Modeling Ionomer Swelling Dynamics of a Sulfonated Polyphenylene, Pentablock Copolymers, and Nafion

Donghui Wang,[1] Chris J. Cornelius[2]

[1]Envorik, Birmingham, Alabama 68588
[2]Department of Chemical and Bimolecular Engineering, University of Nebraska, Lincoln, Nebraska 68588
Correspondence to: C. J. Cornelius (E-mail: ccornelius2@unl.edu)

ABSTRACT: The water swelling behavior of Nafion, sulfonated poly(phenylene) (sPP), and poly[t-butyl styrene-b-hydrogenated isoprene-b-sulfonated styrene-b-hydrogenated isoprene-b-t-butyl styrene) was studied in order to understand microscopic molecular interactions. Ionomer swelling was modeled using the Flory-Rehner relationship to predict solvent-ionomer interaction parameter (χ_{12}) and effective number of elastically active chains (n). Water swollen PBC had a decreasing χ_{12} from 1.146 to 0.516 when its ion-exchange capacity (IEC) increased from 1.0 to 2.0. Nafion 117 and sPP χ_{12} values were 0.93 and 0.807 at an IEC of 0.91 and 1.8. Polymer water uptake was inversely dependent upon n and IEC or sulfonic acid-group concentration. The following trend was noted for ionomer type, n, and water uptake: PBC-2.0 (159 wt % and 7.89e-4 mol/cm^3) > sPP (48.6 wt % and 1.40e-3 mol/cm^3) > Nafion 117 (23 wt % and 1.24e-3 mol/cm^3). The ionomer's Gibb's total free change (ΔG_{Tot}) due to water swelling for Nafion 117 was -15.3 J, sPP was -28.5 J, and PBC-2.0 was -53.2 J. An empirical equation was created to estimate a material's total solubility parameter (δ); and dispersion (δ_d), dipolar ($\delta_{p'}$), and hydrogen bonding (δ_h) forces. The δ values for Nafion 117, sPP, and PBC-2.0 were 19.9 (J/cm^3)$^{1/2}$, 21.3 (J/cm^3)$^{1/2}$, and 21.0 (J/cm^3)$^{1/2}$. Idealized swelling within an ionomer due to solvent. Ion domains are comprised of fixed sulfonated acid groups (—SO$_3$H) along the polymer's backbone. These functional groups provide interaction sites for molecules to diffusion and swell chains. The total change in free energy ΔG is dominated by ΔG_{mix} that is attributed to hydrogen bonding and the concentration of elastically active chains n, which directly impacts its chemical potential $\Delta \mu$. © 2017 Wiley Periodicals, Inc. J. Polym. Sci., Part B: Polym. Phys. **2017**, 55, 435–443

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INTRODUCTION Ionomer applications in electrochemical devices, such as fuel cells, batteries, and sensors, require a better understanding of the relationships between microscopic interactions and macroscopic ionomer properties related to its ion-exchange capacity (IEC), swelling, solubility parameter (δ), and the effective number of elastically active chains (n). Polymer δ experiments are continually being performed in order to explain and predict interrelationships between physical properties and chemical composition. Hildebrand (1950)[1] and Hansen (1967)[2] developed a group contribution method to predict δ using the material's chemical structure. Flory-Huggins model[3] and Flory-Rehner Theory[4] provide an indirect method to describe polymer swelling. However, δ calculation and predictive methods corresponding to thermodynamic properties, and molecule transport are still needed. These properties may have correlations with a material's rheological and optical properties, molar mass, surface energy, and dielectric constant that are based upon sulfonic acid group concentration.

A group contribution method (GCM) was developed to estimate a material's δ by various investigators such as Hildebrand (1916), Small (1953), Van Krevelen (1965), Hoy (1970), Fedors (1974), and Hoftyzer and Van Krevelen (1976).[5] Hansen[2] advanced this theory by considering the individual δ contributions due to dispersive, polar, and hydrogen bonding forces, which was used to describe the interaction between a polymer and solvent. However, deviations were still observed for predicted δ values using GCM when compared to experimental methods. Several techniques have been used to predict a polymer's δ using swelling,[6] turbidimetric titration,[7] specific volume,[8] intrinsic viscosity,[6] and inverse gas chromatography.[9]

