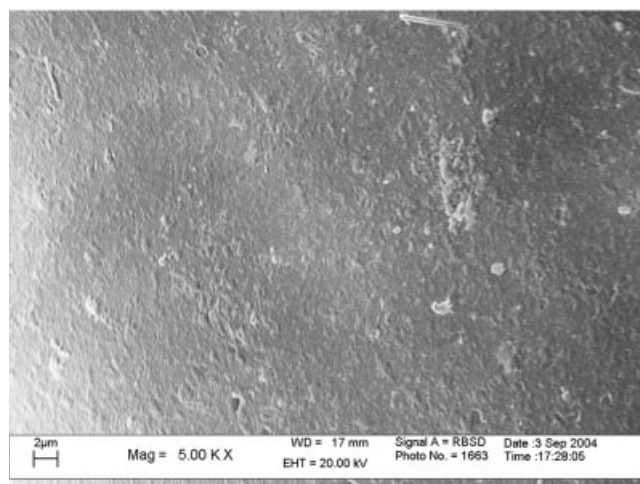


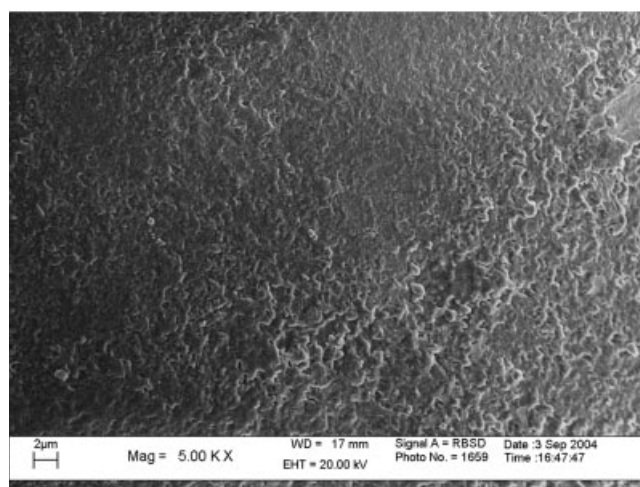
Figure 2 IEC_{SO_3H} versus temperature plot for sulfonated ST-MA copolymers of varying MA content.



(a)



(b)



(c)

Figure 3 (a) SEM microphotographs for polystyrene bead; (b) SEM microphotographs for ST-MA bead with 20 wt % MA; (c) SEM microphotographs for ST-MA bead with 50 wt % MA.

network structure and thereby facilitates the sulfonation reaction.

During the sulfonation, hydrolysis of the ester groups of ST-MA copolymer also takes place leading to the formation of the carboxyl groups. The generation of the carboxyl groups is quantified as IEC_{CO_2H} , and the values are presented in Figure 4, as a function of temperature for the copolymers of varying MA contents. As mentioned earlier, the copolymers containing less than 20% MA react very slowly at lower temperature. We note that up to 60°C, no carboxyl generation was detected for ST-MA copolymer beads containing 10% of MA. For copolymers containing 20% or above MA content, the IEC_{CO_2H} increases with an increase in temperature attains a maximum and decreases thereafter. It was also observed that the maximum IEC value was significantly lower than the theoretical value calculated for a particular composition. The difference between the theoretical and the experimental values increased with the increase in the MA content. This can be explained by considering the participation of the $-CO_2H$ groups in the cyclization as shown briefly in Figure 5. The detailed discussion on the cyclization has been presented in our previous publications.^{18,19} The cyclization requires a presence of alternating segments of the copolymer and possibility of formation of such a segment increases with the increase in the MA content up to 50%. Hence, more and more carboxyl groups participate in the cyclization for the copolymer of higher MA content, leading to the more and more deviation of the IEC_{CO_2H} value from the respective theoretical value.

