Polymer Electrolyte Membrane with Nanomatrix Channel Prepared by Sulfonation of Natural Rubber Grafted with Polystyrene

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Received 6 August 2010; accepted 10 February 2011
DOI 10.1002/app.34352

ABSTRACT: High-proton-conductive polymer electrolyte with a nanomatrix channel was prepared by graft copolymerization of styrene onto deproteinized natural rubber followed by sulfonation with chlorosulfonic acid. First, natural rubber latex was purified with urea in the presence of surfactant to remove almost all proteins present in the rubber. Second, graft copolymerization of styrene onto deproteinized natural rubber was carried out with *tert*-butyl hydroperoxide/tetraethylenepentamine as an initiator at 30°C in latex stage. The graft-copolymerized natural rubber (DPNR-*graft*-PS) was sulfonated with chlorosulfonic acid in chloroform solution at an ambient temperature. The resulting sulfonated DPNR-*graft*-PS was characterized by FTIR spectroscopy, solid state ^{13}C CP/MAS NMR spectroscopy, elemental analysis, and transmission electron microscopy. High proton conductivity of about 0.1 S/cm, less water uptake of 24 wt % and comparatively good stress at break of 9 MPa were accomplished at suitable contents of styrene units and sulfur, i.e., 32 wt % and 75 mol %, respectively. The high proton conductivity, excellent stability, and good mechanical properties were associated with not only the formation of the nanomatrix channel but also a specific concentration of sulfuric acid group. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 122: 2403–2414, 2011

Key words: nanomatrix channel; graft-copolymerization; deproteinized natural rubber; sulfonation; polystyrene

INTRODUCTION

Polymer electrolyte membrane (PEM) is recognized to be indispensable for a PEM fuel cell to transport protons. Many studies on the proton-transport of the PEM have been performed with perfluorosulfonic acid membrane, which consists of a fluorocarbon backbone containing sulfonic acid groups, due to its outstanding proton conductivity and chemical stability.[1–7] However, some drawbacks of the membrane prevent applying it to the fuel cell as a PEM. For instance, a dramatic decrease in the proton conductivity at high temperature above 140°C has been associated with high water uptake and thermal fluctuation of ion-cluster.[8–10] Furthermore, less fluorocarbon unit content is required for the PEM to suppress destroying an ozone layer of the earth planet, despite high proton conductivity and good chemical stability as well as high mechanical strength.

Sulfonated block copolymer,[11–15] comprising hydrophilic and hydrophobic polymers, has attracted much attention to be an alternative of perfluorosulfonic acid membrane. The good proton transport was attributed to hydrophilic polymer, and the chemical stability and the excellent mechanical strength were to hydrophobic polymer. Cylinder, gyroid, and lamellar structures formed by self-assembly were considered to be useful for the proton-transport. However, recent studies on a morphology-control in nanometer scale for the block-copolymers revealed a limitation of alignment of microphase separated structure, due to a grain boundary of the structures.[16,17] The grain boundary of the sulfonated block copolymer was found to reduce the proton conductivity. To accomplish the high proton conductivity, therefore, it is necessary to form a uniform channel structure for the PEM in nanometer scale.

In the previous work,[18] we proposed a nanomatrix channel as a novel nano-phase separated structure to transport ionic molecules. The nanomatrix channel was formed by sulfonation of polystyrene nanomatrix as a minor component, which linked to natural

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Contract grant sponsor: Monbukagakusho scholarship from the ministry of Education, Science and Culture Japan and Nagaoka University of Technology, Japan.

Journal of Applied Polymer Science, Vol. 122, 2403–2414 (2011)

rubber dispersoid as a hydrophobic major component. The proton conductivity and electrochemical stability of the PEM with the nanomatrix channel were found to be higher than those of perfluorosulfonic acid membrane. Thus, it is quite important to investigate a relationship between the proton conductivity and morphology, to understand a fundamental concept of the effect of the nanomatrix channel structure on the excellent proton conductivity; in other word, it must be clarified whether the completely connecting proton channel as a matrix without any defect in nanometer scale is a necessary requirement for the high proton conductivity or not. Furthermore, an attention has to be paid to investigate a relationship between not only the morphology but also a primary structure and the electrochemical stability, as well as the mechanical strength. The proton conductivity and water uptake may be dependent on a content of the sulfonic acid group; hence, we have to determine a suitable content of the sulfonic acid group.

The nanomatrix channel may be formed by sulfonation[15,19] of polystyrene linking to hydrophobic polymer particle, in which a chemical linkage between polystyrene and the hydrophobic polymer particle is formed by graft-copolymerization of styrene onto the particle. It is necessary that the hydrophobic polymer particle is a naturally occurring carbohydrate, to reduce a carbon emission. In the previous work,[18] we prepare a PEM with nanomatrix channel by sulfonation of natural rubber grafted with polystyrene through the following procedure. First, we prepared deproteinized natural rubber-*graft*-polystyrene (DPNR-*graft*-PS) through graft copolymerization of styrene onto DPNR with *tert*-butyl hydroperoxide (TBHP)/tetraethylenepentamine (TEPA) as an initiator in latex stage.[20–23] Second, the DPNR-*graft*-PS was sulfonated with chlorosulfonic acid to prepare PEM. The morphology observation of the sulfonated DPNR-*graft*-PS by transmission electron microscopy (TEM) revealed that, after sulfonation, cyclized natural rubber particles of about 1.0 μm in diameter were well dispersed into the sulfonated polystyrene matrix of about 80 nm in thickness. In the present work, the resulting DPNR-*graft*-PS is characterized by FTIR spectroscopy, solid state ^{13}C CP/MAS NMR spectroscopy, elemental analysis and transmission electron microscopy (TEM). The primary structure and morphology of the resulting sulfonated DPNR-*graft*-PS is associated to the proton conductivity, electrochemical stabilities and mechanical properties.

EXPERIMENTAL

Materials

Natural rubber latex used in the present study was commercial high-ammonia natural rubber (HA-NR) latex (Golden Hope, Malaysia) of about 60% dry rubber content (DRC). Sodium dodecyl sulfate (SDS: 98%), TBHP and TEPA were purchased from Kishida Chemical Co., Ltd. Chloroform-d (99.8%), chloroform (99%), chlorosulfonic acid (97%), lithium aluminum hydride ($LiAlH_4$) were purchased from Wako Pure Chemical Industry Ltd. Styrene monomer (99%), urea (99.5%), 2-butanone, acetone (99.5%), dichloromethane, potassium iodide, diethyl ether, sodium thiosulfate were purchased from Kanto chemical Co., Inc. Methanol (99.5%), toluene (99.5%), sodium chloride (NaCl: 99.5%), sodium hydroxide (NaOH: 97%) were purchased from Nacalai tesque Inc. Ruthenium tetroxide (RuO_4) was prepared by oxidation of ruthenium (III) chloride hydrate ($RuCl_3 \cdot H_2O$) with sodium hypochlorite solution (NaClO) purchased from Aldrich and Nacalai tesque Inc., respectively.

Deproteinization of natural rubber

Deproteinization of natural rubber was performed by incubation of the natural rubber latex with 0.1 wt % urea in the presence of 1 wt % SDS at room temperature for 1 h followed by centrifugation at 10^4 rpm. The cream fraction after centrifugation was redispersed in 0.5 wt % SDS solution to make 30 wt % DRC latex and it was washed twice by centrifugation to prepare deproteinized natural rubber (DPNR) latex. The DRC of the DPNR latex was adjusted to 30 wt % with distilled water and SDS was added up to 0.1 wt %.

