

Preparation and Characterization of Cation-Exchange Media Based on Flexible Polyurethane Foams

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ABSTRACT: Continuous electrodeionization (CEDI) is used to deionize a solution to a level attained by mixed bed ion exchange without chemical regeneration. However, handling of ion-exchange beads is laborious for a large-scale CEDI system. In this study, a new type of ion-exchange polyurethane foam containing sulfonic acid groups was synthesized by bulk condensation polymerization for use as a cation-exchange medium. Polyurethanes are synthesized by the reaction between a diisocyanate and a polyol. Toluene diisocyanate 2,4-80%, 2,6-20% (<http://www.tciamerica.com/>) was reacted with poly(propylene glycol) to synthesize a polyurethane prepolymer and then *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES) was added to give a foam containing sulfonic acid groups. The functional polyurethane prepolymers were characterized by proton nuclear

magnetic resonance spectroscopy (¹H NMR), Fourier transform infrared spectroscopy (FT-IR), elemental analysis (EA), and gel permeation chromatography (GPC). The ion-exchange capacity was measured as 2.5 meq/g, and the equiconductance point of the polyurethane foams were 14, 19, 29, and 33 μ /cm for BES molar ratios of 0.5, 0.7, 1.0, and 1.5, respectively. The porous plug model shows that the current flows dominantly through the solution phase of the polyurethane foam, which indicates the polyurethane foam is a suitable medium for use in a CEDI operation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 1773–1781, 2002

Key words: ion exchangers; electrodeionization; polyurethanes; conducting polymers

INTRODUCTION

Porous polymeric materials with interconnected macrochannels filled with ion-exchange media are currently of major interest for the production of ultrapure water by electrodialysis (ED). ED cannot be economically applied for the treatment of dilute solutions because of their high electrical resistances and the development of polarization phenomena. The concentration polarization limits the amount of electrical current that can be applied and thus increases the necessary membrane area. To overcome this problem, ion-exchange media such as ion-exchange resins, which are more conductive than the solutions to be treated, were introduced into the ion-depleting compartments of an ED stack. These media significantly reduce power consumption because of the decrease of stack resistance while increasing the available surface area for ion exchange. This concept was proposed a long time ago, and various embodiments of the basic idea have been tested by a number of groups.^{1–9} This hybrid separation process combining ion-exchange media and ion-

exchange membranes is known as continuous electrodeionization (CEDI). The process is used to deionize solutions to levels attained by mixed bed ion-exchange resins without chemical regeneration.¹⁰ However, packing the resin beads in the compartment is laborious work to assemble the stack. To overcome this problem, a porous ion-conducting spacer is considered in this study. Polyurethane foam, often used as support matrix, may replace the resin bed if ion-exchange capacity is introduced. Because of their structure, ion-exchange polyurethanes have the following advantages in continuous CEDI applications: convenient handling for a large scale CEDI system, lower fouling by the hydrophobic macroions because of the macroporous structure, and easier storage. Moreover, because of their shape (i.e., in sheets), they provide a good contact surface with ED membranes.

The aim of this study is to develop a method for preparing a cation-exchange media, based on flexible polyurethane foams, which will reduce the electric resistance of the cell in the diluate compartment of the CEDI stack.

In this study, we prepared functionalized polyurethane for cation-exchange media. Flexible polyurethane foams are microcellular structures, produced by gas bubbles formed during the polyurethane polymerization process. These foams are prepared by the con-

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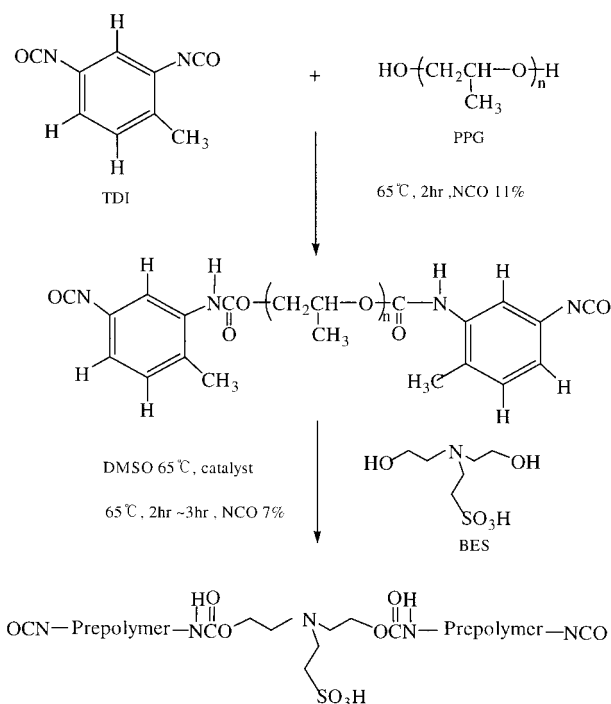


Figure 1 Synthesis of the polyurethane prepolymer containing sulfonic acid groups.

