Preparation and Characterization of 4-Vinyl Pyridine-Grafted SBS Triblock Copolymer

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Synopsis

Study on the graft of 4-vinyl pyridine to styrene-butadiene-styrene triblock copolymer by solution polymerization shows that the catalyst concentration, temperature, and reaction time are the major influencing factors. Graft efficiency increases with temperature and time but levels off when temperature is higher than 65°C. Increasing concentration of catalyst also promotes graft, but when it is higher than 1.0×10^{-2} M, the reaction system begins to gel.

A cast film of the graft copolymer was dried, cross-linked with S_2Cl_2 in nitromethane solution, sulfonated, and chloromethylated. The water content of the membrane is 13.5%. Its anionic and cationic exchange capacities are 0.066 mEq per dry gram and 0.273 mEq per dry gram, respectively. The anionic-cationic capacity ratio is thus 0.26.

The nitrogen content of the graft copolymers was determined with a CHN elemental analyzer, and qualitative analysis was carried out with infrared spectroscopy. Transmitting electronic microscopy was used to study the morphology and feasibility of preparing a charged mosaic membrane for piezodialysis.

INTRODUCTION

In certain two-component ionic polymer materials, salt might be induced to diffuse faster than water, thus allowing an alternate mode of product recovery. This process, operated by means of an externally applied pressure, is usually referred to as piezodialysis or negative reverse osmosis.[1] In the charged mosaic membrane (CMM), small elements of opposite fixed charge are in alternate order in a mosaic structure. In this case, one can expect partial or complete short circuits of the membrane potentials caused by neighboring elements with opposite fixed charge, and thus an unhindered flow of counterions in each element is permitted. This effect greatly increases the overall salt permeability[2,3] but decreases the membrane potential.

Sollner[4] predicted that membranes displaying bifunctional ion-exchange properties may also exhibit specific transport properties, which are evoked by the electrical interaction of oppositely charged ion-exchange resins. Since there exists a strong interaction between the mobile ions and the water molecule contained in the ion-exchange regions, it is possible to initiate a forced transmembrane flow of a solution with a concentration similar to the internal concentration of the membrane.[5] There are several papers dealing with the properties of CMM.[6-10]

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EXPERIMENTAL

Materials

SBS

The trade name is Kraton 1101, produced by Shell company. The weight ratio of styrene to butadiene is 3:7, and the density is 0.94 g/cm³. Purification was necessary to wash out the antioxidants.

4-Vinyl Pyridine

This is the first-grade reagent of Hukung and was stabilized with phenyl-β-naphthylamine. It was distilled under reduced pressure immediately before use. The boiling point is 54°C at 5 mm Hg.[11]

Other Reagents

Benzoyl peroxide (BOP), sulfur monochloride, nitromethane, chlorosulfonic acid, methyl iodide, methylene blue, and carbon disulfide are all of reagent grade and were used directly without further purification.

INSTRUMENTS

We used an infrared spectrometer (Perkin-Elmer Co. Model 567), a CHN elemental analyzer (the Chung San Scientific Research Institute was entrusted to determine the nitrogen content of the graft copolymers for us), a microtome (Reichent-Jung Co. Model FC-4 Microcut), and a transmitting electronic microscope (Joel Model 100SX).
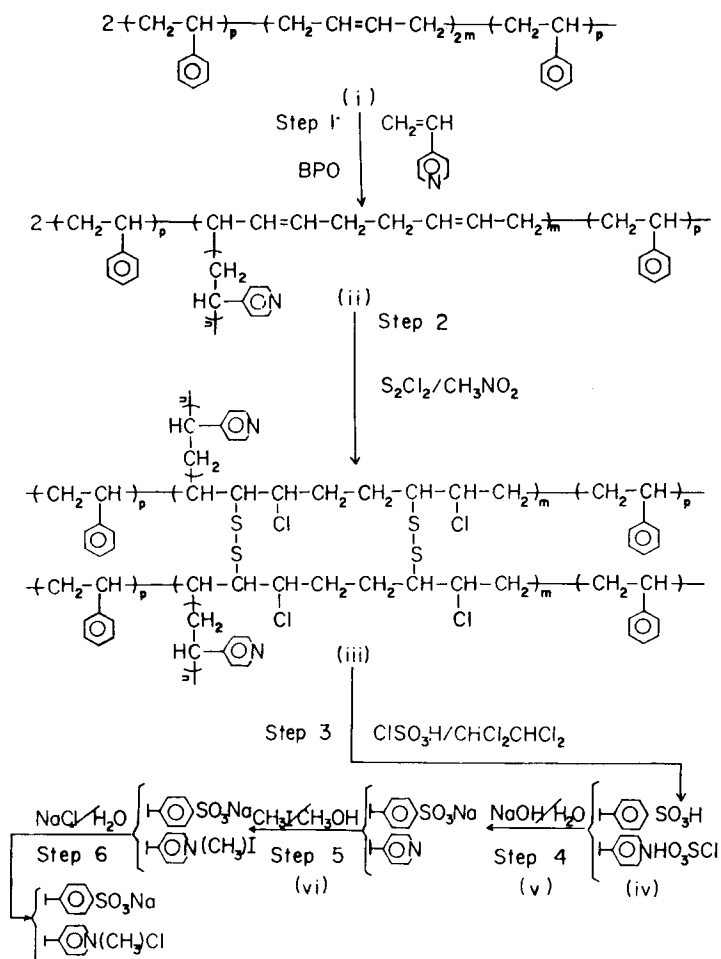
EXPERIMENTAL PROCEDURE