Graft-copolymerization

Graft-copolymerization of DPNR latex was carried out with styrene as a monomer, using TBHP/TEPA as an initiator. DPNR latex was charged with N_2 gas for an hour at 30°C. The initiator and monomer were added in turn to the latex, respectively. The reaction was carried out by stirring the latex at about 400 rpm for 5 h at 30°C. The un-reacted styrene was removed by using a rotary evaporator under reduced pressure. The as-cast film of the graft copolymer (DPNR-*graft*-PS) was prepared by casting the gross polymer latex into a petridish and it was dried under reduced pressure at ambient temperature for more than a week. The as-cast film was extracted with acetone/2-butanone 3 : 1 mixture in a soxhlet apparatus under nitrogen atmosphere in the dark and dried under reduced pressure for a week, in which the removal of almost all free-polystyrene, isolated from the graft copolymer, was completed by the extraction for 24 h.

Ozonolysis

Ozonization was carried out by blowing an equimolar amount of ozone in ozonated oxygen through a

0.4 w/v % methylene chloride solution of the extracted graft-copolymer at 30°C. Reductive degradation of the resulting ozonide was performed by reaction with $LiAlH_4$ in diethyl ether solution followed by decomposition of residual $LiAlH_4$ with water. After reductive degradation, PS, thus isolated from graft copolymer, was dissolved into a small amount of chloroform. The chloroform solution was centrifuged, and the polymer was precipitated with methanol.

Sulfonation

Sulfonation of DPNR-*graft*-PS was performed by the following procedure. The DPNR-*graft*-PS film (32 wt % of polystyrene or styrene feed of 5.5 mol/kg-rubber with 20×10^{-5} mol/g-rubber) of 5×5 cm^2 was immersed in chloroform for 5 min until swollen. The sulfonation of the DPNR-*graft*-PS was carried out with a solution of 0.2, 0.4, 0.8, 1.0, and 2.0*N* chlorosulfonic acid in chloroform at 30°C for 5 h. After completion of the sulfonation, the resulting membrane was immersed into methanol for 30 min, followed by washed several times with ion-exchange water until water was neutral. The resulting sulfonated DPNR-*graft*-PS was dried under reduced pressure at 50°C. Before characterizations of the sulfonated DPNR-*graft*-PS the membranes were acidified with 0.5*M* H_2SO_4 solution at 80°C for 1 h and rinsed with water. Then, they were boiled with ion exchange water at 80°C for 1 h, twice, followed by dried under reduced pressure at 50°C for a week.

Instrumentation and characterization methods

Measurements of molecular weight of the ozonolysis-product were made with a TOSOH GPC, consisting of a TOSOH CCPD pump, RI-8012 Differential Refractometer, and UV-8011 UV detector. The measurement was made at 30°C and the flow rate of the mobile phase, THF, was 0.5 mL/min.

Solid state ^{13}C CP/MAS NMR measurement was carried out with a JEOL ECA-400 NMR spectrometer at room temperature with spin rate of 7 kHz, scan time of 1000 scans, and contact time of 5 s. Hexamethylbenzene was used as an external standard (17.3 ppm). The samples were crushed by JFC-300 cryogenic sample crusher before the measurement.

Differential scanning calorimetry (DSC) measurements for the samples were performed with a SII SSC/5200 DSC 220 differential scanning calorimeter (Seiko instruments, Japan) at a constant heating rate of 10°C/min between temperature range of −120 to 200°C. Before DSC measurement, the samples were annealed at 150°C for 10 min, and then quenched in liquid N_2.

The gel content of samples was measured by soaking 0.16 g of the sample in 80 g of toluene for a week and then passing the solution through a wire mesh. The weight of gel remaining on the mesh was weighed after drying under reduced pressure at 50°C. The gel content was calculated from the following equation:

$$\%\text{Gel content} = \frac{W_{\text{dry gel}}}{W_{\text{dry rubber}}} \times 100 \tag{1}$$

where $W_{\text{dry gel}}$ is the weight of dry gel and $W_{\text{dry rubber}}$ is the weight of dry rubber before determination of gel content.

Sulfur content of the samples was determined by elemental analysis (YANACO MT-6 and MSU-32 microanalyzers). The sulfur content was estimated as follows:

$$\text{Sulfur content(wt\%)} = \frac{\text{mol of sulfur}}{\text{mol of styrene}} \times 100 \tag{2}$$

Water uptake of the samples was determined by the following method. The membranes were soaked in water at room temperature for a week to reach the saturated point of the membrane. Water-droplets on the surface of swollen membranes were removed by wiping with tissue paper. The weight of the swollen membranes was measured, and the water uptake was calculated through the following equation:

$$\text{Water update(wt\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{3}$$

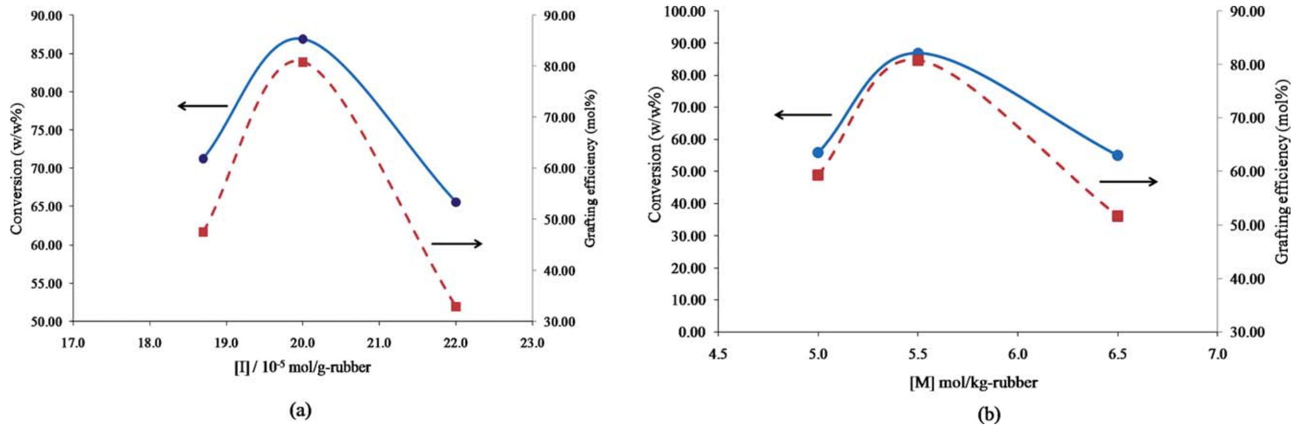
where W_{wet} is the weight of swollen membrane and W_{dry} is the weight of the dry membrane.

Ion exchange capacity (IEC) of the samples was determined by titration. The samples were immersed in 2*N* NaCl solution for a week to replace H^+ to Na^+ ions. The H^+ ions in the solution were titrated with 0.1*N* of NaOH solution in the present of phenolphthalein as an indicator. The IEC (meq/g) was calculated through the following equation:

$$\text{IEC(meq/g)} = \frac{N_{\text{NaOH}} V_{\text{NaOH}}}{W_d} \tag{4}$$

where N_{NaOH}, V_{NaOH}, and W_d are the normality of NaOH, the volume of NaOH solution consumed in the titration, and the weight of dry membrane (g), respectively.

Proton conductivity was measured with a Solartron SI 1260 impedance/gain-phase analyzer and potentiostat (Solartron SI 1287 electrochemical interface) in a range of the frequency between 10 mHz and 10^6 Hz at AC voltage amplitude of 10 mV at room temperature. The membranes were hydrated by immersion in ion-exchange water for 3 h before measurement. The conductivity (σ) of the membranes was calculated as follows:



(a) (b)

Figure 1 Conversion and grafting efficiency of styrene versus (a) initiator concentration and (b) monomer concentration for DPNR-*graft*-PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\sigma = \frac{d}{RA} \tag{5}$$

where d is the sample thickness, R is the membrane resistance, and A is surface area of the membranes.

Two-dimensional observations of morphology for the samples were made with a transmission electron microscope (TEM), JEOL JEM-2100 at accelerating voltage of 200 kV. The ultra thin sections for the TEM experiments were prepared with a microtome (Ultracut N, Reichert-Nissei FC S) between −40 and −90°C. The thin sections with the thickness of about 100 nm were stained with RuO_4 at room temperature for 1 min.