It is generally accepted that an intrinsic relationship exists between polymer properties and its δ parameter. A solution-diffusion model was used by LaPack[10] to correlate molecule transport within particle filled elastomeric membranes with Hildebrand solubility parameters. Ravindra used GCM to

predict chitin and chitosan's δ and compared it with intrinsic viscosity, surface tension, and dielectric constant corresponding to the Flory-Huggins interaction parameter between component one and two (χ_{12}).[11] Lindvig's used Hildebrand Solubility Parameter (HSP) correlations that were coupled with the Flory-Huggins model. This work enabled material predictive results that were independent of molecular structure.[12] Jung showed that dissimilar chemical structures caused large δ differences between a liquid crystal and resin, and high crosslink density within the same polymer-solvent system.[13] Guan showed that surface morphology was impacted by polymer-solvent interactions using solvent-cast sulfonated polyethersulfone (SPES). SPES film surface irregularity decreased with increasingly favorable polymer-solvent interaction for SPES-Dimethylacetamide (DMAc) versus Dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP).[14] Lu used a polystyrene based shape-memory polymer (SMP) and an interactive solvent in order to modulate its shape recovery behavior and glass transition temperature.[15]

Numerous experimental efforts in the literature have explored relationships between polymer solubility and properties. A prior knowledge of an ideal solvent-polymer system corresponding to δ and composition are still needed. In this paper, solubility parameters were evaluated for a series of ionomers using various approaches. These results were used to probe ionomer-swelling relationships corresponding to IEC, composition, chemical potential, n, solvent-polymer interaction, and predicted δ.

THEORY AND MODELS

Hildebrand Solubility Parameter

A substance's cohesive energy (E_{coh}) in a condensed state is defined as the change in its in internal energy per mole of substance (ΔU). This correlation is proportional to the latent heat of vaporization (ΔH_{vap}), universal gas constant (R), and absolute temperature (T), which excludes intermolecular forces (eq 1)[5]

$$E_{coh} = \Delta U \approx \Delta H_{vap} - RT \tag{1}$$

This relationship is directly related to the cohesive energy density (e_{coh}) and proportional to Hildebrand's solubility parameter (δ) and liquid molar volume (V) shown in eq 21

$$\delta = \left(\frac{E_{coh}}{V}\right)^{1/2} \equiv e_{coh}^{1/2} \ @ \ 298 \ K \tag{2}$$

These relationships provide important quantities for characterizing the physical state of a given polymer. The cohesive energy has a significant role associated with describing the interactions between a polymer and solvent.

Three-Component Hansen Solubility Parameter

Hansen proposed an empirical equation that predicts the δ of a polymer in an organic liquid by assuming that δ_d, δ_p, and δ_h represent the energy from dispersion, dipolar, and hydrogen bonding between molecules. These three

parameters can be treated as co-ordinates for a point within a three-dimensional volume known as the Hansen space. The distance between two Hansen parameters in this space is defined as R_a. A geometric-like mean is assumed for the solvent (1) and polymer (2) intermolecular contributions to R_a given by eq. 3

$$R_a = \sqrt{\begin{array}{l} 4(\delta_{d2} - \delta_{d1})^2 \\ + (\delta_{p2} - \delta_{p1})^2 \\ + (\delta_{h2} - \delta_{h1})^2 \end{array}} \tag{3}$$

In order to validate the solvent and polymer prediction, an interaction radius (R_0) is attributed to the substance being dissolved. R_0 is the maximum affinity difference associated with good solvent-polymer interactions. This value determines the Hansen space sphere's radius defined by δ_d, δ_p, and δ_h. The relative energy difference (RED) of this system is the ratio R_a and R_0 given by eq 4

$$RED = R_a / R_0 \tag{4}$$

RED < 1 system will dissolve

RED = 1 system partially dissolve

RED > 1 system will not dissolve

Indirect Method-Swelling

Several experimental techniques have been used to determine a polymer's δ. Indirect test methods include solvency screening, turbidimetric titration, inverse gas chromatography, Matrix Assisted Laser Desorption Ionization (MALDI), dilute polymer solution properties corresponding to a solution's osmotic pressure; and polymer swelling, specific volume, intrinsic viscosity[16]