trolled entrapment of an expanding gas during the polymerization. This polymerization involves the formation of urethane linkages between a polyfunctional alcohol, or polyol, which has a hydroxyl functionality, and the polyisocyanate so that the polyurethane forms a crosslinked network.¹¹ The polyurethane foam can be sulfonated with *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid according to the method of Santerre et al.¹²

EXPERIMENTAL

Materials

Poly(propylene glycol) (PPG; $M_n = 1000$; Aldrich Chemical Company) was dried at $100\text{ }^{\circ}\text{C}$ under a vacuum before use. Toluene diisocyanate (TDI; 2,4-80%, 2,6-20%; Tokyo Chemical Industry Company, Ltd.; purity 99.0+%), dimethyl sulfoxide (DMSO; Oriental Chemical Company; purity 99.0+%), *N,N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid (BES; Acros Organics), dibutyltin dilaurate (Aldrich Chemical Company) and L-5614 silicone surfactant (Halla Chemical Company, Ltd.) were used without purification.

Synthesis of polyurethane containing sulfonic acid groups

The procedure for synthesis of polyurethane containing sulfonic acid groups is shown in Figure 1. A four-

necked flask, equipped with a condenser, a mechanical stirrer, a nitrogen inlet adapter, and a dropping funnel, was initially charged with TDI under saturated nitrogen and constant temperature ($70\text{ }^{\circ}\text{C}$) in an oil bath, as shown in Figure 2. PPG was slowly added by dripping, and the reaction was allowed to proceed until the theoretical isocyanate content, 11%, was reached as determined by the di-*n*-butylamine method. A BES solution, dissolved in DMSO at a 55% w/v concentration and at $65\text{ }^{\circ}\text{C}$, was then slowly added to the polyurethane prepolymer followed by the slow addition of dibutyltin dilaurate. The reaction was allowed to proceed until reaching the theoretical isocyanate content of 7%. The prepared polyurethane prepolymer was sealed under a nitrogen atmosphere and stored at $4\text{ }^{\circ}\text{C}$ in the refrigerator.

Preparation of polyurethane foam containing sulfonic acid groups

Polyurethane prepolymer (20 g) was mixed with deionized water (2 g) and L-5614 silicone surfactant (0.24 g) at an agitation speed of 4000 rpm for 7 s. As soon as the blowing was finished, the polyurethane prepolymer was poured into a warm mold and placed in an oven at $45\text{ }^{\circ}\text{C}$ for 6 h.

Ion-exchange polyurethane foams were soaked in distilled water or 2 N NaCl solution to condition them according to preplanned time and temperature. Polyurethane foams require the homogeneous rearrangement of its polymeric bonds through water conditioning because the foam does not experience stress-free conditions after manufacturing. Therefore, the effect of water conditioning was investigated in terms of the conductivity within a flow cell with 0.086 mN NaCl.

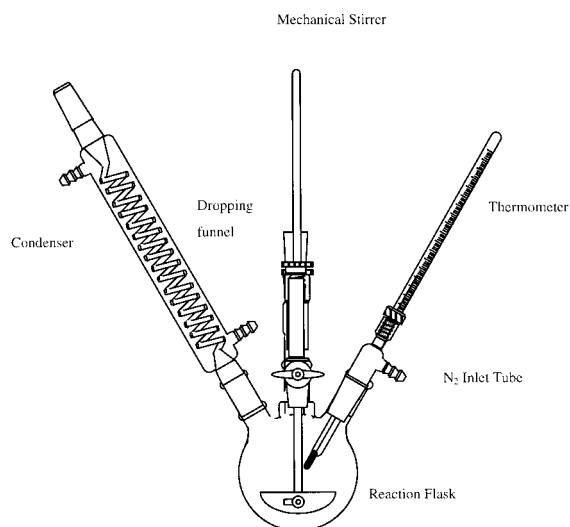


Figure 2 Apparatus for synthesis of the polyurethane prepolymer.

Characterization

Nuclear magnetic resonance (NMR) spectroscopy

Proton (^1H) NMR spectra were measured on a JEOL JNM-LA 300 WB FT-NMR in D_2O , DMSO, or CDCl_3 depending on the solubility of the materials being analyzed. Proton chemical shifts were referenced to tetramethylsilane (TMS) at 0 ppm.

Fourier transform infrared (FT-IR) spectroscopy

The structures of the monomers and synthesized prepolymers were confirmed by FT-IR spectroscopy (Perkin Elmer IR 2000 series). The spectra were recorded at 4 cm^{-1} resolution and measured from 4000 to 400 cm^{-1} using KBr pellets for solid samples and KBr pellets cast with samples for liquid samples under nitrogen at room temperature.

Elemental analysis

Elemental analysis of carbon, hydrogen, oxygen, nitrogen, and sulfur was done with an Elemental Analyzer (FISON, EA 1106/ EA 1108/ EA 1110). The sample size of the foam was 20 mg.

Gel permeation chromatography (GPC)

Molecular weights were analyzed by GPC (WATERS M77251, M510). The mobile phase was HPLC grade tetrahydrofuran (THF). Polymer solutions were 0.2 w/v % in THF and were syringe-filtered through a $0.2\ \mu\text{m}$ Teflon membrane filter. One milliliter of the filtered solution was injected into the chromatograph. The flow rate of the eluent was 1.0 mL/min. From calibration curves of the injected polystyrene standard samples, the number-average molecular weight (M_n) and molecular weight distribution (MWD) of the synthesized prepolymers were determined. Signals from the samples were detected with differences in the refractive index.