The tensile properties of the samples were measured by 3365Q5414 Instron universal tester. The crosshead rate was 500 mm/min.

RESULTS AND DISCUSSION

Graft-copolymerization

It is necessary to accomplish high conversion and grafting efficiency of styrene, as well as large amount of styrene units, to completely cover the natural rubber dispersiod with polystyrene. Figure 1(a) shows the conversion and grafting efficiency of styrene versus initiator concentration, at a styrene-feed of 5.5 mol/kg-rubber. The conversion of styrene and the grafting efficiency were estimated as follows:

$$\text{Styrene conversion}(\%) = \frac{\text{Weight of polystyrene in gross polymer} \times 100}{\text{Feed of styrene}}$$

$$\text{Grafting efficiency}(\%) = \frac{\text{Mole of polystyrene linked to natural rubber} \times 100}{\text{Mole of polystyrene produced during graft copolymerization}}$$

where the weight of polystyrene in the gross polymer and the feed of styrene were determined by gravimetric method. The conversion and grafting efficiency of styrene were dependent upon initiator concentration ([I]), and their values were maxima at 20×10^{-5} mol/g-rubber of initiator concentration. The smaller values of the conversion and grafting efficiency at low initiator concentration may be explained to be due to a deactivation of radicals, in which the number of active sites on the dispersoid is too small to react with all styrene. In contrast, at high initiator concentration, the number of active sites on the dispersoid is so large that a chain transfer occurs. Figure 1(b) shows a plot of the conversion and grafting efficiency of styrene versus styrene concentration ([M]), at the initiator concentration of 20×10^{-5} mol/g-rubber. The conversion of styrene and the grafting efficiency were also dependent upon the feed of styrene, in which the maxima were achieved at 5.5 mol/kg-rubber of the styrene concentration. Consequently, the suitable initiator concentration and styrene-feed condition for the high conversion and grafting efficiency were found to be 20×10^{-5} mol/g-rubber and 5.5 mol/kg-rubber, respectively, at which the conversion of styrene and the grafting efficiency were 85 wt % and 81 mol %. In this case, the highest styrene content was 32 wt %, as shown in Table I, which was quite higher than 12 wt % at 3.3×10^{-5} mol/g-rubber of initiator concentration and 1.5 mol/kg-rubber of styrene-feed, reported in the previous article.[20,21,23]

TABLE I
***Tg*, Gel Content, Grafting Efficiency, Styrene Conversion, and Styrene Content of Graft Copolymerization of DPNR with 5.5 mol/kg-Rubber of Styrene Concentration**

Sample	[Styrene] mol/kg-rubber	$\overline{M_n}/10^4$ g/mol	$\overline{M_w}/10^4$ g/mol	$\frac{\overline{M_w}}{\overline{M_n}}$	T_g°C	Gel content (wt %)	Grafting efficiency (mol %)	Styrene conversion (wt %)	Styrene content (wt %)
DPNR-*graft*-PS	5.5	1.0	1.2	1.2	−61.0	50.9	80.8	85.4	32.0

Morphology

In the previous work,[18] a hierarchical phase-separated structure of the DPNR-*graft*-PS containing 32 wt % styrene units was observed by TEM, in which the DPNR dispersoids of about 1 μm in average diameter were well dispersed in the polystyrene matrix composed of the particles of about 60 nm in average diameter. In the present work, we prepared PEM from the DPNR-*graft*-PS containing 32 wt % styrene units. Figure 2 shows TEM images for the DPNR-*graft*-PS containing 32 wt % styrene units after sulfonation with various amounts of chlorosulfonic acid. The ultra thin sections were stained with RuO_4. As for the DPNR-*graft*-PS sulfonated with 0.2*N* chlorosulfonic acid, the polystyrene particles of about 60 nm in average diameter individually existed in the nanomatrix, as in the case of the DPNR-*graft*-PS as a source, in which the bright domains represent DPNR and the gloomy domains represent polystyrene [Fig. 2(a)]. This may be attributed to the 0 mol % sulfur of the sulfonated DPNR-*graft*-PS, due to the less amount of chlorosulfonic acid for the sulfonation; that is, the sulfonation did not occur. The polystyrene particles, itself, remained in its shape. When the amount of chlorosulfonic acid was 0.4*N*, the polystyrene particles fused slightly to each other in the nanomatrix [Fig. 2(b)]. Since the DPNR-*graft*-PS, sulfonated with 0.4*N* chlorosulfonic acid, contained about 2 mol % sulfur, both affinity of polar groups and interaction of sulfonated polystyrene are expected to play an important role in the formation of the continuous nanomatrix. The formation of the continuous nanomatrix was quite

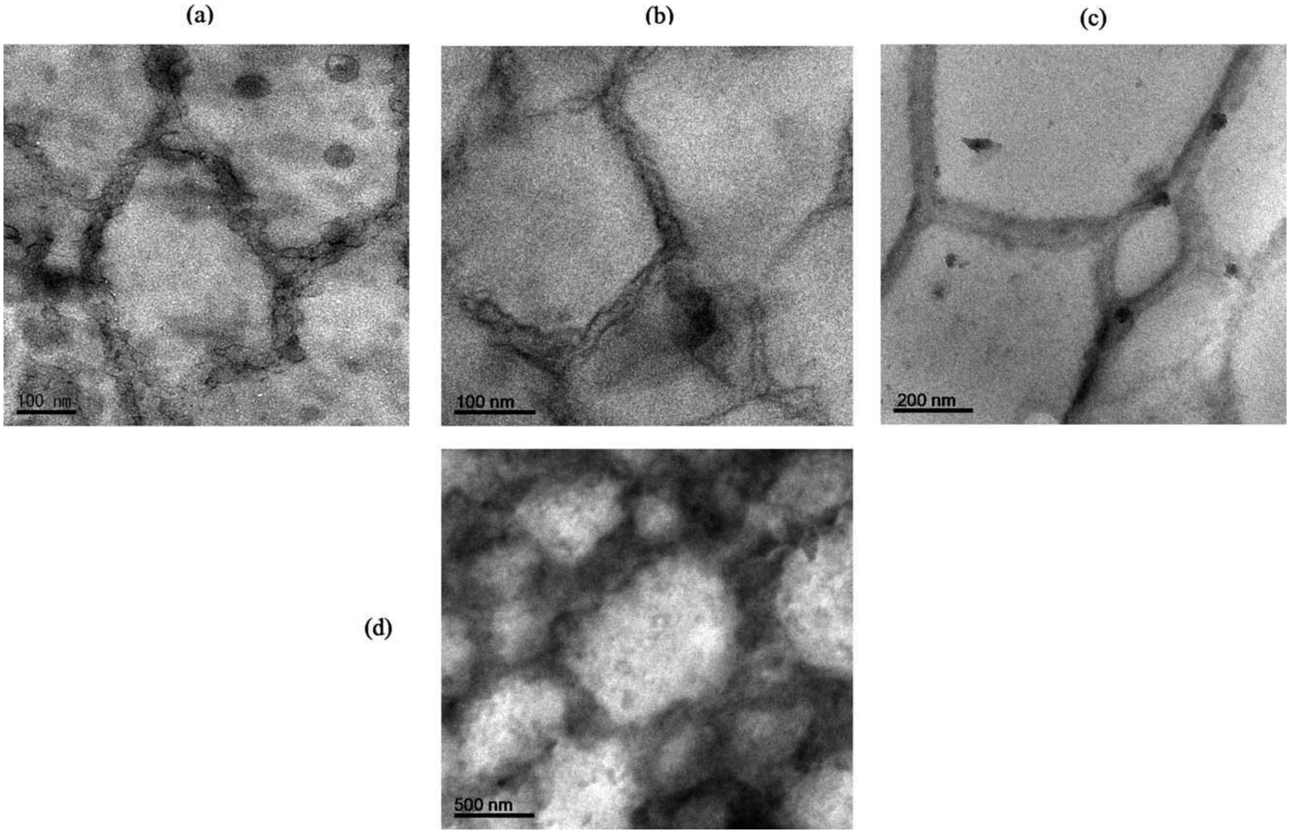


Figure 2 TEM images for DPNR-*graft*-PS sulfonated with (a) 0.2, (b) 0.4, (c) 0.8, and (d) 2.0*N* $ClSO_3H$ at 30°C for 5 h. The ultra thin section of about 100 nm in thickness was stained with RuO_4 at room temperature for 1 min, in which bright domains represent natural rubber and gloomy domains represent the PS.

