Self-Assembly of Surface-Charged Latex Nanoparticles: A New Route to the Creation of Continuous Channels for Ion Conduction

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Department of Physics and Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada, and Institute for Fuel Cell Innovation, National Research Council Canada, 3250 East Mall, Vancouver, BC V6T 1W5, Canada

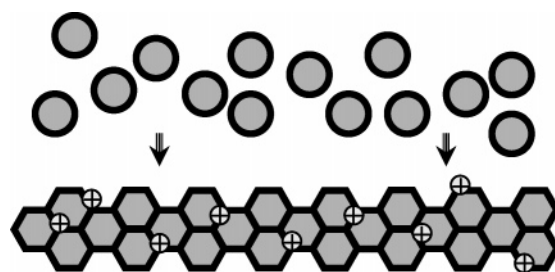The self-assembly of monodispersed colloidal spheres has been observed as a natural phenomenon in both mineral[1] and animal[2] systems. Scientists have exploited this behavior[3a] to mimic natural nanocomposites[4a] and to fabricate artificial opals,[5a,6a] functional materials such as photonic papers[3b] and chemical sensors,[5b] nanoparticle networks for controlled drug delivery,[6b] ordered mesoporous[4b]/macroporous[7] materials, and photonic band gap materials.[8,9] The use of colloidal self-assembly to manipulate electrical conduction has also been reported: Hamilton et al. used chemically etched microporous silicon networks to create size-controlled percolation pathways for electrical conduction,[10] and Mezzenga et al. exploited the self-assembly of polystyrene particles to template doped π-conjugated polymers to decrease the percolation threshold for electrical conductivity.[11]

A related topic of current interest is ion conductivity, which is important to the development of materials for batteries, sensors, electrochromic and photoelectrochemical devices, and, in particular, the ion-conducting membranes that are the essential component of the polymer electrolyte membrane fuel cell.[12] It is recognized that the ion conductivity and mechanical integrity of these membranes are enhanced by nanoscale phase separation of ionic and nonionic components into bicontinuous structures,[13,14] although a complete understanding of the relationship between morphology and conductivity is still lacking. To improve upon and design novel ion-conducting membranes, it is important to be able to understand and model this relationship.[15]

In this work, we present a new model system designed to test the relationship between morphology and proton conductivity. We discuss the concept and practice of using surface-charged latex nanoparticles as building blocks for proton conductive membranes, wherein the particles are packed and physically linked together. In this way, a proton conductive membrane of controlled micro/nanoscale structure is formed.

Our model system consists of lightly cross-linked spheres with hydrophobic cores and proton-conducting surfaces. As shown schematically in Figure 1, continuous ionic channels form naturally upon annealing closely packed spheres. Cohesion of the spheres can be achieved through either intersphere cross-linking and/

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Figure 1. Schematic diagram showing precursor particles with hydrophobic cores (gray) and ionic surfaces (dark) and a film formed by self-assembly of the particles.

or intersphere chain tangling. The formation of latex films, particularly from latex water dispersions, has been investigated extensively[16,17] and provides guidance for this method.

To demonstrate this concept, two hydrophobic monomers, butyl acrylate (BA) and methyl methacrylate (MMA), a cross-linker, N,N'-methylenebis(acrylamide) (BIS), and a charged monomer, sulfonate styrene sodium salt (NaSS), were chosen for nanoparticle syntheses using the standard technique of free-radical emulsion copolymerization in water. Synthesis in aqueous emulsions should result in the charged groups being attached to the surface of the particles.[19] Different quantities of NaSS were introduced to change the charge content of the particles. The low-T_g component, BA, was chosen to ensure a low enough T_g of the final particles to obtain a suitable minimum film temperature.[18] The BIS concentration used was sufficiently low that interparticle chain tangling could occur upon annealing but high enough to maintain the integrity of the particle structure.[17b] The size and solid density of the precursor nanospheres were characterized by a combination of static and dynamic laser light scattering with an ALV DLS/SLS-5000E spectrometer. Data for one series of particles are presented in Table 1. As the charge content in the syntheses increases, the final size and solid density of the particles decrease, as expected in charged latex[19] and gel nanoparticle syntheses.[20] The exception is sample 6, synthesized in salt solution, where the resultant particle size increases due to charge screening by the ions.

Free-standing membranes were obtained by casting aqueous particle dispersions followed by incubation at ∼110 °C for 2 h for film formation. The membranes were then treated with 2 M HCl overnight and washed with DI water for 2−4 h to prepare for proton conductivity, ionic content, and water uptake measurements. For comparison, membranes with similar composition but a more uniform distribution of ions were fabricated by casting post-sulfonated MMA, BA, and styrene terpolymer ionomer chains from tetrahydrofuran solutions. The terpolymers were prepared by free-radical polymerization and were post-sulfonated at 50 °C with sulfuric acid as the sulfonation agent. No cross-linker was added to the terpolymer system.

