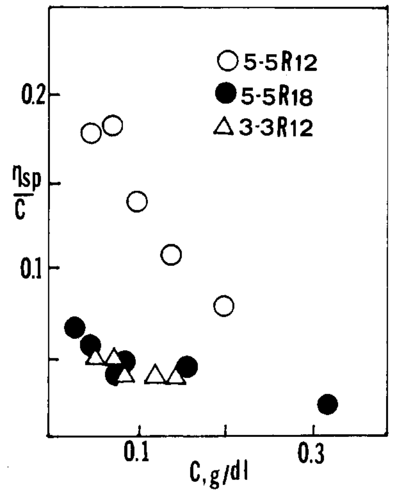

Figure 2. Reduced viscosities in a 0.0050 M KBr 50/50 water–ethanol mixture.

in extremely dilute salt solutions. On dilution in such solvents, the charges in the ionic atmosphere about the polyion distribute themselves at large distances from the chain causing decreased shielding of the backbone charges with concomitant elongation. It is interesting that 3-3R12 and 5-5R12 show this polyelectrolyte effect to the same extent, indicating that while the linear charge density is important, another effect is dominant. The reduced viscosities at a definite concentration can be used to compare the effective hydrodynamic volumes of the polymer molecules if the contour degrees of polymerization of the polymers are similar. Linear 3–3 and 4–4 ionene bromides are reported[8] to have molecular weights over a small range when they are prepared by the method used to prepare the ionene polysoaps. In our laboratory, [η] in aqueous 0.40 M KBr for samples of linear 3–3 and 4–4 ionene bromides were found to be 0.13 and 0.12 dL/g, respectively. There is no reason to expect that the main backbone of the ionene polysoaps would have lengths differing greatly from those of their linear analogues. Then the relative effective hydrodynamic volumes of the ionene polysoaps presented here could be compared at the same concentration even if this approximation is somewhat crude. The results in Figure 1 indicate that each of the ionene polysoaps has the same degree of compactness in ethanol solution regardless of whether the alkyl side chain is a dodecyl or an octadecyl group. This indicates that the apolar interactions of these alkyl branches are not only dominant over the electrostatic effect of the linear charge density of the chain, but are independent of the length of the alkyl branches and independent of the charge density of the chain. It would be of interest to investigate ionene polysoaps with smaller alkyl branches.

Figure 2 shows the reduced viscosity results of 3-3R12, 5-5R12, and 5-5R18 in 0.0050 M KBr, using a 50/50 ethanol–water mixture. Here the 5-5R18 and the 3-3R12 appear to have the same degree of compactness over the concentration range employed. It is interesting that *linear* 3–3, 4–4, and 6–6 ionene bromides prepared in our laboratory had reduced viscosities at 0.3 g/dL in 0.005 M KBr in 50/50 ethanol–water mixtures of 0.29, 0.38, and 1.31, respectively, indicating a more extended structure than the ionene polysoaps compared in Figure 2. Upon comparison with the reduced viscosity values for these polysoaps in Figure 1, it is noted that above 0.1 g/dL the reduced viscosities are essentially the same as those in absolute ethanol and in 50% ethanol, while below this polysoap concentration the rise in the curve with dilution is steeper in pure ethanol. Similar findings have been reported for poly(2-vinyl-*N*-*n*-dodecylpyridinium bromide) in water and in 92.80% ethanol,[3] where the greater rise in the reduced viscosity curves was found with the lower dielectric solvent. In Figure 2 it is apparent that the 5-5R18 is more compact than the 5-5R12 polysoap, probably due to greater apolar interactions. Analogously, it was reported that the greatest reduced viscosity decrease occurred in increasing the percent of polysoap character of poly(4-vinyl-*N*-ethylpyridinium bromide).[6]

Interesting and potentially useful ionene polysoap structures can be synthesized without great difficulty. They may provide useful models for cell membranes.

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On the Poly(β-DL-aspartic acid)

The determination of the ratio of α and ω linkages in aspartyl, glutamyl, and lysyl residues in polypeptides or poly(amino acids) is an important problem. However, until recently no general method for the determination of α- and ω-amino acid residues in poly(amino acids) has been reported. In the previous study from this laboratory, the determination of α- and ω-amino acid residues of aspartic acid,[1] glutamic acid,[2] and lysine[3] in poly(amino acids) by potentiometric titration has been reported. In a series of studies of the α- and ω-linkage determination, it is necessary to characterize authentic poly(β-DL-aspartic acid) (β-PAA) in order to test the applicability of the analytical method. The β-PAA was prepared by two different methods.[4,5] However, the structure of both β-PAAs prepared was a mixture of α- and β-aspartyl residues. The fact is an unexpected result, and we would like to report the analytical results in this communication.