remarkable when the amount of chlorosulfonic acid was 0.8*N* [Fig. 2(c)], in which the nanomatrix was completely connected to each other. Thickness of the connected nanomatrix was about 80 nm, which was a little bit thicker than the average diameter of the DPNR-*graft*-PS, i.e., 60 nm.[18] This may be explained to be due to the fusion of the polystyrene particles gathering in the nanomatrix to form the completely connected nanomatrix, where the PS particles are dissolved into chloroform solution with chlorosulfonic acid. Since almost all polystyrene in the nanomatrix may be converted to the sulfonated polystyrene containing a phenyl group substituted with a sulfonic acid group, the nanomatrix becomes a nanomatrix channel to transport ion, i.e., proton, in which the interface between the bright and gloomy domains was very clear. In contrast, when the amount of chlorosulfonic acid was 2.0*N*, a rugged nanomatrix was formed in the sulfonated DPNR-*graft*-PS, in which thickness of the nanomatrix was about 100 nm. The rugged nanomatrix may come from incomplete dissolution of polystyrene into chlorosulfonic acid/chloroform solution, due to hydrophilic nature of the solution. Consequently, the amount of chlorosulfonic acid was found to be a key factor to control the morphology of the sulfonated DPNR-*graft*-PS.

Molecular weight distribution for deproteinized natural rubber grafted with polystyrene

Average molecular weights of polystyrene linking to DPNR were determined by size-exclusion chromatography, after ozonolysis of the DPNR-*graft*-PS, since all carbon–carbon double bonds were cleaved by ozonization followed by reduction.[21,23,24] The chemical structures of the grafted DPNR after ozonolysis were confirmed by ^{1}H-NMR spectroscopy in our previous work.[23] Table I shows number average molecular weight, $\overline{M_n}$, weight average molecular weight, $\overline{M_w}$, and polydispersity index, $\overline{M_w}/\overline{M_n}$ of polystyrene obtained from the DPNR-*graft*-PS. The values of $\overline{M_n}$, $\overline{M_w}$, and $\overline{M_w}/\overline{M_n}$ were 1.0×10^4 g/mol, 1.2×10^4 g/mol, and 1.2, respectively. These are quite low compared with the values of $\overline{M_n}$, $\overline{M_w}$, and $\overline{M_w}/\overline{M_n}$ of polystyrene, which is solely polymerized by ordinary emulsion polymerization. The lower values of $\overline{M_n}$, $\overline{M_w}$, and $\overline{M_w}/\overline{M_n}$ may be associated with interactions of the radicals with *cis*-1,4-isoprene units and the vitrification of polystyrene during polymerization.

From the value of $\overline{M_n}$, we estimated a radius of gyration (R_g)[25] of polystyrene and the number of polystyrene included in polystyrene dispersoid. R_g of polystyrene can be calculated as following:

$$R_g = \left(\frac{1}{6}a^2N\right)^{\frac{1}{2}}$$

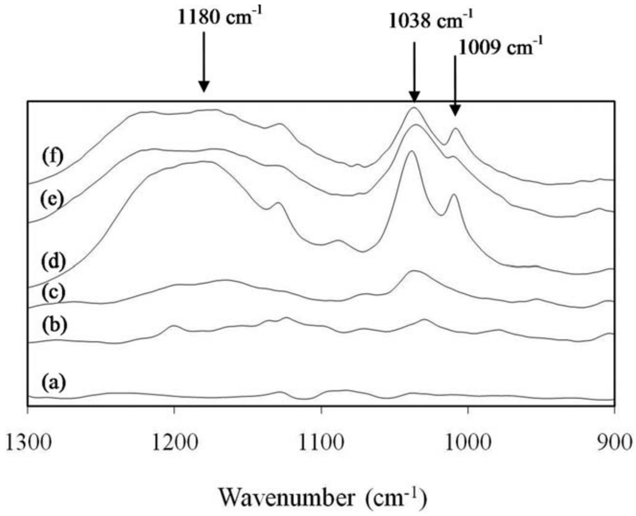


Figure 3 FTIR spectra for (a) DPNR-*graft*-PS and sulfonated DPNR-*graft*-PS prepared from 32 wt % PS with (b) 0.2, (c) 0.4, (d) 0.8, (e) 1.0, and (f) 2.0*N* $ClSO_3H$.

where *a* is the statistical segment lengths for polystyrene (0.68 nm)[26] and *N* is degree of polymerization of polystyrene. The estimated value of the radius of gyration of polystyrene was 2.8 nm. The volume of polystyrene particles (*V*) is estimated by the following expression:

$$V = \frac{4}{3}\pi R_g^3$$

Since the average diameter of the polystyrene dispersoid was about 60 nm, the volume of grafted polystyrene was about 1.1×10^5 nm^3. Assuming that the DPNR particles are surrounded by the polystyrene particles, the number of grafted polystyrene per polystyrene particle, which was estimated from the volume of grafted polystyrene per the volume of polystyrene particles, was 1230 molecules. Thus, we may estimate the number of sulfonic acid ($-SO_3H$) groups per unit volume from the number of repeating units per chain, the conversion of sulfonation and the number of polystyrene per polystyrene particle. The estimated value of the number of $-SO_3H$ per unit volume was 8.9×10^4 molecules (nm^{-3}).

Characterization of sulfonated DPNR-*graft*-PS

Figure 3 shows FTIR spectra for the DPNR-*graft*-PS and the sulfonated DPNR-*graft*-PS, which were sulfonated with the various chlorosulfonic acid concentrations. After sulfonation with 0.8, 1.0, and 2.0*N* chlorosulfonic acid, absorbance peaks appeared at 1180 and 1038 cm^{-1} that were identified to S=O asymmetric and symmetric stretching vibrations of the sulfonated polystyrene, respectively, while the characteristic absorption peak appeared at 1009 cm^{-1} that was

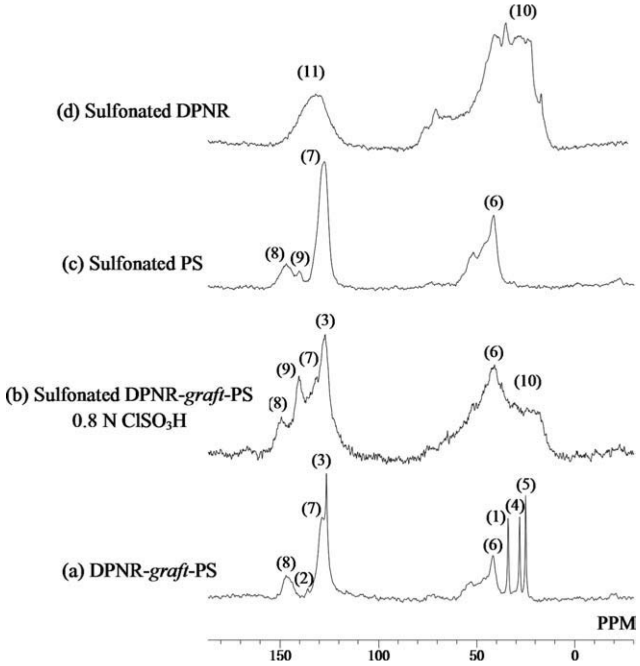


Figure 4 ^{13}C CP/MAS NMR spectra for (a) DPNR-*graft*-PS, (b) sulfonated DPNR, (c) sulfonated PS, and (d) sulfonated DPNR-*graft*-PS prepared from 32 wt % PS with 0.8*N* $ClSO_3H$.

identified to in-plane bending vibration of *para*-substituted aromatic ring of the sulfonated polystyrene.[12] This suggests that the sulfonic acid groups are incorporated into styrene units of the DPNR-*graft*-PS, after sulfonation with chlorosulfonic acid.