The effect of structural design on the conductivity is evident upon comparing the conductivity of membranes made from self-assembled surface-charged particles and membranes cast from ionomer solutions. The measured proton conductivity of the films is shown in Figure 2 as a function of charge content, which is expressed in terms

**Table 1. Particle Synthesis Components and the Resulting Sizes and Solid Densities, Which Were Measured at 25 °C for Dilute Water Dispersions**

particle sample	NaSS [mg]	$\langle R_h \rangle$ [nm]	ρ [g/cm³]
1	0	135	0.53
2	145	46	0.37
3	288	36	0.23
4	576	31	0.18
5	967	26	0.12
6[a]	1440	89	0.09

[a] Synthesized in 0.1 M NaCl aqueous solution.
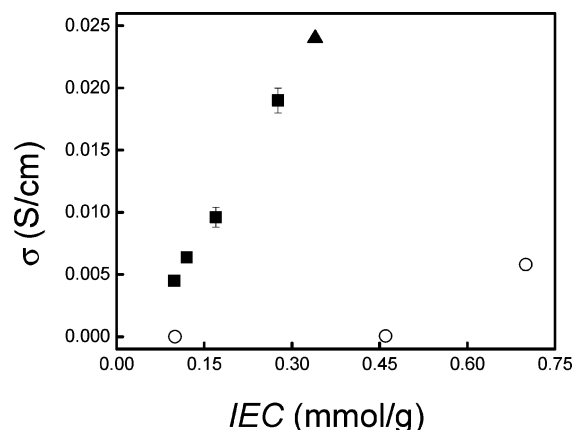
Figure 2. Proton conductivity as a function of IEC for membranes prepared from poly(MMA-BIS−BA-NaSS) particles (solid squares for samples 2−5 and triangle for sample 6) and sulfonated poly(MMA-BA-St) solutions (circles). The error bars indicate the variation between membranes prepared from the same particles as represented by the uncertainty of the mean. Conductivity was obtained by measuring ac imped-ance spectra at room temperature in the frequency range 100 Hz−40 MHz using a gold-plated coaxial probe attached to a Hewlett-Packard 8753 A network analyzer, and IEC was determined by titration.

of the ion exchange capacity (IEC). The conductivity of the particle membranes is significant even for IECs as low as 0.1 mmol/g and increases with IEC, reaching 0.02 S/cm for IECs of 0.3 mmol/g. Without the advantage of structural design, membranes simply prepared from solution-cast ionomers show much lower conductivity for the same or even higher charge content. The conductivity of the particle membranes is even higher than that expected for membranes known to contain ion channels made from a grafted polymer PS-*g*-macPSSA at a similar charge content.[22]