The procedures for the preparation of membranes are shown in Scheme 1. Details of the description of the experimental are given by the following.

Graft Polymerization

Purified SBS (I) (10 g, dried) was dissolved in 130 ml benzene, and the stirred mixture was purged with a slow stream of nitrogen. 4-Vinyl pyridine (12 ml) was added, and 0.12 g benzoyl peroxide was then added after 5 min. The mixture was stirred and bubbled with nitrogen at 50°C (the temperature controlled with an oil bath) for 3 h. The solid was dissolved in 130 ml benzene, poured dropwise with stirring into a solution of 1300 ml methanol, and then the mixture was filtered. The procedure was repeated three times to wash out the homopoly (4-vinyl pyridine). The solid was washed again with methanol in a Soxhlet extractor for 24 h. The graft copolymer (II) was dried in a vacuum oven for 24 h and then stored in a refrigerator.

Cast Film

Graft copolymer (II) (3.4 g dry weight) was dissolved in 20 ml benzene. The mixture was filtered under reduced pressure to wash out any gel or dust

$2 + CH_2\text{-}CH \xrightarrow{}_p \text{---} + CH_2\text{-}CH=CH\text{-}CH_2 \xrightarrow{}_{2m} + CH_2\text{-}CH \xrightarrow{}_p$

(i)

Step 1 $CH_2=CH$

BPO

(ii)

Step 2

S_2Cl_2/CH_3NO_2

(iii)

Step 3 $ClSO_3H/CHCl_2CHCl_2$

Step 6 $NaCl/H_2O$ Step 5 CH_3I/CH_3OH Step 4 $NaOH/H_2O$

(vi)   (v)   (iv)

Scheme 1. Schematic diagram of the experimental procedure.

particles. Thickness of the wet film was regulated by adjusting the height of the casting knife (washed with benzene before use). If the thickness of the wet film was 0.5 mm, then the dry film would be 0.05 mm thick.

The filtered mixture was poured evenly onto the glass plate (30 × 12 cm) and swept by casting knife; a film then adhered to the glass plate. The glass plate was taken into the oven and dried at 50°C for 30 min. It was then dipped into methanol solution, and after a few minutes the film was removed from the glass plate. The film was dried in a vacuum oven for 12 h.

Cross-linking, Sulfonation, and Chloromethylation of the Membranes

Cross-linking of the film (step 2) was carried out by placing the film in a closed container filled with a 3% (by volume) solution of freshly distilled sulfur monochloride in dry nitromethane. After 72 h at −4°C the film was washed in n-heptane containing 10% (by volume) carbon disulfide.

In order to sulfonate (step 3) the polystyrene part of the copolymer, the cross-linked film was swelled in chloroform and placed in a 5% (by volume) solution of chlorosulfonic acid in chloroform at $-28°C$ for 24 h. During the sulfonation reaction, the film turned purple but the color disappeared when washed with chloroform. In order to transform the poly(styrene sulfonic acid) into its salt form (V), the sulfonated film was placed in 0.5 N sodium hydroxide solution.

The cross-linked and sulfonated film was swollen in methanol and chloromethylated in a 15% (by volume) solution of methyl iodide in methanol at room temperature. After 48 h the film (VI) was placed in 0.5 N sodium chloride solution.