Figure 4 shows ^{13}C CP/MAS NMR spectra for (a) DPNR-*graft*-PS, (b) sulfonated DPNR-*graft*-PS, (c) sulfonated PS, and (d) sulfonated DPNR. As for the DPNR-*graft*-PS, signals at 24.1, 27.3, and 33.1 ppm characteristic of methyl and methylene carbon atoms of *cis*-1,4-isoprene units are shown in the ^{13}C CP/MAS spectrum [Fig. 4(a)], which are marked as, (5), (4), and (1) in the proposed structure of the DPNR-*graft*-PS [Fig. 5(a)], respectively. The other signals at 126.0 and 135.5 ppm were assigned to C=C of *cis*-1,4-isoprene units, as marked as (3) and, (2) respectively. Furthermore, three signals appeared at 40.8 ppm (6), 128.1 ppm (7), and 146.5 ppm (8), respectively, which were assigned to aliphatic carbon of methylene group and aromatic carbons of styrene unit, respectively. The small signal at 128.1 ppm for the aromatic carbon of the styrene unit (7) appeared to overlap with the signal of unsaturated methane and quaternary carbons of *cis*-1,4-isoprene units at 126.0 ppm (3) and 135.5 ppm, (2) respectively. Values of half width and signal-to-noise (S/N) ratio of the signal at 24.1 ppm were 24.1 Hz and 18.2, respectively.

After sulfonation [Fig. 4(b)], new signals appeared. In olefinic region, a new signal of 497.8 Hz in half width appeared at 140.0 ppm (9), which overlapped with the signals at 130.8 ppm (7) and 148.8 ppm (8). The proposed structure of the sulfonated DPNR-*graft*-PS is shown in Figure 5(b). The signal at 140.0 ppm (9) is, thus, expected to be associated to the resulting functional groups after sulfonation. In contrast, in aliphatic region, very broad signals (10) appeared, ranging from 10 ppm to 80 ppm, reflecting that many signals overlapped with each other. The signals at 24.1, 27.3, 33.1, and 40.8 ppm may, perhaps, be included in these broad signals. To assign the signals (9) and (10), shown in Figure 4(b), we prepared sulfonated PS and sulfonated DPNR as a model. ^{13}C CP/MAS NMR spectra for the sulfonated PS and the sulfonated DPNR are shown in Figure 4(c,d). As for the sulfonated PS [Fig. 4(c)],

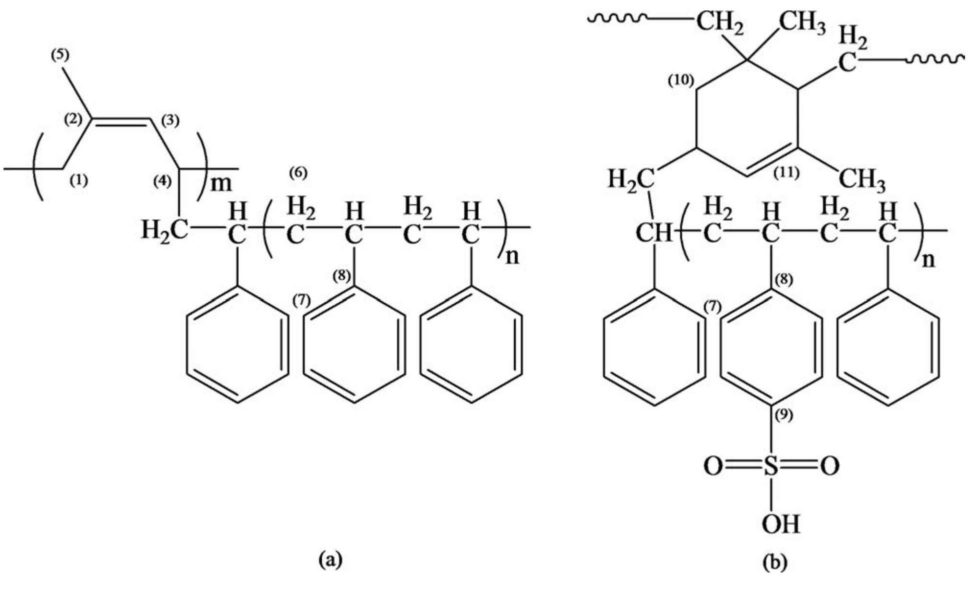


Figure 5 Proposed structures of (a) DPNR-*graft*-PS and (b) sulfonated DPNR-*graft*-PS.

TABLE II
***Tg*, Gel Content, Sulfur Content, and Electrochemical Properties of Sulfonated DPNR-*graft*-PS, Sulfonated PS, and Nafion®117**

Sample	Chlorosulfonic acid (*N*)	Solvent	T_g (°C)	Gel content (wt %)	Sulfur content (mol %)	IEC (meq/g)	Conductivity (S/cm)	No. SO_3H per unit volume (cm^{-3})	Water uptake (wt %)
DPNR-*graft*-PS	0.0	–	−60.4, 103.1	50.9	0	0.00	–	0	0.0
DPNR-*graft*-PS	0.2	$CHCl_3$	79.9, 108.8	75.4	0	0.00	3.0×10^{-5}	0	0.8
DPNR-*graft*-PS	0.4	$CHCl_3$	80.4, 110.6	88.6	2	0.16	4.7×10^{-5}	6.3×10^{18}	5.7
DPNR-*graft*-PS	0.8	$CHCl_3$	83.3, 154.6	90.4	75	2.43	9.5×10^{-2}	2.4×10^{20}	24.3
DPNR-*graft*-PS	1.0	$CHCl_3$	84.1, 166.4	100.0	97	3.71	1.0×10^{-1}	3.1×10^{20}	240.0
DPNR-*graft*-PS	2.0	$CHCl_3$	84.6, 166.6	93.0	100	3.89	2.7×10^{-1}	3.2×10^{20}	396.0
Sulfonated PS	0.8	$CHCl_3$	157.3	81.0	100	1.50	3.2×10^{-2}	1.2×10^{16}	340.0
Sulfonated DPNR	0.8	$CHCl_3$	96.8	–	–	–	–	–	–
Nafion®117	–	–	169.2	90.6	–	1.02	8.0×10^{-2}	7.2×10^{20}	18.6

three signals characteristic of styrene group appeared at 40.6 ppm (6), 127.3 ppm (7) and 146.5 ppm (8), which were assigned to methylene carbon and phenyl carbons of styrene units, respectively. Furthermore, a new signal appeared at 139.8 ppm (9). According to the previous literatures,[27,28] the signal at 139.8 ppm was assigned to aromatic carbon linking to sulfonic acid groups. Based upon the assignment of the sulfonated PS, we assigned the signal at 140.0 ppm in the spectrum [Fig. 4(b)] for the sulfonated DPNR-*graft*-PS to aromatic carbon linking to sulfonic acid group. In contrast, for the sulfonated DPNR [Fig. 4(d)], two overlapped broad signals appeared: one being between 10 ppm and 80 ppm and the other between 110 ppm and 155 ppm. The broad signals may be explained to be due to a presence of complicated structural units in the resulting polymer after sulfonation of the DPNR. According to the previous study,[29] the overlapped broad signals in aliphatic region ranging from 10 ppm to 50 ppm were assigned to methyl and methylene carbons of cyclized *cis*-1,4-isoprene units, and the overlapped signals in olefinic region ranging from 110 ppm to 155 ppm were assigned to olefinic methine and trisubstituted carbons. The cyclization of the DPNR was supported by high temperature shift in glass transition temperatures (T_g) and increase in gel contents, as shown in Table II. The cyclization may concretize the nanomatrix channel of the sulfonated DPNR-*graft*-PS.