We believe that the difference between the conductiv-ity of the particle membranes and the others mentioned above lies in the connectivity of the conduction path-ways. In a membrane made from random or graft copolymers, conductivity only occurs above a minimum charge content, often associated with a percolation threshold, where there is enough connection between charged regions for a continuous pathway to exist. This leads to minimal ionic conduction at low charge content. For surface charged latex membranes, the channels are expected to form naturally as the charged surfaces of adjacent particles touch and provide continuous pathways even at low charge content. In this case, it seems that the percolation threshold either disappears or shifts to much lower values. In effect, the huge difference in proton conductivity can be attributed to a more efficient organization of the charges within the membrane.
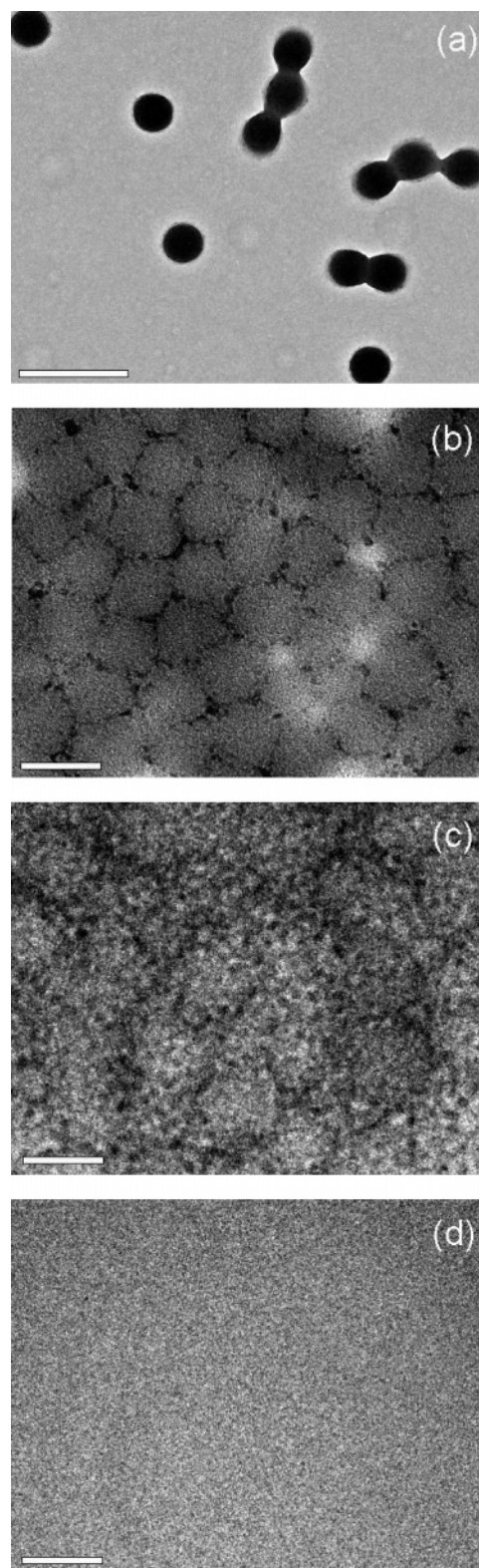
Figure 3. TEM images of (a) dilute precursor particles with zero charge content (sample 1), (b) closely packed, lightly charged particles (sample 2), (c) a film of moderately charged particles (sample 6) incubated at 102 °C, and (d) a film with an IEC of 0.46 mmol/g that was cast from ionomer solution. The tendency of these polymer particles to coalesce can be seen in the neutral particles as shown in (a). The contrast observed in (b) and (c) corresponds to charged and uncharged regions. Image (d) indicates a more amorphous structure with charges uniformly distributed through the film. Bar lengths are 500 nm in (a) and 100 nm in (b), (c), and (d). TEM images were obtained using a Tecnai FEI 20 scanning transmission electron microscope at either 200 or 80 keV.

Unfortunately, we were not able to produce particle membranes with higher charge content. We made particles with initial IECs as high as 1.2 mmol/g, but films made from these particles swelled excessively in water, preventing measurement of conductivity and IEC. This is expected since the particles should become more hydrophilic as the charge content is increased. It is also likely that particle formation will be compromised at charge contents above 10 wt %.[19]

These data imply differences in the way the charges are localized within the different membranes and offer indirect evidence that we have produced surface-charged nanospheres. Transmission electron microscopy (TEM) offers further evidence of these structural differences. Several representative images are shown in Figure 3. The uniformity in size found for isolated neutral particles from sample 1, which contained no NaSS, and the deformation of these particles as coalescence occurs is shown in Figure 3a. Deformation of the spheres is a sign of intersphere chain tangling, which leads to fusion of the spheres and prevents the particles from redispersing in water. An image of closely packed particles is shown in Figure 3b; this image is from particles from sample 2, made with 0.145 g of NaSS. The contrast seen in this figure is between the hydrophobic cores and the charged surfaces of the individual particles, making it possible to see the morphology even without staining the polymer film. An example of an incubated film is shown in Figure 3c; this film is composed of particles from sample 6, made with 1.44 g of NaSS, which were cast directly onto a TEM grid and incubated at 102 °C for 2 h. The image shows that the contrast between the hydrophobic cores and the charged surfaces persists after incubation. A closer look at Figure 3c indicates that the charged groups do not form completely continuous channels but are present as isolated clusters that appear as black dots in the image. It is possible that some degree of phase separation can occur during the drying of the particles and the incubation of the membrane because the hydrophobic and charged components are incompatible. However, once the thin film swells in water, these isolated but localized charge clusters may diffuse to form continuous channels. Neutron scattering experiments have been performed using hydrated thin films in order to confirm the persistence of particle structure in the incubated membrane and will be presented in a future paper. In contrast to the bicontinuous structure observed for the particle membranes, the charges in the membranes cast from ionomer solution are uniformly distributed, as is shown in Figure 3d. This membrane was stained with lead acetate. No phase separation morphology is observed, which is consistent with the significantly lower proton conductivity.

In summary, ion-conducting membranes formed through the assembly of surface-charged latex spheres into closely packed structures have been realized for the first time. These membranes show conductivity orders of magnitude higher than that of amorphous membranes possessing the same charge content. TEM images provide direct evidence of nonhomogeneous structures. The combined evidence indicates that continuous charged hydrophilic channels form naturally during self-assembly of the particles. Although further effort is required to increase the ionic content of the precursor particles and to suppress excessive swelling of the latex membranes, this precisely engineered model system allows for the investigation of the relationships between membrane nanostructure and ion conductivity.