Acid-base titration

The degree of sulfonic acid group integration into the polyurethane prepolymer was measured by acid-base titration. Isopropyl alcohol (50 mL) was added to the polyurethane prepolymer (3 g). After the sample was melted, 2–3 drops of phenolphthalein were added to the solution, and this solution was titrated with a 0.05 N NaOH solution.

Ion-exchange capacity

Polyurethane foams containing the sulfonic acid groups were dried in a vacuum oven at 50°C , and their weights were measured. The foam was washed with

deionized water and then immersed in 1 N HCl solution for 1 day to ensure all sulfonic moieties were protonated. The foam was washed with a AgNO_3 solution until AgCl no longer precipitated, and then immersed in a 0.1 N NaOH solution for 1 day to exchange H^+ for Na^+ . A given amount of this solution (50 mL) was titrated with 0.1 N HCl. Phenolphthalein was used as an indicator. The ion-exchange capacity of the foam was calculated using the following equation:

$$\text{IEC} = \frac{\{200\text{ mL} \times 0.1\text{ N (NaOH)}\} - \{4 \times A\text{ mL} \times 0.1\text{ N (HCl)}\}}{W_d} \quad (1)$$

where IEC is the ion-exchange capacity (meq/g), A is the volume of 0.1 N HCl (mL), N is the molar concentration (mol/L), and W_d is the weight of the dried foam (g).

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

The thermal properties of the synthesized prepolymer were determined with a TA instrument 2100 series. Thermal degradation temperatures were measured in the range $30\text{--}800^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under ambient atmospheric conditions. The glass transition temperatures (T_g) of the synthesized prepolymers were also measured in the range $-100\text{--}150^\circ\text{C}$ at a heating rate of $10^\circ\text{C}/\text{min}$ under a pure nitrogen atmosphere.

Swelling ratio and the permeability coefficient

Polyurethane foams, in 1 cm width and 0.4 mm thickness, were immersed into deionized water at room temperature. The weight of the swollen foams was measured at preset times after removing excess water on the foam surface. The swelling ratio was calculated using the following equation:

$$\text{Degree of Swelling} = \frac{(W_s - W_D)}{W_D} \quad (2)$$

where W_D and W_s denote the weights of the dry and swollen polyurethane foams, respectively.

The permeation of deionized water through the polyurethane foams was measured using the permeability coefficient equation:

$$\text{Permeability coefficient} = \frac{(J \times L)}{\Delta P} \quad (3)$$

where J is the flux (i.e., the amount of permeate per unit area), L is the length of the polyurethane foam, and ΔP is the applied pressure.

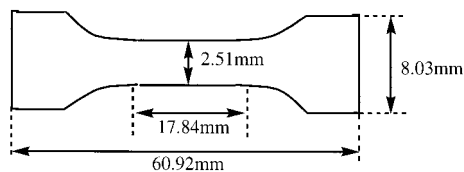


Figure 3 Schematic of the dog bone.

Mechanical properties

A Universal Test Machine (INSTRON) was used to measure modulus, stress, and strain using an ASTM-1822-L, as shown in Figure 3. The thickness of each specimen was 0.5 mm. At least five separate tensile specimens were used for each polyurethane foam sample. The modulus, strain, and stress were obtained at room temperature at a crosshead speed of 25.4 mm/min.

Electric conductivity

A flow cell was used for the measurement of the polyurethane foams electric conductivity when saturated with a solution of sodium chloride. As shown in Figure 4, the foams were placed between a pair of perforated platinum electrodes and flushed with a sodium chloride solution at a desired concentration until equilibrium was reached. The electric conductivity of the ion-exchange polyurethane foam was measured with a LCZ meter (NF electronics) with the flow cell set at 1.5 cm/s. The feed solution was circulated through the flow cell until it reached equilibrium with the packed resin in the flow cell.

The cell constant was calculated using a solution having a known k value. The LCZ meter provides the resistance; R . Therefore, k can be determined from the following equation:

$$R = \frac{1}{k} \frac{l}{A} \quad (4)$$

where, l is the distance between the electrodes, and A is the area of the electrode. If ' k ' is the known value of

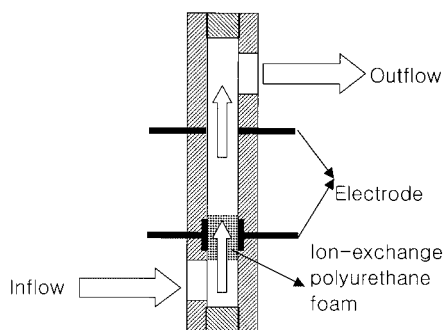
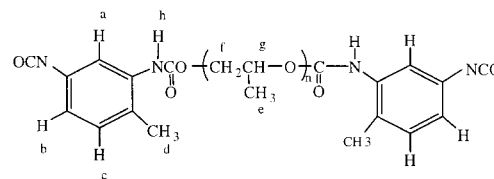