Figure 6 shows expanded olefinic region of ^{13}C CP/MAS NMR spectra for (a) DPNR-*graft*-PS and DPNR-*graft*-PS sulfonated with (b) 0.2, (c) 0.4, (d) 0.8, (e) 1.0, and (f) 2.0*N* chlorosulfonic acid. Before sulfonation [Fig. 6(a)], two sharp signals at 126.0 ppm (3) and 135.5 ppm (2) and two broad signals at 128.1 ppm (7) and 146.5 ppm (8) appeared, which were assigned in Figure 4. After sulfonation of the DPNR-*graft*-PS with 0.2*N* chlorosulfonic acid, the signals at 126.0 ppm, (3) 128.1 ppm (7) and 135.3 ppm (2) overlapped with each other to make a broad signal of 543.4 Hz in half width between 120 ppm and 140 ppm (12). When we use 0.4*N* chlorosulfonic acid, the half width of the signal (12) increased to 706.0 Hz and the small shoulder appeared between 110 and 120 ppm, which overlapped with the broad signal (12). Further increase in the amount of

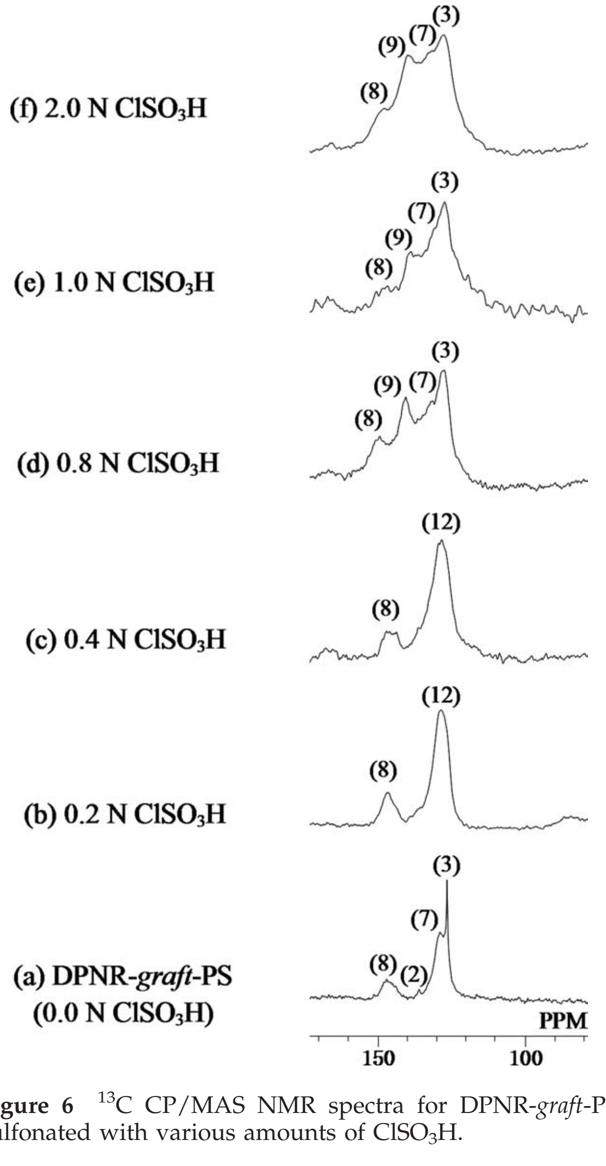


Figure 6 ^{13}C CP/MAS NMR spectra for DPNR-*graft*-PS sulfonated with various amounts of $ClSO_3H$.

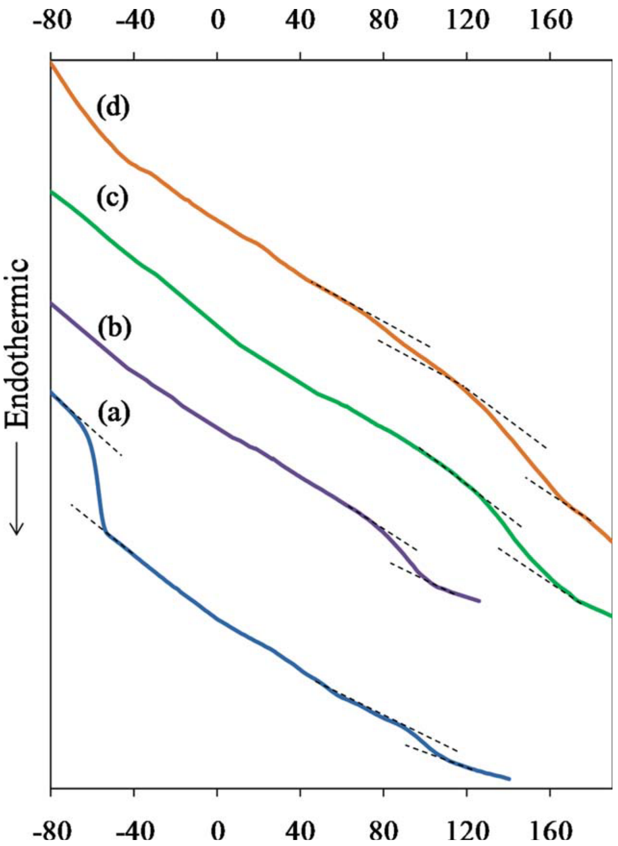


Figure 7 DSC thermograms of (a) DPNR-*graft*-PS, (b) sulfonated DPNR, (c) sulfonated PS, and (d) DPNR-*graft*-PS sulfonated with 0.8*N* $ClSO_3H$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chlorosulfonic acid, i.e., 0.8, 1.0, and 2.0*N*, dramatically changed the feature of the spectra ranging from 110 to 150 ppm. It became the same as the signals shown in Figure 4(b). In addition, an overlapped broad signal (9) appeared between 115 and 155 ppm, which was assigned to aromatic carbon linking to sulfonic acid groups. Consequently, we determined that a critical concentration of chlorosulfonic acid was 0.8*N* for sulfonation of styrene units and cyclization of the DPNR.

DSC analysis

Figure 7 shows DSC thermograms for (a) DPNR-*graft*-PS, (b) sulfonated DPNR, (c) sulfonated PS, and (d) sulfonated DPNR-*graft*-PS, in which the sulfonation was carried out with 0.8*N* chlorosulfonic acid. In thermogram (a), two endothermic drops were shown for the DPNR-*graft*-PS at about −60°C and 100°C, which were attributed to the glass transition of the DPNR and the polystyrene,[30,31] respectively. Since the DPNR is immiscible with the polystyrene, two phases may exist in the DPNR-*graft*-PS, which results in two glass transitions in the thermogram. After sulfonation, in thermogram (d), two endothermic drops were also shown for the sulfonated DPNR-*graft*-PS at about 80°C and 150°C, which were distinguished from those for the DPNR-*graft*-PS. To assign these endothermic drops, we prepared the sulfonated DPNR and the sulfonated PS. In thermogram (b) and (c), one endothermic drop appeared at about 80°C for the sulfonated DPNR and about 150°C for the sulfonated PS. To investigate the glass transition, more accurately, we determined T_g as a point of the inflection of the curves. The determined values of T_g were tabulated in Table II. For the DPNR-*graft*-PS, the two T_g's were determined to be −60.4°C and 103.1°C, respectively. After sulfonation, the two T_g's of the DPNR-*graft*-PS increased with increasing amount of chlorosulfonic acid. When the amount of chlorosulfonic acid was 0.8*N*, the two T_g's drastically increased to 83.3°C and 154.6°C. As for the sulfonated DPNR and the sulfonated PS, the determined values of T_g were 86.8°C and 157.3°C, respectively. Natural rubber may undergo cyclization after reaction with a strong acid such as chlorosulfonic acid, based on previous literatures.[29] This may result in the elevation of T_g of natural rubber. In contrast, the sulfonation is effective to introduce the sulfonic acid groups into polystyrene through an aromatic electrophilic substitution. This may raise T_g due to the intermolecular interaction of sulfonic acid groups and steric hindrance effect of polystyrene.[32] The values of T_g of the sulfonated DPNR and the sulfonated PS were quite similar to those of the DPNR-*graft*-PS sulfonated with 0.8*N*. Consequently, two T_g's of the sulfonated DPNR-*graft*-PS were assigned to T_g of the sulfonated DPNR and the sulfonated PS, respectively.