One preparation of β-PAA was carried out by using the six-membered *N*-carboxyanhydride (NCA).[4] In this preparation, α-methyl DL-aspartate was converted to its corresponding NCA, and the NCA was polymerized in dioxane, using triethylamine as an initiator. The resulting poly(α-methyl β-DL-aspartate) was hydrolyzed partially with KOH–methanol at room temperature to obtain poly(β-DL-aspartic acid) [β-PAA(OH)]. The other poly(β-DL-aspartic acid) [β-PAA(H)] was synthesized by the active ester method.[5] The β-PAA(H) was prepared by polycondensation of α-benzyl β-pentachlorophenyl DL-

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Table I
Physical Properties of PAA

sample	$\overline{\mathrm{DP}}$[a]	IR,[b] cm^{-1} COOH	amide I	amide II
β-PAA(OH)	20	1720	1650	1520
β-PAA(H)	90	1720	1650	1530
α-PAA(H)	60	1720	1630	1550

[a] Determined by the titration of *N*-terminal amino groups with perchloric acid. [b] Measured in a KBr disk.

aspartate. The resulting poly(α-benzyl-β-DL-aspartic acid) was subjected to hydrogenolysis to yield β-PAA(H). Poly(α-DL-aspartic acid) [α-PAA(H)] was also prepared by the NCA method, using β-benzyl DL-aspartate. The benzyl group of the polymer was removed by hydrogenolysis. The physical properties of three PAA samples are summarized in Table I.

The potentiometric titration was carried out using 30 mL of sample solution containing 30 mg of polymer at 25 °C in an atmosphere of nitrogen with a Hirama Automatic Titration Apparatus. The ionic strength of the titration system was adjusted with NaCl to 0.5. The molar concentrations of α- and β-carboxyl groups, represented by C_α and C_β, can be calculated from the titration data by the following equation[2]

$$(1/K_\alpha)(K_\alpha + C_{\mathrm{H}^+})\alpha_{\mathrm{d}}^{\mathrm{t}}C_{\mathrm{M}} = C_\alpha + \{K_\beta(K_\alpha + C_{\mathrm{H}^+})/K_\alpha(K_\beta + C_{\mathrm{H}^+})\}C_\beta$$

where K_α and K_β are the dissociation constants of the α- and β-carboxyl groups, respectively, C_{H^+} is the molar concentration of proton, $\alpha_{\mathrm{d}}^{\mathrm{t}}$ is the degree of dissociation of all of the carboxyl groups, and C_{M} is the total carboxyl group concentration. If K_α and K_β are known, C_α and C_β can be respectively determined by means of the intercept and the slope of a straight line which was obtained by plotting $(1/K_\alpha)(K_\alpha + C_{\mathrm{H}^+})\alpha_{\mathrm{d}}^{\mathrm{t}}$ vs. $K_\beta(K_\alpha + C_{\mathrm{H}^+})/K_\alpha(K_\beta + C_{\mathrm{H}^+})$. The values of K_α(3.1 ± 0.1) and K_β(4.2 ± 0.1) used for the determination were the intrinsic dissociation constants at ionic strength of 0.5 for α- and β-carboxyl groups in PAA, which were estimated and discussed previously.[1] The conformity of the above-mentioned plots to a straight line was evaluated by the correlation coefficient, which was more than 0.998 in all analyses.

The summarized analytical results are listed in Table II. The results show that 98% of the authentic α-PAA is composed of α-aspartyl residue. This indicates that the analytical method for α- and β-aspartyl residues in the polymer by the potentiometric titration method is adequately applied to α-PAA(H). However, the analysis indicates that β-PAA(OH) contains 66% of the α-aspartyl residue, and the content of the β-aspartyl residue is smaller than that of the α-aspartyl residue. It was also found that β-PAA(H), which was prepared by the active ester method, consisted of 43% of the β-aspartyl residue. The content of the β-aspartyl residue is again smaller than that of the α-aspartyl residue.

