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Nanomatrix Channel for Ionic Molecular Transportation

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Although thousands of studies have been performed on the ionic molecular transportation[1−3] on the membrane, a novel concept on high ability of the membrane to transport the ionic molecule is anxiously desired in a fabrication of high performance battery as an energy source, i.e., fuel cell, lithium ion battery, and so forth. In particular, morphology-control in nanometer scale attracts much attention in regard to the formation of a path of the molecule to accomplish more rapid transportation. Furthermore, a necessary requirement for the membrane is what is made of green-renewable resources such as a carbon-neutral biomass-origin product, in order to establish a global carbon cycle. It is well-known that the products made in the second metabolism of higher plants are effective to prevent releasing CO_2 into atmospheric air, but not products made in the first metabolism. One of the green-renewable resources is natural rubber made in the second metabolism of *Hevea brasiliensis*, which is comprised of *cis*-1,4-isoprene units.

The nanomatrix channel is a three-dimensional molecular vessel, which provides infinite number of paths along with the channel to transport a lot of ionic molecules through the membrane (Figure 1). It is required to make a completely continuous matrix without any defect in the three-dimensional molecular vessel, in order to secure the infinite number of paths in the nanomatrix channel. The channel is, thus, distinguished from nanophase separated structures formed for block and graft copolymers, i.e., cylinder, gyroid, and lamellar structures, which inherently include a grain boundary as a defect.[4,5] It is different also from a nanomatrix structure proposed in our previous paper.[6−8]

The nanomatrix channel may be formed by covering particles of hydrophobic polymer with a nanolayer of hydrophilic polymer followed by coagulation or solidification (Figure 1). The particles are required to be cross-linked and chemically liked to the nanolayer, in order to stabilize the nanomatrix channel in equilibrium state. The chemical linkages are formed in principle by graft-copolymerization of a suitable monomer onto the particles in latex stage, since the particles in the latex are dispersed in water. Natural rubber is a typical hydrophobic polymer, which is isolated from *H. brasiliensis* as the latex. The rubber has reactive carbon−carbon double bonds in constitutive repeating *cis*-1,4-isoprene units. However, it contains nonrubber constituents such as proteins[9] that make side reactions during the graft-copolymerization. In fact, as long as we use natural rubber without purification, conversion and grafting efficiency of vinyl monomer are less than 30 and 60 mol %,[6] respectively. In the previous work,[6−8,10] we made a break-through to attain high grafting efficiency and high conversion of styrene for the graft-copolymerization through purification of natural rubber with urea in latex stage. The resulting hydrophobic polystyrene partially covered the hydrophobic natural rubber particles. On the basis of the our previous results, when we completely cover the natural rubber particles with polystyrene and convert polystyrene from hydrophobic to hydrophilic in nature, it becomes possible to form the nanomatrix channel.

Sulfonation[11−13] is well-known to be effective to convert polystyrene from hydrophobic to hydrophilic in nature, in which sulfonic acid ($-SO_3H$) groups are incorporated into polystyrene through aromatic electrophilic substitution with chlorosulfonic acid. The sulfonic acid groups on a phenyl ring may contribute to the rapid transportation of the proton, as in the case of a proton-conductive perfluorosulfonic acid membrane, such as Nafion117. Furthermore, the sulfonation makes cyclization on natural rubber; hence, the membrane becomes tough. Here, first, we prepare 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. Second, the resulting DPNR-*graft*-PS is sulfonated with chlorosulfonic acid to prepare the proton-conductive membrane.

A hierarchical phase-separated structure of DPNR-*graft*-PS is found in an image of transmission electron microscopy (TEM), which consists of DPNR particles of about 1 μm in average diameter and PS particles of about 60 nm in diameter (Figure 2B and Supplementary Movie S1). The bright DPNR particles are well dispersed into discontinuous matrix of gloomy PS particles that are densely close to each other in the matrix; although no phase separated structure is shown for DPNR, itself (Figure 2A). This implies that one DPNR particle is surrounded by about 10^3 PS particles; that is, it is surrounded by about 2×10^8 PS molecules, since a number average molecular weight, $\overline{Mn}$, of PS is about 10^4 g/mol (Table S1), which is determined by size exclusion chromatography of an ozonolysis product of the DPNR-*graft*-PS. The hierarchical structure is artificially concreted with the chemical linkages, as is evident from high gel content of DPNR and high grafting efficiency of styrene (Table S1), which represent large amount of three-dimensional DPNR network and a large number of PS molecule linking to DPNR particles, respectively. Conversion of styrene is also high under a suitable condition of the graft-copolymerization, as shown in Table S1.