Elemental Analysis

The nitrogen content of the graft copolymer was determined with a CHN analyzer. The percentage graft-on may be calculated by the equation

$$\text{Graft-on\%} = \frac{N\%}{14.01} \times 105.14$$

where $N\%$ is the weight percentage of nitrogen in the graft copolymer, 14.01 is the atomic weight of nitrogen, and 105.14 is the molecular weight of 4-vinyl pyridine.

Film Prepared for Infrared Spectroscopy

SBS and SBS-g-(4-vinyl pyridine) (0.1 g dry weight) were dissolved in 10 ml benzene. The mixture was poured into a Petri dish prelayered with a sheet of glutinous rice. After drying in air, the Petri dish together with the film was dried in a vacuum oven at room temperature for 8 h. The film was removed from the rice paper by dissolving the paper in water. The film was dried in a vacuum oven at room temperature. After 8 h the film could be analyzed by infrared spectroscopy.

A film of poly(4-vinyl pyridine) was prepared with a mixture of tetrahydrofuran and methanol (3 : 1 volume ratio) as solvent.

Film Prepared for Transmission Electron Microscope

Sectioning was carried out with a microtome (Reichert-Jung Co. Model FC-4) at $90°C$. The thickness of the film was 700 Å. The sectioned film was placed on a copper mesh. Phase contrast was obtained by staining the poly(4-vinyl pyridine) phase with a 0.02% aqueous solution of methylene blue.[6] The polystyrene phase was not wet and remained clear after excessive dyestuff was rinsed off. The stained film was used directly as a negative for making the print.

Properties of the Charged Mosaic Membrane

The water content of the CMM was carried out by immersing it in distilled water. After it was completely swollen, the wet weight of CMM (W_w) was determined by wiping off the surface water with filter paper. The wet CMM

TABLE I
Effect on Reaction Time on % Graft-on[a]

Code of sample	Reaction time (h)	Nitrogen (wt%)	Graft-on (%)
H-1-3	3	0.35	2.63
H-1-8	8	0.44	3.30
H-1-12	12	0.47	3.53
H-1-16	16	0.53	3.98
H-1-24	24	0.65	4.88
H-1-36	36	0.79	5.93
H-1-48	48	1.05	7.88

[a]Concentration of SBS = 70.42 g/L; concentration of 4-vinyl pyridine = 7.83 mol/L; concentration of initiator = 3.49×10^{-3} mol/L; and temperature of graft copolymerization = 50°C.

was dried in a vacuum oven at room temperature for 24 h to determine its dry weight W_d. Thus, $W\% = (W_w - W_d/W_d) \times 100$, where $W\%$ is the percentage water content of the CMM.

A membrane containing sulfonic acid groups (a mEq) and quaternary pyridinium groups (b mEq) was treated with a hydrochloric acid solution followed by washing with water and left immersed in 0.1 N NaOH containing 1 N sodium nitrate (x ml). The solution was titrated with 0.1 N HCl (y ml at the equivalent point, and y' ml in total), and then with 0.1 N AgNO$_3$ (z ml).[12]

$$a = 0.1x(x - y) \qquad b = 0.1x(z - y')$$

RESULTS AND DISCUSSION

Grafting Polymerization

Effect of Grafting Time

The grafting of 4-vinyl pyridine as a function of time is shown in Table I. As observed, the percentage of graft-on increases with time.

Effect of the Reaction Temperature

The effect of the reaction temperature on the percentage of graft-on is shown in Table II. It can be seen that it increases with temperature at first

TABLE II
Effect of Reaction Temperature on % Graft-on[a]

Code of sample	Reaction temperature (°C)	Nitrogen (wt%)	Graft-on (%)
H-2-50	50	0.35	2.63
H-2-65	65	1.25	0.38
H-2-80	80	1.24	9.31

[a]Concentration of SBS = 70.42 g/L; concentration of 4-vinyl pyridine = 7.83 mol/L; concentration of initiator = 3.49×10^{-3} mol/L; reaction time = 3 h.

TABLE III
Effect of Initiator Concentration of % Graft-on[a]

Code of sample	Initiator concentration $(mol \times 10^3 \ L^{-1})$	Nitrogen (wt%)	Graft-on (%)
H-3-0.06	1.74	0.38	2.85
H-3-0.12	3.49	0.47	3.53
H-3-0.24	6.98	0.54	4.05
H-3-0.36[b]	10.47	2.16	16.21
H-3-0.48[c]	13.96	3.60	gel

[a]Concentration of SBS = 70.42 g/L; concentration of 4-vinyl pyridine = 7.83 mol/L; temperature of graft copolymerization = 50°C; reaction time = 12 h.