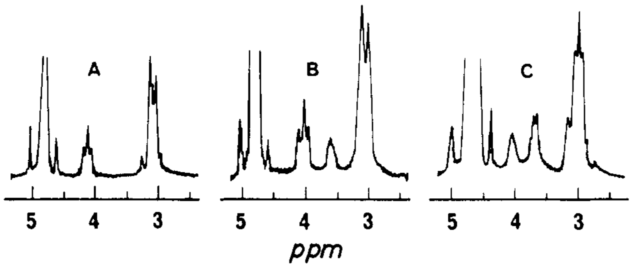

Figure 1. NMR spectra of three PAAs: (A) α-PAA(H) at pD 3.31; (B) β-PAA(OH) at pD 4.16; and (C) β-PAA(H) at pD 3.90. The spectra were measured at 25 °C, using a Hitachi MM-HM-100 instrument.

In order to confirm the structure of β-PAA(H) prepared by the active ester method, the diagram of the potentiometric titration described in the literature[5] was analyzed to determine the ratio of α- and β-aspartyl residues of PAA(H). The results indicate that the β-PAA(H) prepared by Kovâcs et al.[5] also contains 58% of the α-aspartyl residue, and the analytical results of the two preparations (by us and by Kovâcs) agree quite well. In addition, the analytical results obtained by the potentiometric titration method indicate that so called "poly(β-aspartic acid)" is not a pure compound but that the polymer contains a considerable amount of α-aspartyl residue.

In order to confirm further the results obtained by the potentiometric titration, three PAA samples were examined by NMR. All samples were dissolved in D_2O and then lyophilized to perform the H–D exchange. The H–D exchanged samples (50–70 mg) were dissolved in 3 mL of D_2O and the pD was adjusted with NaOD or DCl. The typical examples of NMR spectra are shown in Figure 1. It was found that the chemical shift of the methine groups of β-PAA split into two peaks (3.7 and 4.0 ppm) in the lower pD region. Moreover, the integral ratio of the two peaks was found to be constant in the pD region below 4. The signal at 4.0 ppm corresponds to the methine group of α-PAA; therefore, the signal at 3.7 ppm could be assigned to the methine group of the β-aspartyl residue. The integral ratio of the methine signals for α- and β-aspartyl residues is represented in Table II. These results also indicate that the β-PAAs prepared by two different methods contain a considerable proportion of α-aspartyl residue.

It was found that the β-PAAs are not all β-linked, even when the polymer is prepared by the active ester method which does not involve alkaline hydrolysis of the protecting group. These results could be interpreted as arising from transamidation during the preparation of β-PAA. The detailed study of the transamidation and the synthesis of pure β-PAA are future problems.

Table II
Analyses of α- and β-Aspartyl Residues in PAA

	titration method			NMR method	
sample	α-COOH, mmol/L	β-COOH, mmol/L	α-linkage, %	α-CH, % (4.0 ppm)	β-CH, % (3.7 ppm)
β-PAA(OH)	2.53 ± 0.04	4.90 ± 0.34	66 ± 0	66	33
β-PAA(H)	1.30 ± 0.16	1.71 ± 0.20	57 ± 5	40	60
α-PAA(H)	0.01 ± 0.00	6.10 ± 0.00	98 ± 0	100	0
β-PAA(H)[a]	0.94 ± 0.15	1.30 ± 0.19	58 ± 7		

[a] Obtained from the diagram of the potentiometric titration in ref 5.

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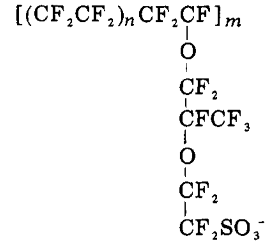
Ion Percolation and Insulator-to-Conductor Transition in Nafion[1] Perfluorosulfonic Acid Membranes[†]

Nafion perfluorosulfonic acid products are made from a copolymer of tetrafluoroethylene (C_2F_4) and a vinyl ether PSEPVE ($CF_2{=}CFOCF_2C(CF_3)FOCF_2CF_2SO_2F$) known as XR resins which are then converted to the ion-exchanged sulfonate form



$$\begin{array}{l}[(CF_2CF_2)_nCF_2CF]_m\\ \qquad\qquad\quad\; | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CFCF_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad O \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CF_2SO_3^-X^+\end{array}$$

by hydrolysis.[2] These materials possess extraordinary electrochemical and mechanical properties and can be used as a membrane separator in a chlor–alkali cell.[2] Their unique transport characteristics are intimately associated with a spontaneous phase separation which occurs in hydrated perfluorosulfonate polymer: the conductive aqueous phase segregates into ion containing clusters which are randomly dispersed in an insulating fluorocarbon matrix.[3,4] In this paper, we apply modern percolation theory[5] to gain insight into the transport processes occurring in this system and identify, for the first time, an (ionic) insulator-to-conductor transition in Nafion. Our theory is very general and can be applied to other ionomeric systems as well.