The sulfonation of DPNR-*graft*-PS makes connection of the PS particles to form completely continuous nanomatrix (Figure 2C), since the PS particles may be dissolved into chloroform before sulfonation with chlorosulfonic acid (Figure S1), but the DPNR particles may not due to three-dimensional network structure. Thickness of the nanomatrix is about 80 nm, reflecting that several PS particles of about 60 nm in diameter fuse to each

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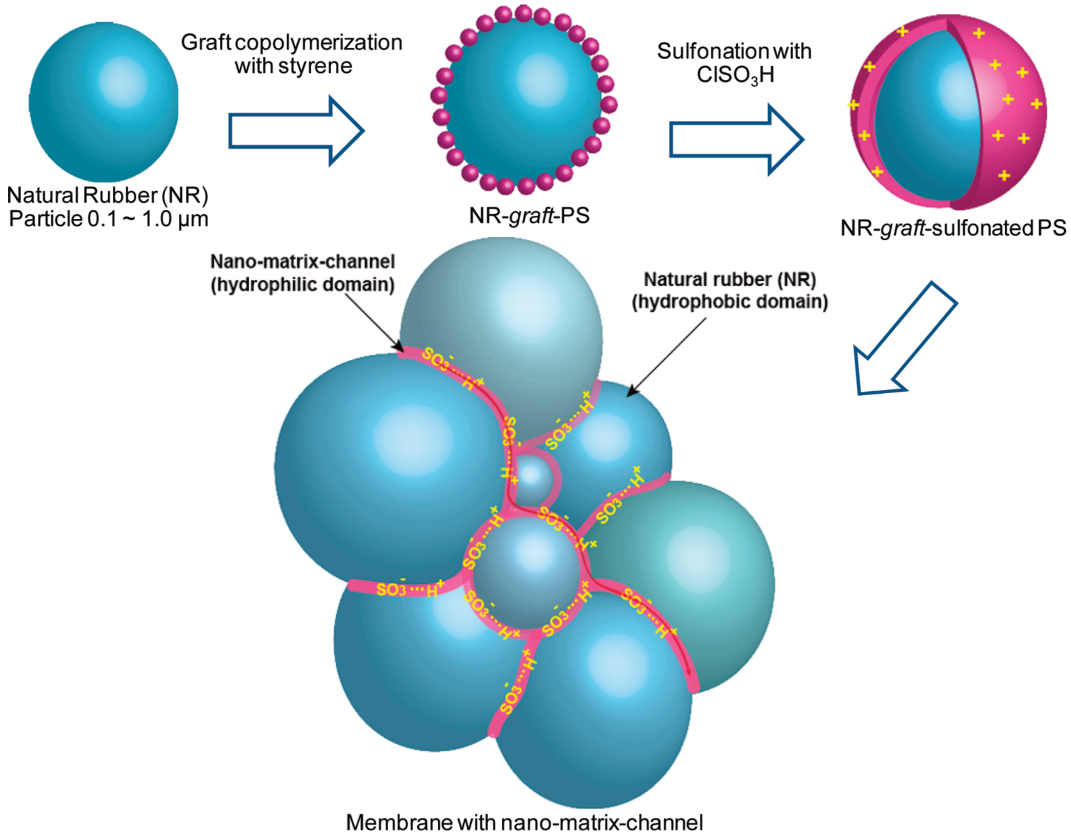

Figure 1. Schematic representation of nanomatrix channel prepared from sulfonation of grafted natural rubber with styrene. The illustration indicates the proton conductive channel of hydrophilic domain in the sulfonated polystyrene, which phase separates from natural rubber (hydrophobic domain) in nanometer scale.