Figure 4 Schematic representation of the flow cell.



a	7.2	f	3.3
b	6.9	g	3.6
c	6.7	h	4.3
d	2.3	Chloroform-d	7.23
e	1.2		

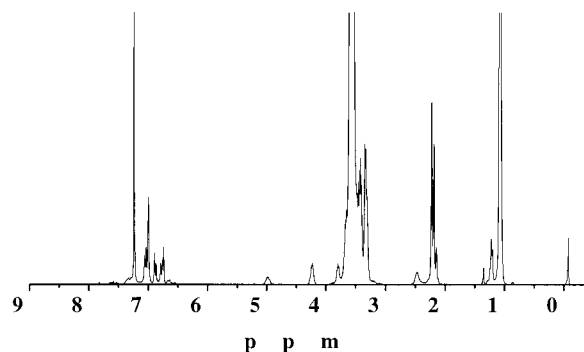


Figure 5 NMR spectrum of the polyurethane prepolymer.

the standard solution of a reference electrolyte, l/A (the cell constant) can be calculated from the observed resistance. When the cell constant is known, the conductivity of any electrolyte can be calculated from its measured resistance using eq. 4. The cell constant of the flow cell was obtained for each electrode pairs with a frequency of either 1 or 100 kHz.

RESULTS AND DISCUSSION

Synthesis of polyurethane prepolymer containing sulfonic acid groups

TDI was reacted with PPG ($M_n = 1000$) via bulk condensation polymerization to form polyurethane prepolymer. The polyurethane prepolymer was characterized by ^1H NMR spectroscopy, FT-IR, and EA. The ^1H NMR spectra of the resulting polyurethane prepolymer are shown in Figure 5. The signal from the NH of urethane bond is apparent at 4.3 ppm. The other peaks are summarized in Figure 5. After confirming the synthesis of the polyurethane prepolymer, BES, dissolved in DMSO and kept at 65°C, was added. FT-IR spectroscopy was employed to confirm that the

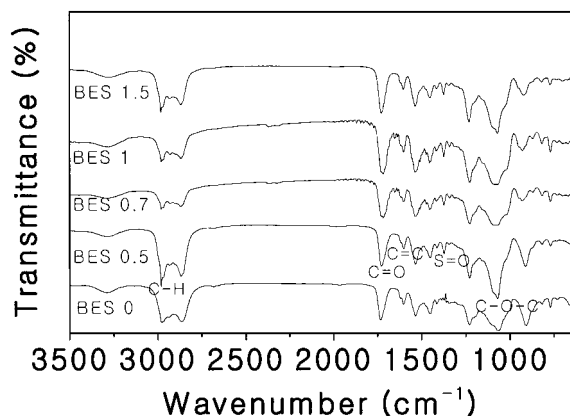


Figure 6 FT-IR spectrum of polyurethane containing sulfonic acid group.

resulting polyurethane contained sulfonic acid groups.

The FT-IR spectrum of polyurethane containing sulfonic acid group is shown in Figure 6. In this figure, BES 0, BES 0.5, BES 0.7, BES 1, and BES 1.5 represent the molar ratios of BES with a constant TDI: PPG ratio of 3:1. In other words, BES 1.5 represents a TDI: PPG: BES ratio of 3:1:1.5. The maximum amount of BES is 1.5 times the PPG in moles. With a mole ratio >1.5 , polyurethane foam was not formed from the prepolymer because of lack of NCO. The O—S—O absorbance peak appears at $\sim 1060\text{ cm}^{-1}$. This peak partially overlaps with the C—O—C band from the polyether soft segment peak at 1100 cm^{-1} . The asymmetrically stretched S=O signal appeared at 1350 cm^{-1} . The NH band ($3000\text{--}3500\text{ cm}^{-1}$) and the hydrogen-bonded NH group appeared at 3286 cm^{-1} . Urethane carbonyl absorbance appears at 1700 cm^{-1} . These results clearly indicate that BES was successfully introduced into the polyurethane prepolymer.

Elemental analysis

The atomic quantity of carbon, hydrogen, oxygen, nitrogen, and sulfur within the polyurethane foam was analyzed with an elemental analyzer and the results are shown in Table I. The measured values agree well with the calculated values based on the materials used

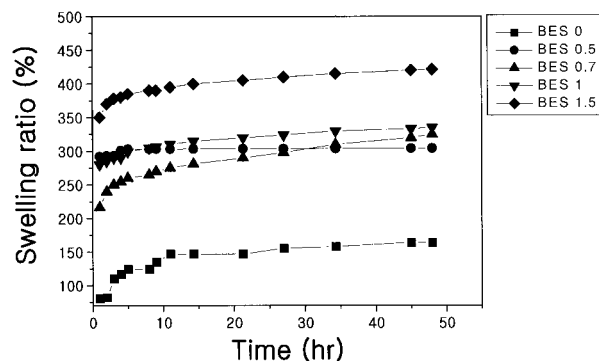


Figure 7 Effect of time and BES ratio on the swelling ratio.

for polymerization. Furthermore, the sulfonic acid content increased as the BES ratio was increased.