Polymer Theory

The Flory-Huggins Solution Theory[3] is a statistical thermodynamic relationship used to describe a polymer solution. The Gibb's free energy of mixing (ΔG_{mix}) relationship takes into account molecule size differences, number of solvent (n_1), and polymer molecules (n_2), solvent (ϕ_1), and polymer (ϕ_2) volume fractions, and χ_{12}. The entropy of mixing ($\Delta S_{mix} = k[n_1 \ln \phi_1 + n_2 \ln \phi_2]$), and enthalpy of mixing ($\Delta H_{mix} = kTn_1\phi_2\chi_{12}$) contributions to ΔG_{mix} summarized by eq 5.

$$\Delta G_{mix} = kT[n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2 \chi_{12}] \tag{5}$$

The change in free energy associated with stretching a polymer chain within a swollen network is defined as ΔG_{elas} (eq 6). This relationship accounts for the effective number of chains within the network referred to as v_e. This network may consist of chain entanglements and/or crosslinking.

$$\Delta G_{elas} = \frac{3}{2}kTv_e\left[\phi_2^{-2/3} + \frac{1}{3}\ln\phi_2 - 1\right] \tag{6}$$

If the total ion concentration within an ionomer matrix is C_{Ti} and solvent molar volume is V_1 then its ion-free energy is
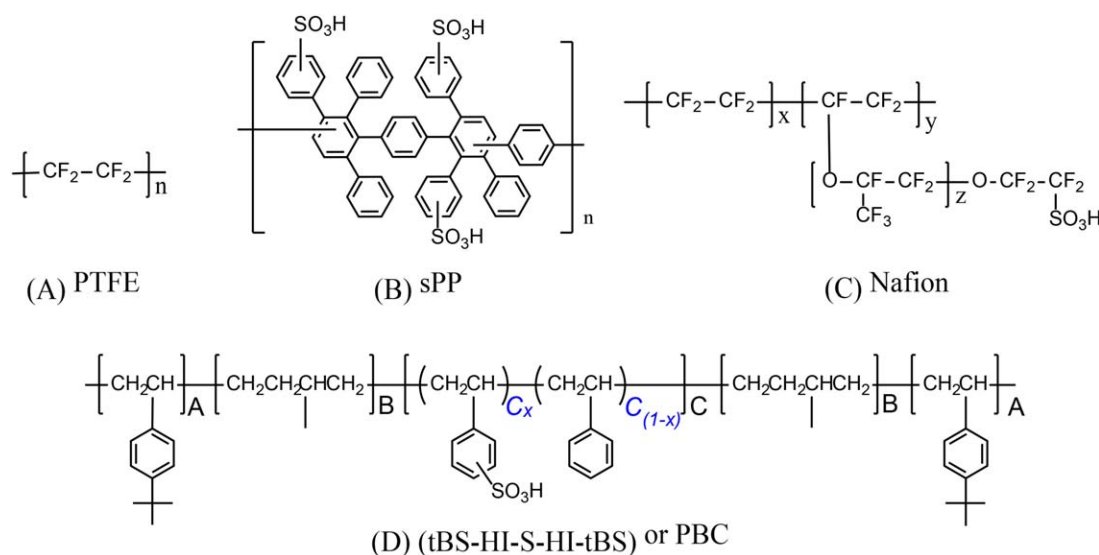
FIGURE 1 Polymer structures. [Color figure can be viewed at wileyonlinelibrary.com]

given by eq 7. This generates an osmotic force within the film due to an ion or solution concentration difference within film versus bulk solution.

$$\Delta G_{\text{ion}} = kTV_1 C_T r_2 n_2 \ln \frac{1}{\phi_2} \tag{7}$$

The χ_{12} parameter is proportional to the energy associated with dispersing polymer and solvent molecules amongst each other. A solvent coordination number z and monomer-solvent contact energy Δw is used to describe χ_{12}. This can predict an ideal polymer-solvent system based upon the solvent's molar volume (V_s), and solubility parameter differences between solvent (δ_1) and polymer (δ_2). This relationship is directly proportional to ΔH_{mix} shown in Fig. 8.

$$\chi_{12} = \frac{z\Delta w}{RT} = \frac{\Delta H_{\text{mix}}}{RTn_1\phi_2} = \frac{V_s(\delta_1-\delta_2)^2}{RT} \tag{8}$$

This correlation only describes "weakly" interacting molecules that have negligible hydrogen bonding and little to no ionic interactions. Unfortunately, ionomers are "highly" charged materials that preclude this relationship from being used to predict χ_{12} using δ parameters.