[b]The nitrogen content was determined on the purified soluble part of the graft copolymer.

[c]Most of the graph copolymer gelled. The poly(4-vinyl pyridine) might have been entrapped in the gel particles, which resulted in high nitrogen content.

but levels off as the temperature goes higher. The maximum grafting level is soon reached. The monomer is likely to take part in homopolymerization rather than grafting polymerization as the temperature increases.

Effect of the Initiator Concentration

The effect of initiator BPO concentration on the percentage of graft-on was evaluated in a series of polymerizations in which the concentration of the initiator varied from 1.74×10^{-3} to $13.96 \times 10^{-3} \ M$. The results are shown in Table III, in which the percentage of graft-on increases with the initiator concentration but gelation occurs when the initiator concentration reaches $10.47 \times 10^{-3} \ M$. The cross-linking reaction occurred strongly as a result of the increased number of branch points on the polymer skeleton.

CHARACTERIZATION OF THE GRAFT COPOLYMER

The difference of absorption bands between SBS and poly(4-vinyl pyridine) is shown in Figure 1a and b. In SBS there are five adjacent hydrogens in the benzene ring and the aromatic C-H absorption band appears at $700 \ cm^{-1}$, whereas in poly(4-vinyl pyridine), there are only two adjacent hydrogens in the pyridine ring and the C-H absorption band appears at $820 \ cm^{-1}$.

The major difference between Figure 1b and c is that the absorption band appears at $820 \ cm^{-1}$ in Figure 1c, which is the bending deformation of the two adjacent hydrogens in the pyridine ring. In the region of $1400-1600 \ cm^{-1}$, as shown in Figure 1c and d, there are five and three absorption bands, respectively. The absorption band at $820 \ cm^{-1}$ is less clear in Figure 1d. From this evidence, it is reasonable to conclude that graft polymerization has occurred.

Figure 1d, the absorption band at $3400 \ cm^{-1}$ may be caused by the moisture absorbed by poly(4-vinyl pyridine). However, it is not present in the graft copolymer shown in Figure 1c.

Carbon double-bond absorption occurs at $1650 \ cm^{-1}$ in the graft copolymer, and these double bonds have been cross-linked to increase the mechanical properties of membrane.
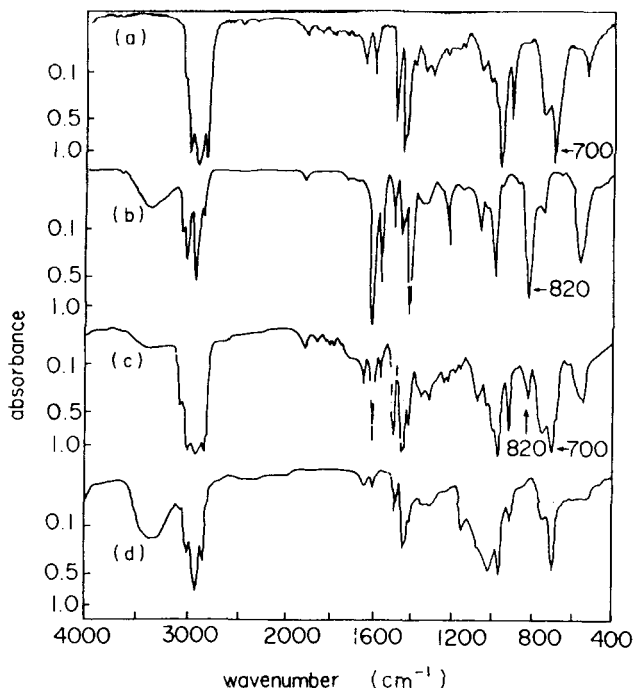
Fig. 1. Infrared spectra of SBS systems. (a) SBS film cast from benzene solution. (b) Poly(4-vinyl pyridine) film cast from mixture of THF and methanol (THF-MeOH = 3 : 1, v/v). (c) SBS-g-(4-vinyl pyridine) film cast from benzene solution (7.88% graft-on). (d) SBS-poly(4-vinyl pyridine) polyblend film cast from mixture of THF and methanol (THF-MeOH = 3 : 1, v/v); poly(4-vinyl pyridine) content = 8%.