Swelling ratio and permeability coefficient

As shown in Figure 7, the swelling ratio increased with a greater amount of BES incorporation because of the hydrophilic characteristics of BES. The foams swelled to only a limited degree (i.e., equilibrium was attained, beyond which swelling did not proceed). Variations in permeability coefficient between BES 0 and BES 1.5 show values from 11.5 to $19.3\text{ l/h} \cdot \text{m} \cdot \text{kPa}$. Permeability through polyurethane foam with BES 1.5 is much greater than that with the other compositions because the higher swelling attained with BES 1.5 foams increases the mobility of the chain segments.

Mechanical properties

The effects of the molar ratio of BES on stress at the maximum load are shown in Figure 8. Stress decreased significantly as the molar ratio of BES increased. As the amount of incorporated BES increased, the strain increased. The effects of the molar ratio of BES on strain at the maximum load are shown in Figure 9. Polyurethane foam containing sulfonic acid groups showed a strain of $>220\%$. The effects of the molar ratio of BES on the modulus are shown in Figure 10. According to the mechanical properties of the polyurethane foams (i.e., low stress, high strain,

TABLE I
Comparison of Theoretical and Measured Values by Elemental Analysis

Sample	Atomic ratio (wt%)									
	Theoretical (calculated)					Measured by elemental analyzer				
	C	H	N	O	S	C	H	N	O	S
BES 0.0	60.6	8.0	5.5	25.0	1.0	60.0	8.6	5.5	24.0	1.2
BES 0.5	58.5	8.0	5.6	26.0	1.9	56.8	8.5	5.1	24.0	2.3
BES 0.7	57.9	8.0	5.6	26.2	2.0	56.4	8.6	5.1	24.4	2.5
BES 1.0	56.9	7.9	5.6	26.9	2.4	55.6	8.6	5.0	24.4	3.8
BES 1.5	55.5	7.8	5.7	27.3	3.5	54.0	8.1	5.1	25.4	3.9

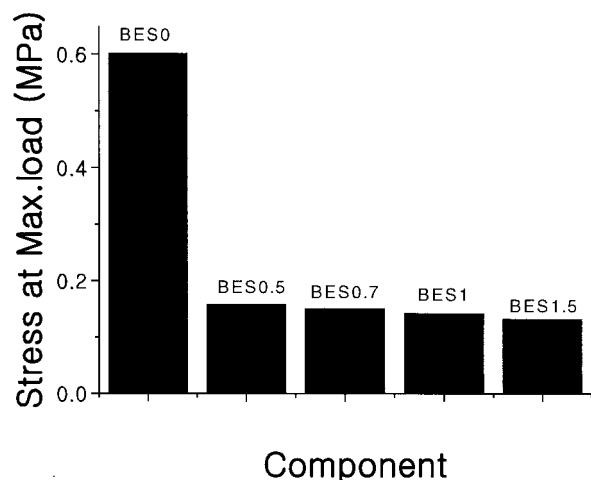


Figure 8 Effect of the molar ratio of BES on the stress at a maximum load.

and low modulus), these foams can be thought of as a flexible plasticizer.

Thermal properties

The thermal stability of the polyurethane prepolymers containing sulfonic acid groups was investigated by TGA at a heating rate of 10 °C/min under ambient atmospheric conditions and the results are presented in Figure 11. The degradation temperatures were 232–237 °C. Polyurethane without a sulfonic acid group, BES 0, was degraded at 258 °C. Addition of BES in polyurethane prepolymer caused a decrease in the stability of the polyurethane foam.

The DSC traces for polyurethane containing sulfonic acid groups are shown in Figure 12. The T_g s were measured by DSC. The lower T_g for the sulfonic acid-containing prepolymer indicates that it has a more phase-separated morphology. This phase separation is enhanced by the greater polarity difference between the sulfonic acid-containing hard segment and soft

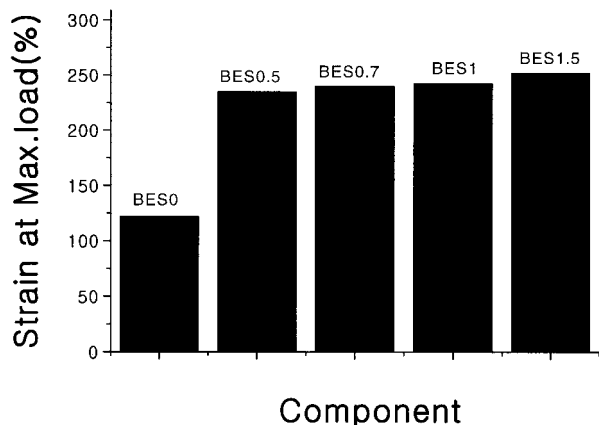


Figure 9 Effect of the molar ratio of BES on %strain at a maximum load.