Flory-Rehner Equation

The Flory-Rehner equation[4] is used to describe polymer equilibrium swelling by a liquid.[4]b The process is described using n, ϕ_2, and χ_{12}. The theory considers forces arising from ΔH_{mix} and ΔS_{mix} that impacts polymer chain confirmation, and the polymer chain's elastic force (ΔG_{elas}). This correlation is given by eq 9,(17 and 18)

$$-\left[\ln(1-\phi_2)+\phi_2+\chi_{12}\phi_2^2\right] = V_1 n\left[\phi_2^{\frac{1}{3}}-\frac{\phi_2}{2}\right] \tag{9}$$

The total free energy (ΔG_{Tot}) associated with mixing a polymer and solvent is made up of ΔG_{mix}, ΔG_{elas}, ΔG_{ion}, and

polymer chain electrostatic interactions (ΔG_{elec}). Typically, ΔG_{elec} is very small compared to ΔG_{ion}, which leads to it being considered negligible. The overall relationship is given by eq. 10

$$\Delta G_{Tot} = \Delta G_{mix} + \Delta G_{elas} + \Delta G_{ion} + \Delta G_{elec} \tag{10}$$

The ΔG_{elas} term is primarily governed by polymer chain elastic restraining forces due to entanglements or crosslinks, which limits swelling. These forces are entropic in nature because polymer chain stretching reduces the number of available chain conformations. The elastic contribution to the chemical potential is determined from the statistical theory of rubber elasticity. The elastic free energy depends upon the number of polymer chains in the network and linear expansion factor (α). The total mobile ion concentration (C_T) within this system and its total change due to swelling is given by $\Delta C = \phi_2 C_T$. The total system chemical potential ($\Delta\mu_{Tot}$) at equilibrium is comprised of mixing, elastic, and ion forces. This is represented as $\Delta\mu_{mix}$, $\Delta\mu_{elas}$, and $\Delta\mu_{ion}$ given by eqs (11–13).

$$\Delta\mu_{mix} = kT\left[\ln(1-\phi_2)+\phi_2+\chi_{12}\phi_2^2\right] \tag{11}$$

$$\Delta\mu_{elas} = kTV_1 n\left(\phi_2^{\frac{1}{3}}-\frac{1}{2}\phi_2\right) \tag{12}$$

$$\Delta\mu_{ion} = kTV_1\Delta C \tag{13}$$

EXPERIMENTAL

Materials

The polymers studied in this work are shown in Figure 1. These materials are the following: polytetrafluoroethylene (PTFE), perfluorosulfonic acid ionomer (PFSA), sulfonated poly(phenylene) (sPP)[19], and poly[*t*-butyl styrene-*b*-hydrogenated isoprene-*b*-sulfonated styrene-*b*-hydrogenated isoprene-*b*-*t*-butyl styrene) (tBS-HI-S-HI-tBS).[20]a The tBS-HI-S-

TABLE 1 Nafion, sPP, and PBC[20]b film properties

	IEC (mmol/g)	Density (g/cm^3)	V_m (cm^3/mol)	C_T (mmol/cm^3)	M_w (g/mol)	Thickness (μm)	Processing Method
NF117	0.91	1.98	550	1.80	10^5–10^6	178	Melting extrusion
NF115	0.91	1.98	550	1.80	10^5–10^6	127	Melting extrusion
NF212	0.91	1.98	550	1.80	10^5–10^6	50.8	Solution dispersion
sPP	1.80	1.25	800	2.24	1.72×10^5	39	Scroll casting
PBC-1.0	1.00	1.01	129	1.01	1.0×10^5	50	Solution casting
PBC-1.5	1.50	1.03	128	1.55	1.0×10^5	50	Solution casting
PBC-2.0	2.00	1.06	123	2.12	1.0×10^5	50	Solution casting

Equivalent weight (EW) is the number of grams of dry polymer per mole of sulfonic acid groups when the material is in the acid form.

HI-tBS ionomer is also referred to as pentablock (PBC). The PBC ionomers referenced were prepared, characterized, and provided by Kraton Polymers LLC, Houston, TX.[20] This anionic polymerized ionomer has a middle styrene block that is selectively sulfonated to a desired IEC (milliequivalents of sulfonic acid per gram of polymer).[20]a PTFE was purchased from VWR International, LLC (catalog NO.89026-098). The PFSA materials were a family of Nafion films with the following properties: NF115, NF117, and NF212. These films were supplied from Ion Power, Inc. The sPP film's synthesis and properties have been previously documented.[19] The ionomer properties are summarized in Table 1.