MORPHOLOGY OF THE GRAFT COPOLYMER

The microstructure of the graft copolymer is shown in Figure 2. From the transmission electron micrograph the mosaic pattern is seen. The dark areas are poly(4-vinyl pyridine) phases packed together closely, and their dimensions are 0.03 μm. The bright areas are polystyrene and polybutadiene phase, and their dimensions are 0.17 μm.
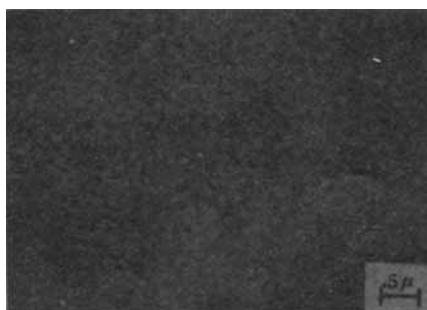

Fig. 2. Transmission electron micrograph of SBS-g-poly(4-vinyl pyridine) film cast from 17% benzene solution (7.88% graft-on). Dark areas represent the poly(4-vinyl pyridine) phases dyed with methylene blue. Light areas represent the polystyrene and poly-polybutadiene phases.
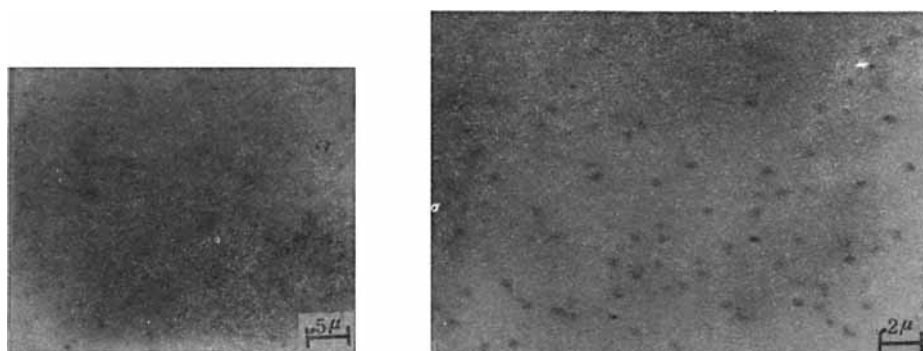
Fig. 3.   Transmission electron micrograph of SBS-poly(4-vinyl pyridine) polyblend film cast from 17% mixture of THF and methanol (THF-MeOH = 3 : 1, v/v). (The poly(4-vinyl pyridine) content = 8%.) Dark areas represent poly-(4-vinyl pyridine) phases dyed with methylene blue. Light areas represent polystyrene and polybutadiene phases.

The transmission electron micrograph of the polyblend is shown in Figure 3. The poly(4-vinyl pyridine) phases are packed dispersively, and their dimensions are 0.068 μm. As far as the mixing effect is concerned, graft polymerization is superior to blending.

PROPERTIES OF THE CHARGE MOSAIC MEMBRANE

It was necessary to use deionized water to decrease the effects of cation and anion in this experiment (see Table IV). The maximum and the true anionic exchange capacities are 0.749 and 0.066 mEq per dry gram respectively, and the percentage of chloromethylation is 8.8%, whereas the maximum and the true cationic exchange capacities are 2.653 and 0.273 mEq per dry gram, respectively, and the percentage of sulfonation is 10.3. The ratio of anionic to cationic exchange capacity is therefore 0.62 (see Appendix). From this quantitative analysis, it can be certain that the charge mosaic membrane prepared in this experiment is endowed with anionic and cationic exchange abilities.

The internal anionic and cationic concentrations of CMM (13.5% water content) are 0.5 and $2M$, respectively. They are higher than the concentration of the salts that naturally occurs in the brine water (0.034 M NaCl). Since there exists a strong interaction between the mobile ions and the water molecules contained in the ion-exchange regions, it is possible to initiate a forced transmembrane flow of a solution whose concentration is similar to the internal concentration of the membrane.[5] Thus a salt enrichment effect occurs that has the characteristics of charge mosaic membrane.

TABLE IV
Properties of the Charge Mosaic membrane

Code of sample	Thickness (mm)	Water content (wt%)	Exchange capacity (mEq/dry g)		Capacity $\gamma = (Q_a/Q_c)$
			Cation (Q_a)	Anion (Q_c)	
H-1-48	0.1	13.5	0.066	0.273	0.26

CONCLUSIONS

From both qualitative and quantitative analyses, it is clear that graft copolymer may be obtained with the method introduced in this report. Transmission electron micrographs indicated that the graph copolymer showed clear microphase separation phenomena. The graft copolymer has the following special features.