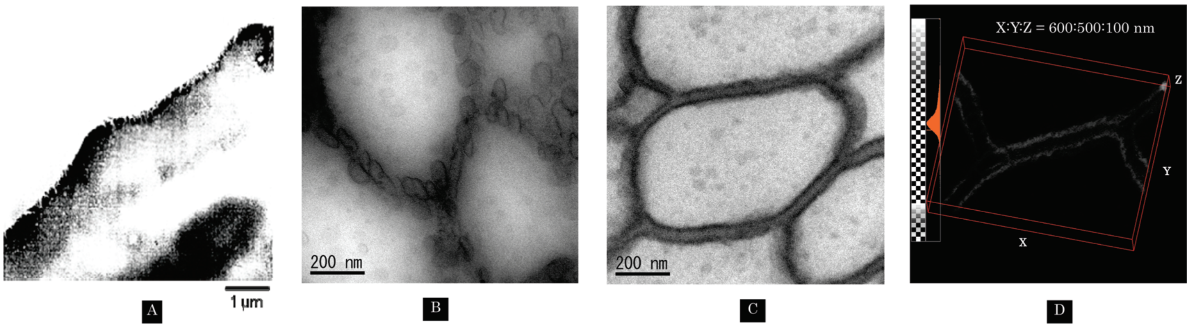

Figure 2. TEM photographs for (A) DPNR, (B) DPNR-*graft*-PS, and (C) DPNR-*graft*-sulfonated PS with chloroform solution of 0.8 N chlorosulfonic acid at 30 °C for 5 h. The ultrathin section of about 100 nm in thickness was stained with RuO_4 at room temperature for 1 min, in which bright domains represent natural rubber and gloomy domains represent the PS (see also Movie S1). The TEM image reveals that the PS matrix was completely connected to each other after sulfonation, whereas it was disconnected before sulfonation. (D) Three-dimensional TEM image for DPNR-*graft*-sulfonated PS with chloroform solution of 0.8 N chlorosulfonic acid at 30 °C for 5 h. The ultrathin section of about 100 nm in thickness was stained with RuO_4 at room temperature for 1 min. The gloomy domains represent natural rubber and the bright domains represent the sulfonated PS (see also Movie S2). The box size of the three-dimensional image is 600 nm, 500 nm, and 100 nm in the *X*, *Y*, and *Z* directions, respectively.

other after sulfonation. A volume fraction of the resulting sulfonated PS is estimated by image-analysis to be about 35 vol % in the DPNR-*graft*-sulfonated PS. The estimated value of the volume fraction is quite similar to 36 vol % of fed styrene for graft copolymerization, as expected from about 90 mol % conversion and grafting efficiency of styrene. The completely continuous nanomatrix of sulfonated PS is proved by transmission electron microtomography (TEMT) observation in Figure 2D. In 600:500:100 nm-size box of three-dimensional image, bright sulfonated PS nanomatrix is completely connected to form the continuous nanomatrix (Movie S2).

The sulfonation of DPNR-*graft*-PS is investigated in molecular order by solid state ^{13}C CP/MAS NMR spectroscopy. Broad signals in solid state ^{13}C CP/MAS NMR spectrum appear to overlap to each other after sulfonation, while signals characteristic of DPNR and PS disappear, as shown in Figure 3. The signal at 139.1 ppm, marked as no.3 in Figure 3, appears after sulfonation, which is assigned to aromatic carbon substituted with sulfonic acid group. The downfield-shifts of the signals at 127.3 and 145.7 ppm occur to 130.1 and 148.0 ppm, marked as no. 2 and no. 4, respectively, which are attributed to an electron-withdrawing effect of the sulfonic acid group linking to the phenyl group (Figure S2). A conversion of the sulfonation, estimated from a sulfur level (mol %) of the sulfonated DPNR-*graft*-PS, increases as a concentration of chlorosulfonic acid increases; for instance, it is 75 mol % at 0.8N chlorosulfonic acid

Table 1. Data of T_g, Gel Content, Elemental Analysis, and Electrical Properties of Sulfonated DPNR-*graft*-PS

chlorosulfonic acid (N)	T_g (°C)	gel content (wt %)	sulfur level (mol %)	IEC (mequiv/g)	conductivity (S/cm)	water swelling content (wt %)
0.2	93.7	75.4	0	0.00	3.0×10^{-5}	0.8
0.4	100.6	88.6	2	0.16	4.7×10^{-5}	5.7
0.8	140.6	90.4	75	2.43	9.5×10^{-2}	24.3
sulfonated PS				1.50	3.2×10^{-2}	340.0
Nafion117	169.2	90.6		1.02	8.0×10^{-2}	18.6

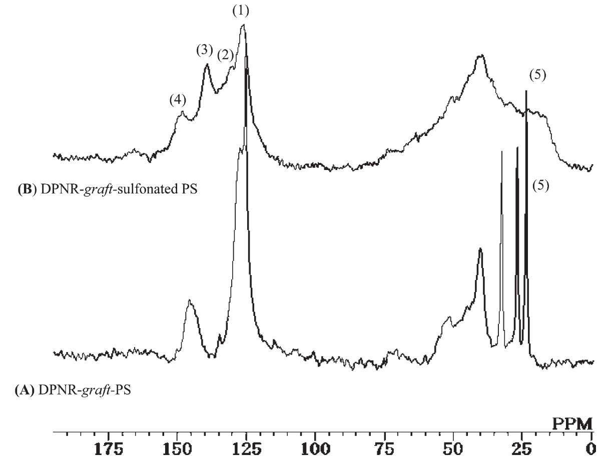

Figure 3. ^{13}C CP/MAS spectra of (A) DPNR-*graft*-PS and (B) DPNR-*graft*-sulfonated PS with chloroform solution of 0.8 N chlorosulfonic acid at 30 °C for 5 h. Broad signals in part B may be explained to be due to the cyclization of *cis*-1,4-isoprene units.