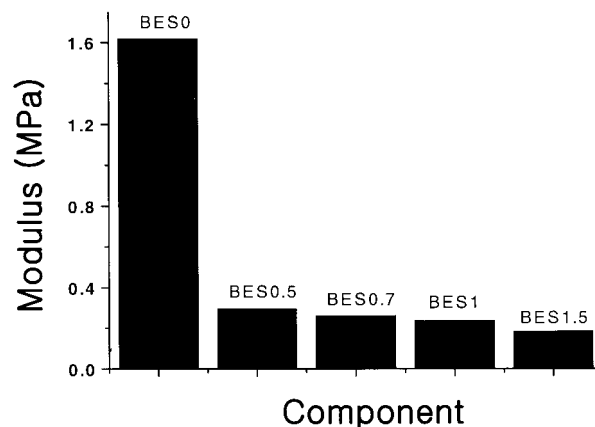


Figure 10 Effect of the molar ratio of BES on the modulus.

segment. As the number of sulfonic acid groups increased, the degree of phase separation initially decreased. At high levels, though, the phase separation increased, with hydrogen bonds providing the driving force, and the resulting morphology was comparable to the unmodified polyurethane. Under these conditions, the urethane groups may have hydrogen bonds with the sulfonic acid groups rather than the urethane carbonyl groups.

Ion-exchange capacity and electric conductivity

The ion-exchange capacity also increased as the number of sulfonic acid groups increased (Table II). The ion-exchange capacity of BES contained polyurethane is lower than that of commercial ion-exchange resins because the amount of addition of sulfonic acid in the polyurethane is limited during the polymerization. Even though the greater content of BES may increase the ion-exchange capacity, the tertiary amine of BES obstructs the reactivity of isocyanate with the hydroxyl group. Also, the foam has a lower capacity

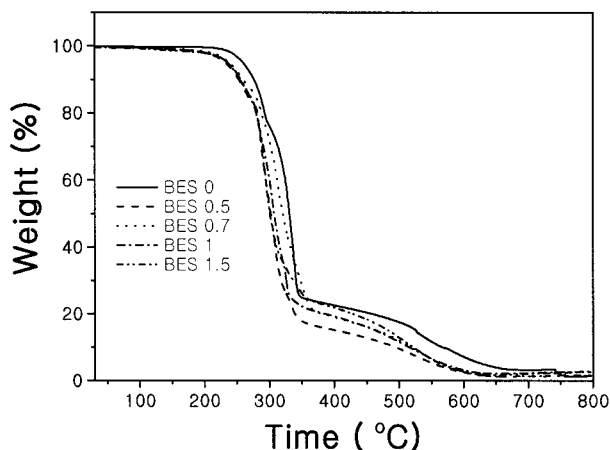


Figure 11 TGA thermograms of the polyurethane foam containing sulfonic acid groups.

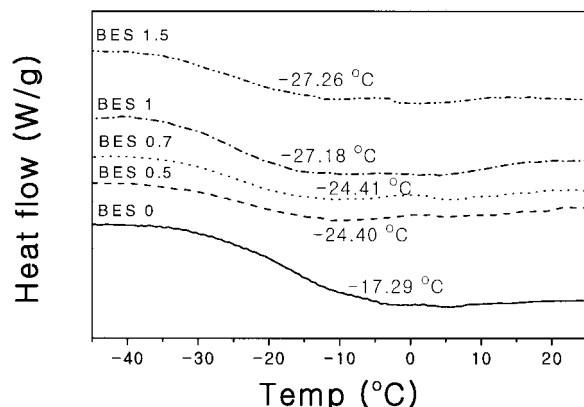


Figure 12 DSC traces for polyurethane containing sulfonic acid groups.

because of a high void volume. The conductivity was measured and BES 1.5 showed the greatest ion-exchange capacity. The conductivity of polyurethane foam was not developed before soaking in hot water, even with ion-exchange capacity.

The conductivity increased eight times after water conditioning, as shown in Table III. This increase was due to the formation of an ion-conducting path as the structure of the polymeric bonds prepared under stress-free conditions. During water conditioning, the effects of the temperature was negligible at temperatures of $\geq 40^\circ\text{C}$. However, conductivity decreased due to degradation of the polymer at 90°C . The optimum condition for water conditioning was to soak for 30 min in deionized water at 40°C . The morphologies before and after water conditioning showed a cavity formed in the treated foam. This cavity formed the ion-conducting path in the insulated polyurethane foam. The swelling pressure of the deionized water was higher than when 2 N NaCl solution was used. Water conditioning with distilled water showed a low specific resistance because of the formation of the large cavity. Also, water conditioning with 2 N NaCl solution resulted in a higher specific resistance due to the formation of a smaller cavity.

Porous-plug model

The flow of electrical current in polyurethane foams is complex because the foams are a mixture of two phases consisting of different properties; namely, polyurethane foam and interstitial liquid. Wyllie suggested an approach for the ion-exchange beds where the distribution of the resin particles constitutes an irregular and discontinuous phase and the liquid is regarded as a continuous one.¹³ The model estimates the electrochemical properties from empirical and geometrical parameters. This "porous-plug" model is based on the principle that the electrical current passes through three different paths within the foams. The first path is alternating layers of foam and interstitial solution, the second is the bridge connecting foam particles or sections that are in contact with each other, and the third is the channel through the interstitial solution (Figure 13). The conductivity of the resin bed is represented by eqs. 5 and 6 in this model:

$$k_b = k_1 + k_2 + k_3 \quad (5)$$

$$k_1 = \frac{ak\bar{k}}{dk + e\bar{k}} \quad k_2 = b\bar{k} \quad k_3 = ck \quad (6)$$

where k_b is the conductivity of the resin bed, \bar{k} is the conductivity of the resin, k is the conductivity of the interstitial solution, k_1 is the conductivity through alternating layers of particles and interstitial solution, k_2 is the conductivity through the resin, and k_3 is the conductivity through the solution.