1. The styrene-butadiene-styrene triblock copolymer has clear phase separation structure in which the polystyrene phases aggregate to form a domain, the precusor of cationic exchange elements. Polybutadiene undergoes graft copolymerization with 4-vinyl pyridine. Owing to the immiscibility between polystyrene and poly(4-vinyl pyridine), the latter aggregates to form another domain, the precusor of the anionic exchange element. After graft copolymerization, the membrane is cross-linked with cold vulcanization to increase its strength.

2. In the graft copolymer, the cationic and anionic exchange elements are linked together by chemical bonds. This arrangement can overcome the stresses developed on the phase boundaries. The formation of small cracks may be avoided.

3. 4-Vinyl pyridine with a secondary amine group is easily chloromethylated, and the amination step is eliminated.
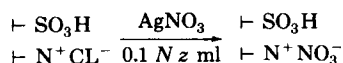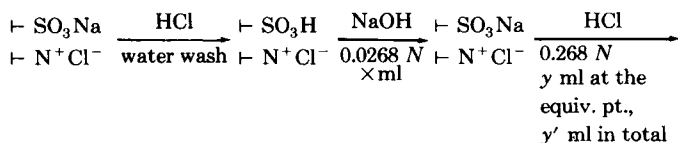
4. The anionic and cationic exchange elements have strong alkaline and acidic exchange groups, respectively.

APPENDIX

Calculations of the Maximum Anionic and Cationic Exchange Capacities

| | | Repeating unit | |
	4-Vinyl pyridine	Styrene	Butadiene
Molecular weight	105.14	104.2	54.1
Weight fraction %	7.88	27.64	64.48
$\dfrac{\text{Mole no. of repeating unit}}{\text{gram copolymer}} \times 10^4$	7.49	26.53	119.19
Max. anionic exchange capacity (mEq per dry gram)	0.749	—	—
Max. cationic exchange capacity (mEq per dry gram)	—	2.653	—

Calculation of Anionic and Cationic Exchange Capacities

$$\begin{array}{c} \vdash SO_3Na \\ \vdash N^+Cl^- \end{array} \xrightarrow[\text{water wash}]{HCl} \begin{array}{c} \vdash SO_3H \\ \vdash N^+Cl^- \end{array} \xrightarrow[\times ml]{NaOH \atop 0.0268\,N} \begin{array}{c} \vdash SO_3Na \\ \vdash N^+Cl^- \end{array} \xrightarrow[\substack{y\ ml\ at\ the \\ equiv.\ pt., \\ y'\ ml\ in\ total}]{HCl \atop 0.268\,N}$$

$$\begin{array}{c} \vdash SO_3H \\ \vdash N^+CL^- \end{array} \xrightarrow[0.1\,N\,z\ ml]{AgNO_3} \begin{array}{c} \vdash SO_3H \\ \vdash N^+NO_3^- \end{array}$$

1. Dry weight of CMM = 0.3926 g
2. Concentration of sodium hydroxide in agueous solution = 0.0268 N (standardized with potassium hydrogen o-phthalate)
3. Concentration of hydrochloric acid = 0.268 N (standardized with sodium carbonate)
4. Concentration of silver nitrate = 0.1 N
5. x = 45 ml
   y = 4.1 ml
   y' = 8 ml
   z = 21.7 ml
6. a = 0.0268 $\times$ − 0.268y
   = 0.107 (mEq)
   b = 0.1z − 0.268y'
   = 0.026 (mEq)
7. Cationic exchange capacity:

$$Q_c = \frac{0.107}{0.3926} = 0.273 \text{ (mEq per dry gram)}$$

Anionic exchange capacity:

$$Q_a = \frac{0.026}{0.3926} = 0.066 \text{ (mEq per dry gram)}$$

Ratio of anionic and cationic exchange capacity:

$$\gamma = \frac{Q_a}{Q_c} = 0.26$$

Thus,

$$\text{Cationic exchange capacity} = \frac{0.107}{0.3926} = 0.273 \text{ (mEq per dry gram)}$$

$$\text{Anionic exchange capacity} = \frac{0.026}{0.3926} = 0.066 \text{ (mEq per dry gram)}$$

$$\%\text{Sulfonation} = \frac{0.273}{2.653} \times 100\% = 10.3\%$$

$$\%\text{Chloromethylation} = \frac{0.066}{0.749} \times 100\% = 8.8\%$$

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