METHODS

Membrane Preparation
PBC[20] films with an IEC equal to 1.0, 1.5, and 2.0 were solution-cast from THF, CHCl$_3$, and equal volume ratio (1:1) of cyclohexane:heptane (CH). Solutions were covered in a Teflon dish to control the rate of evaporation over a 24 h period at 25 °C. sPP films were formed using a scroll casting method. Nafion films were either melt extruded or created from a solution-dispersion (Table 1).

Solvent Weight Uptake
Nafion, PBC, and sPP films were pretreated in 1 M sulfuric acid and rinsed with DI water. All films were dried in a vacuum oven overnight prior to storing and testing. Treated films were exposed to various solutions, ethanol (EtOH), ethylene glycol (EG), de-ionized water to 18 MΩ (DI H$_2$O), and vol % mixtures of EtOH/EG (100/0, 90/10, 80/20,70/30, 10/90 vol %) and EG/water (0/100, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10, 100/0). These mixtures were used to modulate the bulk solution apparent solubility parameter δ. Film mass changes during swelling were used to calculate solvent weight uptake.

Volumetric Swelling
Nafion, PBC, and sPP films were pretreated in 1 M sulfuric acid and rinsed with DI water. All films were dried in a vacuum oven overnight at room temperature (~25 °C) prior to storing and testing. Volumetric swelling changes were measured using a dry 2 cm × 2 cm film was placed within an

optical transparent container. The process of exposing a film to DI water and its subsequent swelling as a function of time was videoed, and the dimensional changes were measured with software from MB-Ruler. The overall water swelling process for Nafion 117 or N117 is shown in Figure 2.

RESULTS AND DISCUSSION

Solubility Parameter from Direct Measurement
The N115, N117, N212, and sPP swelling behavior in solutions of EtOH/EG and EG/H$_2$O were used in order to predict δ. N117 and N115 had a mass uptake of 76.0 wt % and 64.2 wt % using pure EtOH, respectively. The variation between these two ionomers with the same IEC is attributed to film processing that would cause a deviation in the orientation and spatial distribution of sulfonic acid groups (—SO$_3$H) due to film thickness. N117 and N115 pure water and EG uptake properties were nearly identical with values ranging between 21.2 wt % (N115 and EG) and 23.1% (N117 and water). These lower values imply that their δ parameters are not 34.9 (J/cm^3)$^{1/2}$ (EG) or 47.9 (J/cm^3)$^{1/2}$ (water). N212 had similar pure EG and water mass uptake values as N117 and N115. However, extreme film swelling was observed using neat EtOH that had a mass uptake of
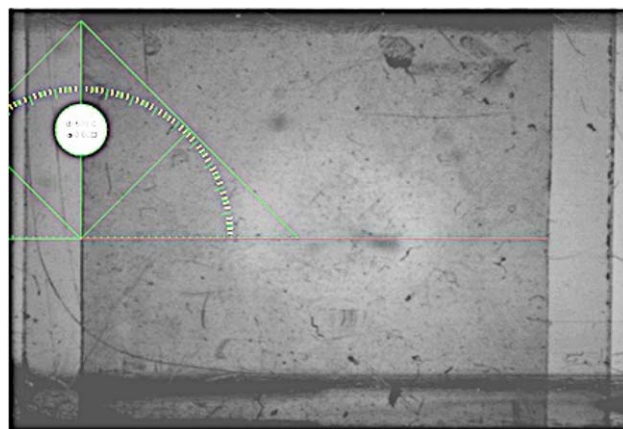

FIGURE 2 Nafion 117 swelling versus time video for measurement using MB-Ruler software. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Polymer solvent uptake

Polymer	Ethanol (wt %)	EG (wt %)	Water (wt %)
NF117	76.0	21.8	23.1
NF115	64.2	21.2	22.5
NF212	344	23.0	22.1
sPP	50.4	373	48.6

344 wt %. This change suggests that N212 has a δ close to 26.3 $(J/cm^3)^{1/2}$ (EtOH). sPP had slightly larger water and EtOH swelling than N117 and N115 with mass uptakes of 50.4 wt % and 48.6 wt %. Its mass uptake was 373 wt % when immersed in pure EG, which suggests its δ parameter is near EG at 34.9 $(J/cm^3)^{1/2}$. The mass uptake results for these ionomers are summarized in Table 2.