References and Notes

(1) Sanders, J. V. *Nature (London)* **1964**, *204*, 1151.
(2) Vukusic, P.; Samples, J. R.; Lawrence, C. R.; Wooten, R. J. *Proc. R. Soc. London B* **1999**, *266*, 1403.
(3) (a) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.* **2000**, *12*, 693. (b) Fudouzi, H.; Xia, Y. *Adv. Mater.* **2003**, *15*, 892.
(4) (a) Sellinger, A.; Weiss, P. M.; Nguyen, A.; Lu, Y.; Assink, R. A.; Gong, W.; Brinker, C. J. *Nature (London)* **1998**, *394*, 256. (b) Lu, Y.; Fan, H.; Stump, A.; Ward, T. L.; Rieker, T.; Brinker, C. J. *Nature (London)* **1999**, *398*, 223.
(5) (a) Weissman, J. M.; Sunkara, H. B.; Tse, A. S.; Asher, S. A. *Science* **1996**, *274*, 959. (b) Holtz, J. H.; Asher, S. A. *Nature (London)* **1997**, *389*, 829.
(6) (a) Hu, Z.; Lu, X.; Gao, J. *Adv. Mater.* **2001**, *13*, 1708. (b) Huang, G.; Gao, J.; Hu, Z.; St. John, J. V.; Ponder, B. C.; Moro, D. *J. Controlled Release* **2004**, *94*, 303. (c) Hu, Z.; Lu, X.; Gao, J.; Wang, C. *Adv. Mater.* **2000**, *12*, 1173.
(7) Imhof, A.; Pine, D. J. *Nature (London)* **1997**, *389*, 948.
(8) Blanco, A.; Chomski, E.; Grabtchak, S.; Ibisate, M.; John, S.; Leonard, S. W.; Lopez, C.; Meseguer, F.; Miguez, H.; Mondia, J. P.; Ozin, G. A.; Toader, O.; van Driel, H. M. *Nature (London)* **2000**, *405*, 437.
(9) Lee, W.; Pruzinsky, S. A.; Braun, P. V. *Adv. Mater.* **2002**, *14*, 271.
(10) Hamilton, B.; Jacobs, J.; Hill, D. A.; Pettifer, R. F.; Teehan, D.; Canhams, L. T. *Nature (London)* **1998**, *393*, 443.
(11) Mezzenga, R.; Ruokolainen, J.; Fredrickson, G. H.; Kramer, E. J.; Moses, D.; Heeger, A. J.; Ikkala, O. *Science* **2003**, *299*, 1872.
(12) Gary, F. M. *Polymer Electrolytes*; Royal Society of Chemistry: Cambridge, 1997; p 31.
(13) Yeager, H. L. In *Transport Properties of Perfluorosulfonate Polymer Membranes* in *Perfluorinated Ionomer Membranes*; ACS Symposium Series Vol. 180; Eisenberg, A., Yeager, H. L., Eds.; American Chemical Society: Washington, DC, 1982; p 49.
(14) Rubatat, L.; Rollet, A. L.; Gebel, G.; Diat, O. *Macromolecules* **2002**, *35*, 4050.
(15) Yang, Y.; Holdcroft, S. *Fuel Cells* **2005**, *5*, 171.
(16) Eckersley, S. T.; Rudin, A. In *Film Formation of Acrylic Copolymer Latices: A Model of Stage II Film Formation* in *Film Formation in Waterborne Coatings*; ACS Symposium Series Vol. 648; Provder, T., Winnik, M. A., Urban, M. W., Eds.; American Chemical Society: Washington, DC, 1996; p 2.
(17) (a) Winnik, M. A. In *The Formation and Properties of Latex Films* in *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons Ltd.: New York, 1997; p 467. (b) Liu, R.; Winnik, M. A. *Macromolecules* **2001**, *34*, 7306. (c) Oh, J. K.; Tomba, P.; Ye, X.; Eley, R.; Rademacher, J.; Farwaha, R.; Winnik, M. A. *Macromolecules* **2003**, *36*, 5804.
(18) Tang, J.; Daniels, E. S.; Dimonie, V. L.; Vratsanos, M. S.; Klein, A.; El-Aasser, M. S. *J. Appl. Polym. Sci.* **2002**, *86*, 2788.
(19) Kim, J. H.; Chainey, M.; El-Aasser, M. S.; Vanderhoff, J. W. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 171.
(20) Gao, J.; Frisken, B. J. *Langmuir* **2005**, *21*, 545.
(21) Weiss, R. A.; Sen, A.; Willis, C. L.; Pottick, L. A. *Polymer* **1991**, *32*, 1867.
(22) Ding, J.; Chuy, C.; Holdcroft, S. *Macromolecules* **2002**, *35*, 1348.

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