The FTIR spectra of sulfonated ST-MA copolymers having 0, 20, and 50% MA content are shown in Figure 6. The sulfonated copolymers show a broad peak in the carbonyl region covering the characteristics peak for carboxylic acid at 1710 cm^{-1} and a peak at 1630 cm^{-1} , which is a characteristic peak for a conju-

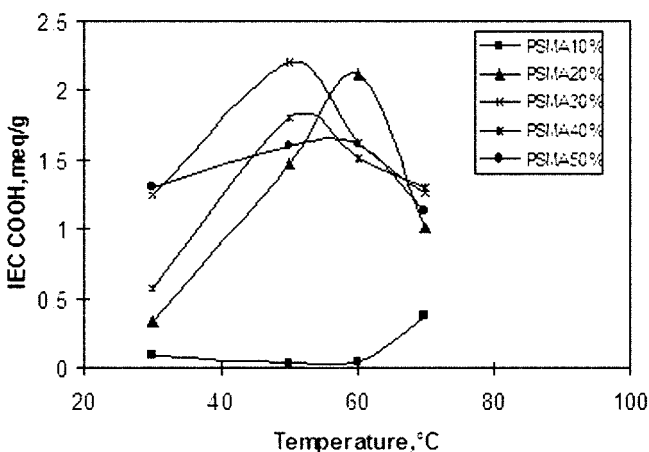


Figure 4 IEC_{COOH} versus sulfonation temperature plots for ST-MA copolymers of varying MA content.

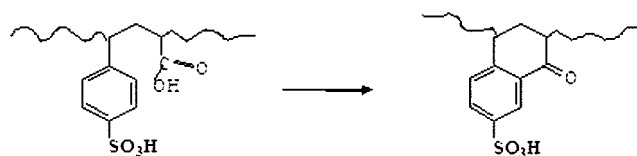


Figure 5 Cyclization of sulfonated ST-MA copolymers.

gated ketone.²² As the concentration of MA increases, the peak broadness increases and the peak shifts towards the characteristic peak for a conjugated ketone. This can be explained in terms of cyclization reaction (Fig. 5). With increase in MA concentration, the number of alternate ST-MA units in the copolymer chain increases, resulting in the formation of a more unsaturated ketone during sulfonation.

To further investigate the chemical structure, the sulfonated copolymers were characterized by ^{13}C NMR spectroscopic analysis in solid state. The resolution in solid state NMR is less compared to a liquid state NMR. Hence, it is difficult to assign the peaks for all the individual carbon atoms. However, a major change in chemical structure can be clearly identified. ^{13}C NMR spectra of unsulfonated and sulfonated ST-MA copolymer of 40% MA content are shown in Figure 7. The peaks at 43.1 and 49.7 ppm are due to the aliphatic carbon atoms. After sulfonation, the peak at 49.7 ppm is shifted to 61.9 ppm, which indicates the involvement of the aliphatic carbon atoms in the cyclization. The peaks at 131 and 151.8 ppm can be attributed to the aromatic carbon atoms. After sulfonation, the peak at 151.8 ppm is shifted to 146.4 ppm. This can be attributed to this fact that during sulfonation $-SO_3H$ group is introduced into the benzene ring. Sulfonic acid, as an electron withdrawing group, reduces the electron density and carbon atoms in the vicinity to this group, and offers lower shielding effect, resulting in a shift of the peak. The electron cloud of benzene ring is also delocalized due to their

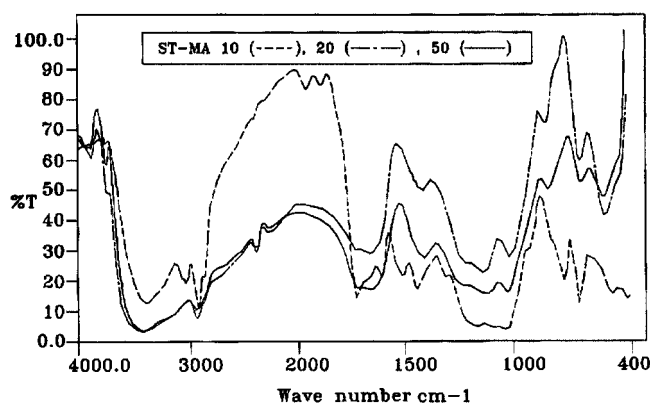


Figure 6 FTIR spectra of sulfonated ST-MA copolymer with MA content: 10% (.....), 20% (-----), and 50% (_____).