A swelling experiment with sPP was done to approximate δ using EtOH/EG and EG/H$_2$O solutions (Methods Section). Utilizing these idealized solutions, the swelling results for sPP are shown in Figure 3.

EG/EtOH and EG/H$_2$O solutions with predicted δ parameters of 30.5 $(J/cm^3)^{1/2}$ and 27.5 $(J/cm^3)^{1/2}$ had that largest mass uptakes of 1020 wt % and 167 wt %. Extrapolating this mass uptake curve provides an estimated value of 29.3 $(J/cm^3)^{1/2}$ for sPP. As previously noted, it is expected that mixed solutions of EG/water and EG/EtOH will partition within an ionomer film such that its concentration is not equivalent to the bulk. Consequently, the predicted δ of this solution would be difficult to determine without measuring it. Furthermore, such an experiment cannot take into account solvent and ionomer
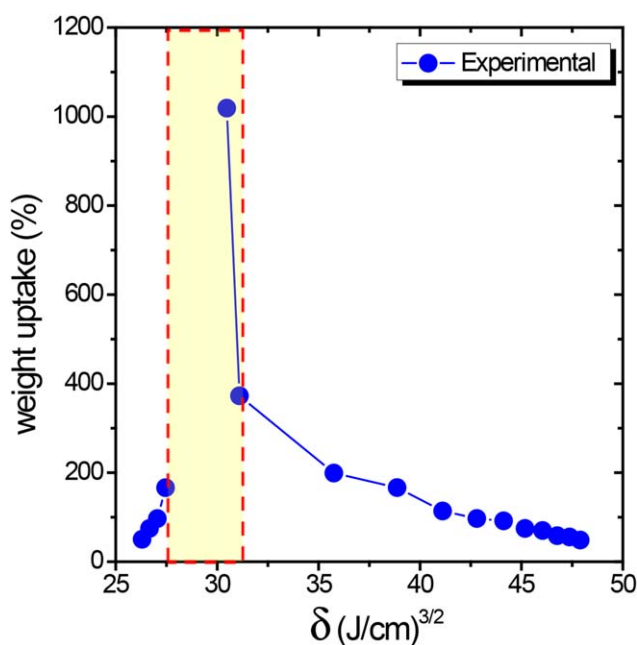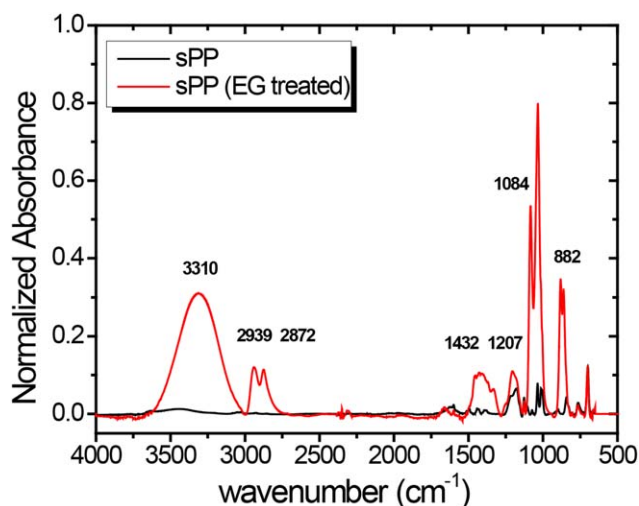
FIGURE 4 FTIR of sPP before and after exposure to EG and its subsequent swelling. [Color figure can be viewed at wileyonlinelibrary.com]

coupling through hydrogen bonding, and interchain interactions due to charged groups.