Elemental analysis

Sulfur content (mol %) of the resulting sulfonated DPNR-*graft*-PS is tabulated in Table II. The sulfur content was dependent upon the amount of chlorosulfonic acid. When the amount of chlorosulfonic acid was 0.2 and 0.4*N*, value of the sulfur content was very small, i.e., less than 2 mol %. When the amount of chlorosulfonic acid was 0.8*N*, the sulfur content increased dramatically to 75 mol %. The abrupt increase in the sulfur content corresponds to the change in the feature of the NMR spectra shown in Figure 5. This demonstrates that the 0.8*N* chlorosulfonic acid is the critical concentration for the sulfonation of DPNR-*graft*-PS. Further increase in the amounts of chlorosulfonic acid resulted in the increase in the content of sulfur; that is, 97 mol % and 100 mol % for 1.0*N* and 2.0*N* chlorosulfonic acid, respectively. The 100 mol % of sulfur content implies that almost all polystyrene links to the sulfonic acid group, which is similar to the sulfur

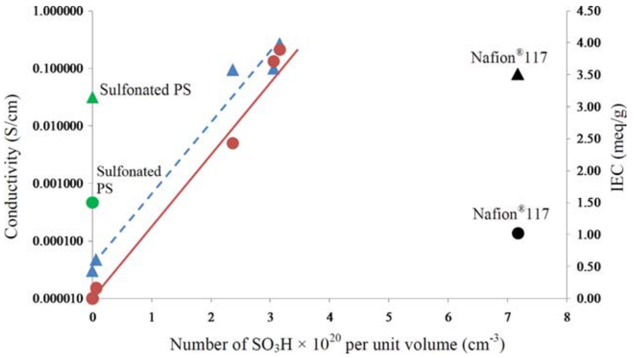


Figure 8 Plots of IEC (●) and proton conductivities (▲ versus number of sulfonic acid (-SO_3H) groups per unit volume (cm^{-3}) for sulfonated DPNR-*graft*-PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

content of the sulfonated PS, itself, which was prepared as a reference.

Electrochemical properties and water uptake content of membranes

Ion exchange capacity (IEC) and proton conductivity (σ) of the sulfonated DPNR-*graft*-PS, the sulfonated PS and Nafion®117 were summarized in Table II. The IEC and proton conductivities were determined by titration and impedance spectroscopy, respectively. Figure 8 shows plots of IEC and proton conductivities versus number of —SO_3H groups per unit volume (cm^{-3}) for the sulfonated DPNR-*graft*-PS. The IEC and proton conductivity of the sulfonated DPNR-*graft*-PS were related to the number of —SO_3H groups. When the number of —SO_3H groups was 0 (0 mol % sulfur content), the IEC of the sulfonated DPNR-*graft*-PS was 0 meq/g, whereas the conductivity was 3.0×10^{-5} S/cm. As the number of —SO_3H groups increased to 6.3×10^{18} (2 mol % sulfur content), the IEC and the conductivity increased to 0.2 meq/g and 4.7×10^{-5} S/cm, respectively. Further increase in the number of —SO_3H groups made the IEC and the conductivities linearly increase. At 2.4×10^{20} of the number of —SO_3H groups (75 mol % sulfur content), the IEC and the proton conductivity were 2.4 meq/g and 9.5×10^{-2} S/cm, respectively. The values of the IEC and the proton conductivity of the sulfonated DPNR-*graft*-PS with 75 mol % sulfur content were quite higher than those of Nafion®117 and the sulfonated PS (100 mol % sulfur content): 1.0 and 1.5 meq/g for the value of IEC and 8.0×10^{-2} and 3.2×10^{-2} S/cm for the value of proton conductivity, respectively. This may be attributed to the formation of the nanomatrix channel. Since, the hydrophilic minor component of the sulfonated PS formed between the hydrophobic major cyclized DPNR particles may contribute to the abrupt increase in the IEC and proton conductivities. Furthermore, an increase in the number of —SO_3H groups up to a percolation threshold in the nanomatrix channel may enhance the transport of protons through hydrophilic pathways.

Figure 9 shows a plot of water uptake versus the number of —SO_3H groups (per unit volume (cm^{-3})) for the sulfonated DPNR-*graft*-PS. The water uptake of the sulfonated DPNR-*graft*-PS was dependent upon the number of —SO_3H groups. The water uptake increased gradually up to 5.7 wt % in the number of —SO_3H groups of 6.3×10^{18} (2 mol % sulfur content). At 2.4×10^{20} of the number of —SO_3H groups (75 mol % sulfur content), the water uptake was 24.3 wt %, which corresponded to that of Nafion® 117, *i.e.*, 18.6 wt %. Further increase in the number of —SO_3H groups made abrupt increase in the water uptake, i.e., 240 wt % at 3.1×10^{20} (97 mol % sulfur content) and 396 wt % at 3.2×10^{20} (100 mol % sulfur content). This may be explained that the water sorption may induce the large deformation in the swollen membrane, as in the case of the sulfonated PS, i.e., 340 wt %. In general, increases in IEC and proton conductivities of the proton conductive polymer electrolyte bring about an increase in water uptake. This results in reduction of the durability of the polymer electrolyte; that is, it may cause a significant damage of membrane. In the present work, we found a suitable condition to achieve high IEC and proton conductivity, in which the water uptake was 1/15 times as low as that of the sulfonated PS, i.e., the sulfonated DPNR-*graft*-PS at 75 mol % sulfur content. This may be explained to be due to the cyclized DPNR part which can suppress the water-uptake to prevent the cell damage from flooding of the cathode, whereas the hydrophilic part of the sulfonated PS enhances the proton transport through the nanomatrix channel. Hence, the high IEC and proton conductivity but low water uptake is the

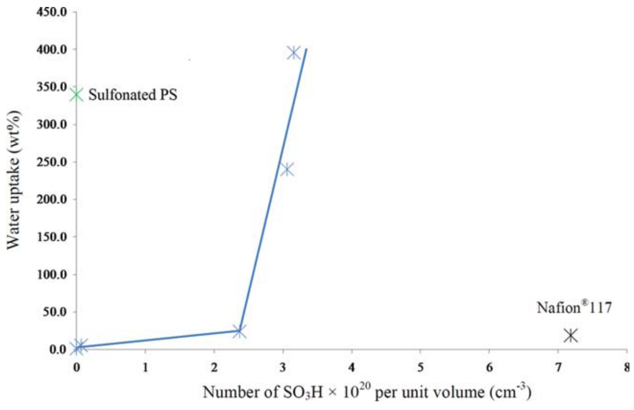


Figure 9 A plot of water uptake versus number of sulfonic acid (-SO_3H) groups (per unit volume (cm^{-3})) for sulfonated DPNR-*graft*-PS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