The geometrical parameters of polyurethane foam can be determined from conductivity data obtained with an electrolyte and plotted as in Figure 13. The specific conductivity \bar{k} of the foam was calculated from the equiconductance point that is, the point where the specific conductivity of the plug and the solution are equal. With \bar{k} determined, the parameters can be calculated from the foam conductivity at $k=0$ and from the slopes of the k_b curve at $k=0$ and $k=\bar{k}$ by use of

TABLE II
Ion-Exchange Capacity

Molar ratio TDI/PPG/BES	Molecular weight			Mol-SO ₃ H/1g PU ($\times 10^{-4}$)		Ion-exchange capacity (meq/g)
	M_n	M_w	M_w/M_n^a	Calc.	Exp. ^b	
3/1/0	2200	2400	1.10	—	—	0
3/1/0.5	2300	2600	1.13	3.07	2.22	1.2
3/1/0.7	2400	2700	1.13	4.19	3.78	1.7
3/1/1	2900	4000	1.38	5.76	5.49	2.1
3/1/1.5	3500	4800	1.37	8.14	7.85	2.5

^a Measured by GPC using a polystyrene standard sample.

^b Measured by acid-base titration.

TABLE III
Electrical Conductivity of Prepared Polyurethane Foams as a Function of Temperature^a

Conditioning time (min)	Conditioning temperature (°C)							
	25		40		60		90	
	I (μs/cm)	II (μs/cm)	I (μs/cm)	II (μs/cm)	I (μs/cm)	II (μs/cm)	I (μs/cm)	II (μs/cm)
0	1.20	1.20	1.20	1.20	1.20	1.20	1.20	1.20
30	9.50	3.04	12.19	4.43	11.98	4.06	11.73	3.68
60	9.52	3.04	12.20	4.44	11.97	4.04	11.74	3.68
120	9.52	3.05	12.21	4.42	11.98	4.05	11.72	3.67
180	9.51	3.03	12.22	4.44	11.97	4.06	11.74	3.66

^a I, Spacer conductivity by conditioning solution (distilled water); II, spacer conductivity by conditioning solution (2 N NaCl).

$$\left(\frac{k_b}{\bar{k}}\right)_{(k=0)} = b \left(\frac{dk_b}{d\bar{k}}\right)_{(k=\bar{k})} = \frac{a}{e} + c \left(\frac{dk_b}{d\bar{k}}\right)_{(k=\bar{k})} = ae + c \quad (7)$$

These relations are obtained from eq. 6 and by differentiation of eq. 5, regardless of the concentration dependence of \bar{k} , and the following relations between the parameters:

$$a + b + c = 1 \quad d + e = 1 \quad (8)$$

Equations 7 and 8 provide five equations for calculating the five unknown parameters.¹⁴

The parameters of the model were estimated in this study to predict the electrochemical properties of the polyurethane foams. The equation for porous-plug model is based on the geometrical configuration of polyurethane foam. The constants a , b , c , d , and e were calculated from the data in Figure 14. These values depend little on the particle size and the nature of the electrolyte. Even though these parameters cannot be compared directly with other ion-exchange media in determining the performance, we can predict the por-

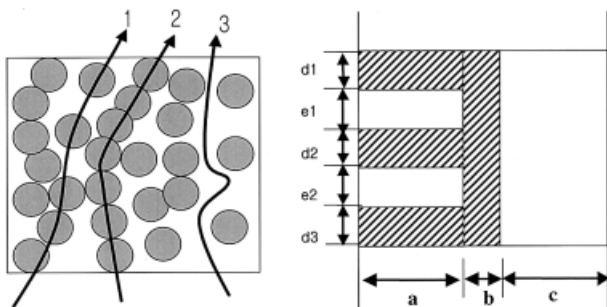


Figure 13 The "porous-plug" model. Left: schematic representation of the three paths that the current can take. Right: the simplified model consisting of three conductance elements in parallel. The geometrical parameters d and e are given by $d1 + d2 + d3 = d$, and $e1 + e2 = e$ (from ref 13).

tion of electric current through the three different paths in the ion-exchange medium.

As shown in Figure 14, the specific conductivities \bar{k} of polyurethane foams were 14, 19, 29, and 33 μs/cm for BES 0.5, 0.7, 1.0, and 1.5, respectively. The results indicate that polyurethane foams made with a BES ratio of 1.5 are electrically more conductive than others when under the influence of an electric potential. Moreover, the value of the equiconductance point allows one to predict the concentration range where the polyurethanes would be efficient in the CEDI process. In a system consisting of a dilute ionic solution in contact with ion-exchange polyurethane foams, ionic transfer driven by an electrical potential will occur almost exclusively through the ion-exchange polyurethane foams and not through the water. The ease of ion transfer will determine the electrical resistivity of the system.