In order to determine if EG-sPP interactions were occurring within sPP, FTIR was used to characterize functional group changes within it due to exposure to EG. Two phenyl group peaks at 700 and 764 cm^{-1} were used to normalize sPP absorption shown in Figure 4. The swollen films revealed an increased functional group intensity at wavenumber 3310 cm^{-1} (—OH), which is associated with hydrogen bonding between the more basic —OH group within EG and acidic group —SO$_3$H. The —CH$_2$ bending, stretching, and rocking within EG were observed at 2939 cm^{-1} and 1432 cm^{-1} (—CH$_2$ bending); 2872 cm^{-1} (—CH$_2$ stretching), and 882 cm^{-1} (—CH$_2$ rocking) are clearly visible. The numerous phenyl groups within sPP underwent several notable Δ wavenumber changes when exposed to EG. The C—C decreased 3 cm^{-1} from 1387 cm^{-1}, =C—H decreased 16 cm^{-1} from 897 cm^{-1}, and the conjugated aromatic groups increased 8 cm^{-1} from 1625 cm^{-1}. The substituted phenyl groups peaks all increased 18 cm^{-1}, 7 cm^{-1}, and 3 cm^{-1} from their initial wave numbers at 843 cm^{-1}, 757 cm^{-1}, and 697 cm^{-1}. These changes are attributed to the swollen material, interaction with solvent, and new environment created for sPP. The peak assignments for sPP are summarized in (Table 3). This result reveals that EG and sPP has significant hydrogen bonding occurring between the basic —OH group within EG and the ionomer's —SO$_3$H group. In addition to this interaction, the aromatic backbone is believed to affect polymer chain and solvent molecule interactions due to configurational entropy changes caused by swelling and interchain interactions.

δ Estimated from Surface Energy

The surface energy (γ) and δ_{Tot} were evaluated for PTFE, Nafion (N117 and N115), PBC-1.0, PBC-1.5, PBC-2.0, and sPP determined based upon eqs (14–16). The total solubility parameter δ_{Tot} was modeled by predicting δ_d, δ_p, and δ_h using the polymer's dispersive and polar forces (γ_d and γ_p),

FIGURE 3 EtOH/EG and EG/H$_2$O solution δ versus its weight uptake by sPP. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Absorption peaks of sPP and sPP treated in the EG

Polymer	Phenyl Group					-SO₃	C-S	O-H	C-O	-CH₂
	C=C	C-C	Conj.	Sub.	=C-H					
sPP	1492–1435	1387	1625–1594	843, 757, 697	3047, 3018, 897	1182, 1033, 1128	1014, 1005	3645, 1594	1207–1084	2939, 2872, 886, 1432
sPP (EG)	1486–1454	1384	1633–1599	861, 764, 700	3047, 3018, 881	1182, 1034, 1128	1014, 1005	3310	1000–1260	2850–3000 (stretch), 882 (rocking), 1350–1480 (bend)
EG Water								3200–3550, 3651 (sym H₂O), 1595 (bend H₂O)		

3b demonstrates three bands.

its average molar volume based on mole fraction (V_m), enthalpy associated with H-bonding is E_h, and empirical constants A and B.

$$\delta_d^{\frac{2}{3}} = A\left(\frac{1}{V_m}\right)^{\frac{1}{3}}\gamma_d \tag{14}$$

$$\delta_p^{\frac{2}{3}} = B\left(\frac{1}{V_m}\right)^{\frac{1}{3}}\gamma_p \tag{15}$$

$$\delta_h = \sqrt{\frac{E_h}{V_m}} \tag{16}$$

A empirical correlation was created in order to predict δ_d, δ_p, and δ_h for PTFE, Nafion (N117 and N115), PBC-1.0, PBC-1.5, PBC-2.0, and sPP using the polymer's γ and δ. This relationship was based upon Jia's work,[21] which used a solvent's and polymer's δ and γ to make property predictions independent of its V_m, or knowledge of constants A or B. This relationship was created by plotting γ_d versus $\gamma_d/\delta_d^{2/3}$, and γ_p versus $\gamma_p/\left(\delta_p^2+\delta_h^2\right)^{1/3}$. In similar fashion, we used experimental results from the literature based upon 37 solvents and 22 polymers with known γ_d, γ_p, and δ[21]; and 46 polymers with known δ_d, which are plotted in Figures 5(a,b). This data was fit with eqs 17 and 18

$$\frac{\gamma_d}{\delta_d^{\frac{2}{3}}} = 0.1322\gamma_d + 0.5231 \tag{17}$$

$$\frac{\gamma_p}{\left(\delta_p^2+\delta_h^2\right)^{\frac{1}{3}}} = 0.142\gamma_p + 0.1913 \tag{18}$$