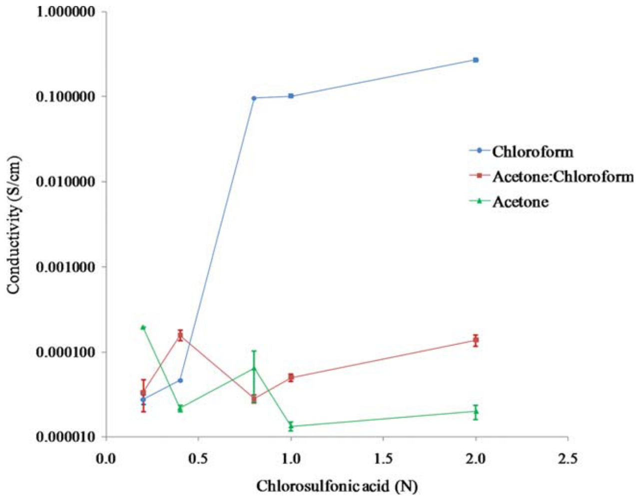


Figure 10 Proton conductivity of sulfonated DPNR-*graft*-PS prepared in (●) chloroform, (■) acetone/chloroform solution, and (▲) acetone as a function of chlorosulfonic acid ($ClSO_3H$) concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

advantage of the sulfonated DPNR-*graft*-PS at 75 mol % sulfur content.

Effect of solvent types for sulfonation

Figure 10 shows a plot of proton conductivity versus chlorosulfonic acid concentration for the sulfonated DPNR-*graft*-PS, which was sulfonated in acetone (▲), chloroform (●), and acetone/chloroform solution (■), respectively. The proton conductivity of the sulfonated DPNR-*graft*-PS was independent of the chlorosulfonic acid concentration, when the sulfonation was performed in acetone and acetone/chloroform solution. In contrast, the proton conductivity was significantly dependent upon the chlorosulfonic acid concentration, when it was sulfonated in chloroform. The proton conductivity increased abruptly at 0.8*N* of chlorosulfonic acid. The proton conductivity of the sulfonated DPNR-*graft*-PS prepared in chloroform was about 2000 times as large as that of the sulfonated DPNR-*graft*-PS prepared in acetone and acetone/chloroform solution. This may be explained to be due to dissolution of the polystyrene particles in the DPNR-*graft*-PS into chloroform, but not into acetone and acetone/chloroform solution; that is, the dissolution of the polystyrene particles resulted in the continuous polystyrene-nanomatrix. In addition, the undissolved DPNR particles, due to cyclization, may contribute to possess the nanomatrix channel structure. Consequently, chloroform was found to be a suitable solvent for the sulfonation of the DPNR-*graft*-PS.

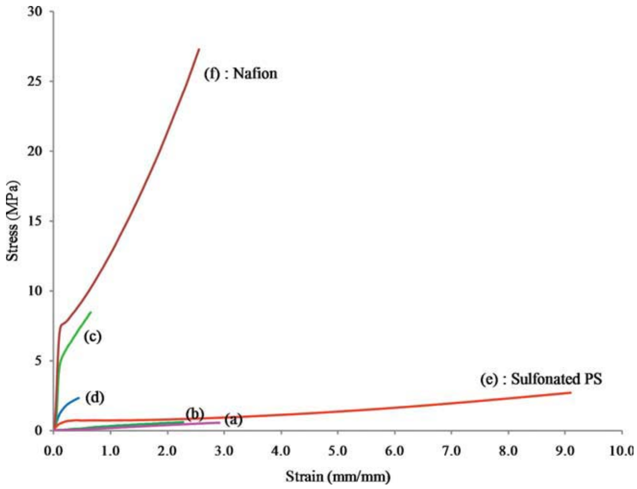


Figure 11 Stress-strain curve for sulfonated DPNR-*graft*-PS prepared from 32 wt % PS with (a) 0.2*N*, (b) 0.4*N*, (c) 0.8*N*, (d) 1.0*N* $ClSO_3H$, (e) sulfonated PS, and (f) Nafion®117. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical properties of membranes

Mechanical properties of the sulfonated DPNR-*graft*-PS, the sulfonated PS and Nafion®117 were summarized in Table III. Figure 11 shows a plot of stress versus strain for the sulfonated DPNR-*graft*-PS with various sulfur contents, the sulfonated PS and Nafion®117. The stress of the sulfonated DPNR-*graft*-PS at strain of 0.4 increased as sulfur content increased, reflecting an increase in Young's modulus. On the other hand, the elongation at break of

TABLE III
Mechanical Properties of Sulfonated DPNR-*graft*-PS, Sulfonated PS, and Nafion®117

Sample	Chlorosulfonic acid (*N*)	Sulfur content (mol %)	Strain (%)	100% Modulus (MPa)	Tensile strength at break (MPa)	Young's modulus (MPa)
DPNR-*graft*-PS	0.0	0	1576	1.5	14.2	4.3 ± 0.2
DPNR-*graft*-PS	0.2	0	291	0.2	0.6	0.3 ± 0.1
DPNR-*graft*-PS	0.4	2	228	0.3	0.6	0.1 ± 0.0
DPNR-*graft*-PS	0.8	75	65	–	8.5	81.2 ± 5.3
DPNR-*graft*-PS	1.0	97	44	–	2.3	11.9 ± 2.7
DPNR-*graft*-PS	2.0	100	–	–	–	–
Sulfonated PS	0.8	100	909	0.7	2.7	4.8 ± 0.4
Nafion®117	–	–	256	12.7	27.3	95.6 ± 0.8

the sulfonated DPNR-*graft*-PS decreased as the sulfur content increased. The maximum values of the stress at break and Young's modulus were 8.5 MPa and 81.2 ± 5.3 MPa, respectively, in which the sulfur content of the sulfonated DPNR-*graft*-PS was 75 mol %. The cyclization of the DPNR part of the DPNR-*graft*-PS may contribute to enhance the mechanical properties, due probably to the dramatic increases in T_g and gel content (Table II). In contrast, the values of the stress at break and Young's modulus decreased to 2.3 and 11.9 ± 2.7 MPa, respectively, as the sulfur content increased to 97 mol % [Fig. 11(d)]. The decreases in the stress at break and Young's modulus at 97 mol % sulfur content may correspond to the abrupt increase of the water uptake (Table II). Furthermore, the Young's modulus of the sulfonated DPNR-*graft*-PS at 75 mol % sulfur content was higher than that of the sulfonated PS, i.e., 4.8 ± 0.4 MPa. The increases in not only the stress at break and Young's modulus but also the proton conductivity and water uptake may be associated to the formation of the nanomatrix channel of the sulfonated PS and dispersoid of the cyclized DPNR.

CONCLUSIONS

The nanomatrix channel was formed by graft-copolymerization of styrene onto the DPNR followed by sulfonation with chlorosulfonic acid at 30°C for 5 h. The conversion and the grafting efficiency of styrene for the graft-copolymerization were about 90 mol % at styrene feed of 5.5 mol/kg-rubber and initiator concentration of 0.2 mol/kg-rubber. The styrene particles of about 60 nm in diameter were fused to each other by sulfonation with chlorosulfonic acid to form the completely continuous nanomatrix channel. The sulfur content, ion exchange capacity, proton conductivity, and water uptake of the sulfonated DPNR-*graft*-PS increased with increasing chlorosulfonic acid concentration. The electrochemical properties of the sulfonated DPNR-*graft*-PS were comparable to Nafion$^{®}$117 and were prominently higher than of that of the sulfonated PS, itself. The sulfonated DPNR-*graft*-PS with 75 mol % sulfur content was found to be the most suitable proton exchange membrane, since it compromises between excellent electrochemical properties for high proton conductivity and good water management to solve the membrane swelling problem from cathode flooding.

The authors express their sincere thanks to Prof. Minoru Umeda of Nagaoka University of Technology and Prof. Hiroshi Jinnai of Kyoto Institute of Technology for their helpful supports on proton conductivity measurement and TEMT observation, respectively.

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