(Table 1). In contrast, the overlapped broad signals, marked as no. 5 in Figure 3, are explained to be due to the cyclization of DPNR, which is supported by a dramatic increase in glass transition temperature, T_g, and gel content (Table 1).

Electro-chemical properties of the DPNR-*graft*-sulfonated PS are compared with those of the proton-conductive perfluorosulfonic acid membrane, Nafion117, as a reference. The nanomatrix of the DPNR-*graft*-sulfonated PS is activated with sulfuric acid solution to the nanomatrix channel. Ion exchange capacity (IEC) and water swelling content of the DPNR-*graft*-sulfonated PS are dependent upon the sulfonic acid group content, as shown in Table 1; the higher the sulfonic acid content, the greater are the IEC and water swelling content. The value of the IEC of the DPNR-*graft*-sulfonated PS is 2.4 mequiv/g at 75 mol % of sulfonated PS/PS, which is larger than the value of the IEC of sulfonated PS, itself, and Nafion117. The nanomatrix channel of the hydrophilic minor component of sulfonated PS formed between the hydrophobic major cyclized DPNR particles is anticipated to contribute to the abrupt increase in the IEC and water swelling content.

Proton-conductivity of the DPNR-*graft*-sulfonated PS is correlated to the IEC. The proton-conductivity of the DPNR-*graft*-sulfonated PS increases as the sulfonic acid content increases. The value of the proton-conductivity of the DPNR-*graft*-sulfonated PS is 9.5×10^{-2} S cm^{-1} at 75 mol % of sulfonated PS/PS, which is about third as large as that of sulfonated PS. It is larger than the value of the proton-conductivity of Nafion117, 8.0×10^{-2} S cm^{-1}, as in the case of IEC. The large values of IEC and proton-conductivity may be associated with the high grafting efficiency of styrene for the graft copolymer, i.e., more than 99 mol %, in which almost all sulfonated polystyrene is covalently linked to cyclized DPNR. If the sulfonated polystyrene had not linked to cyclized DPNR particles, we could not accomplish the high values of IEC and proton conductivity.

The advantage of the DPNR-*graft*-sulfonated PS at 75 mol % sulfur level is quite low water swelling content, in spite of the excellent proton conductivity and high IEC, which corresponds to those of Nafion 117. It is 1/15 times as low as the water swelling content of sulfonated PS. This may be explained to be due to an effect of the cyclized DPNR part of DPNR-*graft*-sulfonated PS, which suppresses water-uptake of the sulfonated PS part while the hydrophilic part of sulfonated polystyrene enables the transport of the ionic molecule through the nanomatrix channel. Consequently, in the term of water management in the cell, DPNR-*graft*-sulfonated PS will solve cathode flooding problems.

In conclusion, the nanomatrix channel is formed by graft copolymerization of styrene onto deproteinized natural rubber followed by sulfonation with chlorosulfonic acid. The conversion and the grafting efficiency of styrene for the graft-copolymerization are about 90 mol % at styrene feed of 5.5 mol/kg of rubber and initiator concentration of 0.2 mol/kg of rubber. The styrene particles of about 60 nm in diameter are fused to each other by sulfonation with chlorosulfonic acid to form the completely continuous nanomatrix of sulfonated PS. The nanomatrix of about 80 nm in thickness is activated with sulfonic acid solution to the nanomatrix channel. The values of the IEC and the proton conductivity of the DPNR-*graft*-sulfonated PS are prominently larger than those of Nafion117.

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Supporting Information Available: Text giving the experimental details and describing the movies available more completely, a table of graft polymerization data, figures showing the preparation procedure and the proposed structure for DPNR-*graft*-sulfonated PS and two movies in .zip format showing the three-dimensional TEMT images for DPNR-*graft*-PS and DPNR-*graft*-sulfonated PS. This material is available free of charge via the Internet at http://pubs.acs.org.

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