The rectangular configurations for the different polyurethane foams are shown in Figure 15, which illustrates the configuration of ratios between the solid and solution portions of the foam, both horizontally and vertically. In this figure, current flows in the vertical direction. Gray filled blocks account for the solid

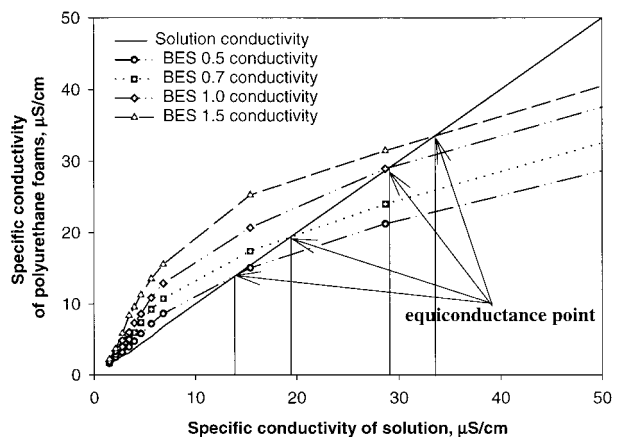


Figure 14 Specific conductivities of polyurethane foams in Co^{2+} or NO_3^- form at equilibrium with $\text{Co}(\text{NO}_3)_2$ solutions.

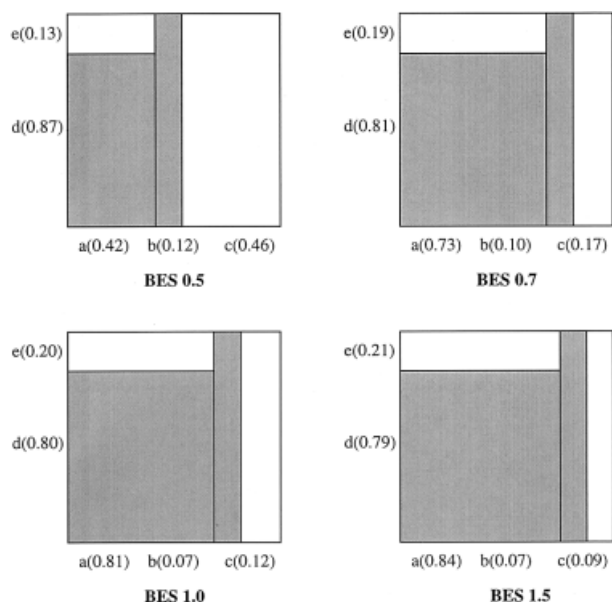


Figure 15 Ratio configuration for conductance through the solid phase and the solution phase (gray blocks are solid phases and white blocks are solution phases).

polyurethane phase and white blocks correspond to the solution phase. From the left, they include transfer through both the solution and solid polyurethane phases, the solid phase, and the solution phase, respectively. In the polyurethane foam made with a BES ratio of 0.5, most of the current flows through the solution phase. The other foams (BES 0.7, BES 1.0, and BES 1.5) show a different trend from BES 0.5, in which most of the current passes through the both the foam and solution phases. Thus, except for BES 0.5, these foams are electrically more conductive than the solutions to be treated. These foams significantly reduce device resistance and increase the available surface area for ion exchange. It is desirable to use such electrically conductive polyurethane foams during CEDI treatment of dilute solutions.

CONCLUSIONS

In this study, polyurethane foams were successfully prepared via bulk condensation polymerization. To synthesize polyurethane prepolymers containing sulfonic acid group, 2,4- and 2,6-TDI and PPG were used. To introduce the sulfonic acid group, BES, which is soluble in DMSO at 65 °C, was added to the isocyanate-terminated polyurethane prepolymer. BES was added up to a 1.5 molar ratio to PPG with a constant diisocyanate mole ratio of 3.

A significant number of sulfonic acid groups were introduced to the polyurethane backbone for application as a cation-exchange media. A tin catalyst was

used because the reactivity of BES with diisocyanate was low. The ion-exchange capacity was measured as 2.5 meq/g. The polyurethane foams were then further studied in terms of their electrical characteristics. From the results it was evident that the polyurethane foam made with a BES ratio of 1.5 is the most conductive polyurethane foam. From the theoretical analyses, the current pattern and the geometric configuration of the polyurethane foams were obtained.

These materials are novel ion-exchange media and show the possibility of new applications of polyurethane foams. Moreover, the combination of a free flowing solution within the device, ease of handling in the field, and use of thin dilute compartments in the stack with the ion-exchange polyurethane foam can make the CEDI system more convenient. Although the capacity of commercialized ion-exchange resins was slightly higher than that of this polyurethane foam, the polyurethane foam-type ion-exchange media may successfully substitute commercial ion-exchange resins. CEDI tests using a preindustrial pilot with polyurethane-type ion-exchange media is currently being investigated.

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