The percolation theory has been investigated thoroughly and extensively applied.[5] Its salient features can be conveniently illustrated on a two-dimensional grid with some of its sites randomly occupied as shown in Figure 1a–d. For our purposes, empty and occupied sites would correspond to the fluorocarbon and the ion cluster phases, respectively. At low concentrations, ion clusters are well separated into "islands" (cf. Figure 1a) so that macroscopic ion flow from one side of the grid to the other is impossible. At a higher concentration (Figure 1b), these "islands" grow in size and interconnect to form extended pathways. However, crucial links (such as those marked L in Figure 1b) are still missing here and there; thus, long range ion transport is still impossible. Eventually, above a threshold value of occupancy, which is approximately 44% for our two-dimensional example, some of these links have been filled (as shown in Figure 1c) to form conductive channels through which ions can now flow. Hence, an ionic insulator-to-conductor phase transition occurs at this threshold and simultaneously the average size of the extended pathways, which is the correlation length of our phase transition problem, becomes macroscopic. At even higher occupancies (cf. Figure 1d), percolation channels crisscross the grid engulfing dead ends and filling missing links which lead to progressively higher conductivities.

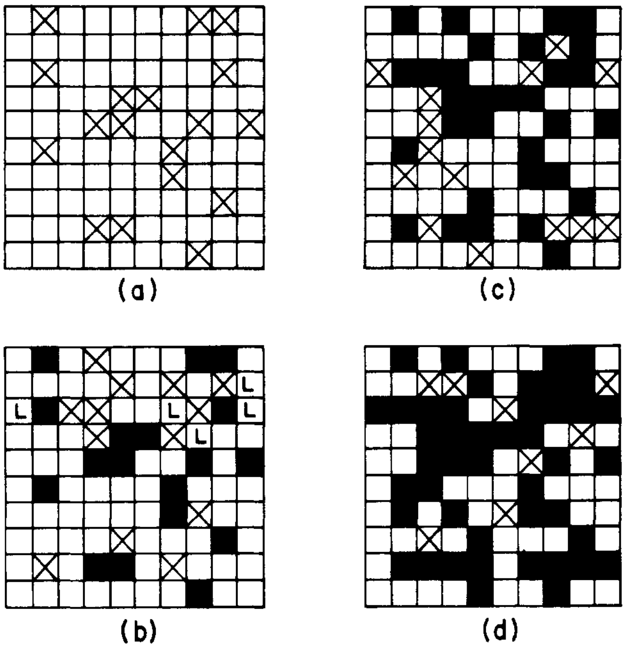


Figure 1. A two-dimensional illustration for the concept of percolation. The shaded and crossed areas correspond respectively to sites that were previously occupied and sites that have just been occupied whereas those marked L in (b) are some empty sites that must be occupied before the onset of ion transport. The percentages of occupancy of the grid for cases (a) to (d) are 18, 31, 45, and 53%, rspectively. For detailed discussions, see text.

The principal conclusion that a threshold value (c_0) exists for the volume fraction (c) of the aqueous phase in the polymer below which ion flow is impossible can be established with the renormalization group technique,[6–8] with a mean field theory (for six dimensions),[9,10] or from numerical computations.[5,11–15] In addition, these analyses showed that above and near the threshold, the conductivity σ obeys a simple power law

$$\sigma = \sigma_0(c - c_0)^n \qquad (1)$$

where the critical exponent n and the prefactor σ_0 are constants. The exponent n is a universal constant which depends on spatial dimensions only and is applicable to any percolative system regardless of its chemical, mechanical, structural, morphological, and statistical properties.[16] For a three-dimensional (3D) system, n was reported to range between 1.3 and 1.7[5,12–15] with 1.5 probably the most reliable value. In contrast, the threshold volume fraction c_0 depends on both the dimensionality and the manner in which the two components are dispersed.[15] For a 3D continuous random system, c_0 is 0.15 according to recent investigations.[14,17,18] It can, however, be larger if ion clusters flocculate into several well-isolated regions;[15] conversely, it may be smaller if they spread out into an

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[†] Contribution no. 2696.