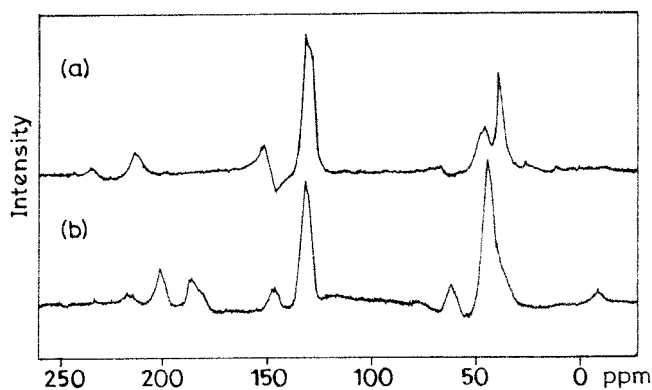


Figure 7 ^{13}C NMR spectra of ST-MA copolymers with 40% MA: (a) unsulfonated and (b) sulfonated.

participation in the cyclization. The peak at 208.2 ppm, observed in unsulfonated copolymer, is because of the presence of the ester carbon. After sulfonation, the peak at 208.2 disappeared and two new peaks at 201.2 ppm and 186.1 appeared. The peak at 201.2 can be assigned to the carboxyl carbon atom and the other peak can be due to the presence of the unsaturated ketone. The electron density of a ketonic carbon atom of an unsaturated ketone is lower than the same of a carboxylic acid due to conjugation, and therefore the former shows a peak at lower ppm compared to the latter.

The copolymer beads are white in color and the color changes to yellow on sulfonation. The sulfonated beads in the acidic form absorb at 450 nm. The absorbance at 450 nm versus MA content plots for the various copolymer beads are shown in Figure 8. The absorbance increases with increasing MA content up to 50%. This can be explained once again in terms of the cyclization leading to the formation of high conjugated structures.^{18,19} The sulfonated beads show a color change from yellow to pink, as the medium changes from an acidic to an alkaline due to the extension of conjugation. In an alkaline medium, the absorption peak undergoes a red shift and absorbs at 630 nm instead of 450 nm in the acid form. The ab-

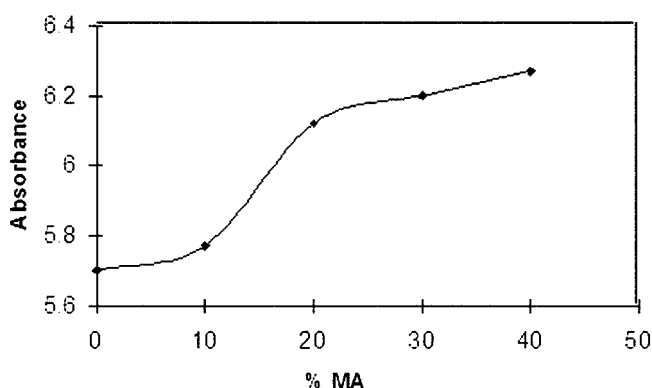


Figure 8 Plot of absorbance (at 450 nm) of sulfonated beads in acid form as a function of MA content.

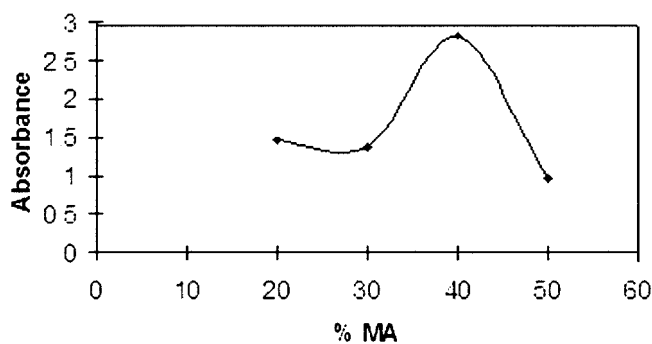


Figure 9 Plot of absorbance (at 630 nm) of sulfonated bead in base medium as a function of MA content.

sorbance at 630 nm versus MA content plots for the various copolymer beads are shown in Figure 9. It was observed that the absorbance is increased up to 40% of MA and then decreased due to the darkening of the color as a result of high level of the cyclization.

CONCLUSIONS

Sulfonation of the ST-MA copolymers was investigated. The ease of sulfonation (in terms of the temperature required for the sulfonation) increases with increasing of MA content due to the increase in the polarity and porosity of the copolymer beads as analyzed by SEM. All the copolymers show an acid-base indicator property due to the cyclization as confirmed by FTIR and solid state ^{13}C NMR spectroscopic analysis. The intensity of yellow color of the sulfonated bead increases up to 50% MA concentration. However, the best indicator property was observed at 40% MA concentration.

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