The experimental values for γ_d and γ_p were previously determined by Wang and Cornelius for PTFE (γ_d = 16.9 mJ/cm² and γ_p = 0 mJ/m²), N117 (γ_d = 16.8 mJ/m² and γ_p = 4.86 mJ/m²), PBC-1.0 (γ_d = 14.4 mJ/m² and γ_p = 4.87 mJ/m²), PBC-1.5 (γ_d = 16.1 mJ/m² and γ_p = 5.94 mJ/m²), PBC-2.0 (γ_d = 13.9 mJ/m² and γ_p = 9.5 mJ/m²), and sPP (γ_d = 13.2 mJ/m² and γ_p = 12.2 mJ/m²). These results were used to predict δ_d, δ_p, and δ_h.[22]

The predicted δ_d, δ_p, δ_h, and δ_{Tot} for PTFE, N117, PBC-1.0, PBC-1.5, PBC-2.0, and sPP are shown in Figure 6. Their overall solubility parameter δ_{Tot} for PTFE, NF117, PBC-1.0, PBC-1.5, and PBC-2.0 was compared with experimental results from the literature and determined experimentally.[22] The δ_{Tot} results were quite good for all these materials except sPP. This exception may be due to the spatial configuration of sulfonic acid groups within sPP, but regardless of this speculation, additional work is necessary for this material. It was surprising that the dispersive component δ_d for all these polymers changed very little with composition or IEC. Their values varied between 14.0 (J/cm³)^{1/2} (sPP) and 15.2 (J/cm³)^{1/2} (PTFE) for very compositionally different polymers. The average δ_d value for these materials is 14.6 (J/cm³)^{1/2}.

The predicted δ_h for sPP was the highest of this series at 10.8 (J/cm³)^{1/2}. Its δ_p energy was 11.8 (J/cm³)^{1/2}, which is

FIGURE 5 (A) $\gamma_d/\delta_d^{\frac{2}{3}}$ versus γ_d, and (B) $\gamma_p/\left(\delta_p^2+\delta_h^2\right)^{1/3}$ versus γ_p for a series of polymers. [Color figure can be viewed at wileyonline-library.com]

nearly equal to PBC-1.0 (12.0 $(J/cm^3)^{1/2}$). The PBC series δ_h increased with IEC from 4.94 $(J/cm^3)^{1/2}$ (PBC-1.0) to 7.81 $(J/cm^3)^{1/2}$ (PBC-2.0) due to increasing sulfonic acid group concentration that leads to greater hydrogen bonding. Its δ_p magnitude improved with $-SO_3H$ concentration (IEC) that led to an elevation in its value from 12.0 $(J/cm^3)^{1/2}$ (PBC-1.0) to 13.2 $(J/cm^3)^{1/2}$ (PBC-2.0). N117 had values from 15.1 $(J/cm^3)^{1/2}$, 8.87 $(J/cm^3)^{1/2}$, and 9.43 $(J/cm^3)^{1/2}$ for its predicted δ_d, δ_p, and δ_h. One of the major differences between PTFE and N117 is the addition of the $-SO_3H$ group. This group increases its polarity and ability to hydrogen bond. The only solubility parameter term associated with PTFE are dispersion forces that produce a δ_d of 15.2 $(J/cm^3)^{1/2}$. The principal differences between sPP, PBC, and N117 are associated with greater

acidity of a fluorosulfuric acid versus an aromatic one, and low surface energy functional groups $-CF_2CF_2-$ within its backbone. This lower surface energy group is not present in the hydrocarbon based membranes sPP and PBC.

Flory-Rehner Equation and Ionomer Properties

Ionomer Swelling in Water and N

Ionomer chains involved with water swelling are influenced by various factors such as film processing method used to control its thickness, ion group concentration (IEC), and ionomer composition. The n for an ionomer is assumed to be equal to $n=IEC*density*\phi_2$ (mol/cm^3). Because the active chain density of these ionomers is known, the Flory-Rhener eq. 9 was used to predict χ_{12} for NF117, NF115, NF212, PBC-1.0, PBC-1.5, PBC-2.0, and sPP summarized in Table 4. The value for n was rather constant for NF117, NF115, and NF212 with a value ranging between 1.24e-3 mol/cm^3 and 1.32e-3 mol/cm^3, which is a 6% variation. The predicted χ_{12} parameter for NF117, NF115, and NF212 were 0.930, 0.941, and 0.944.

Interestingly, the approximately constant n and χ_{12} for the series of Nafion had similar water uptakes ranging from 22.1 wt % to 23.1 wt % (4% variation). This similar behavior for N212 with N117 and N115 is attributed to the
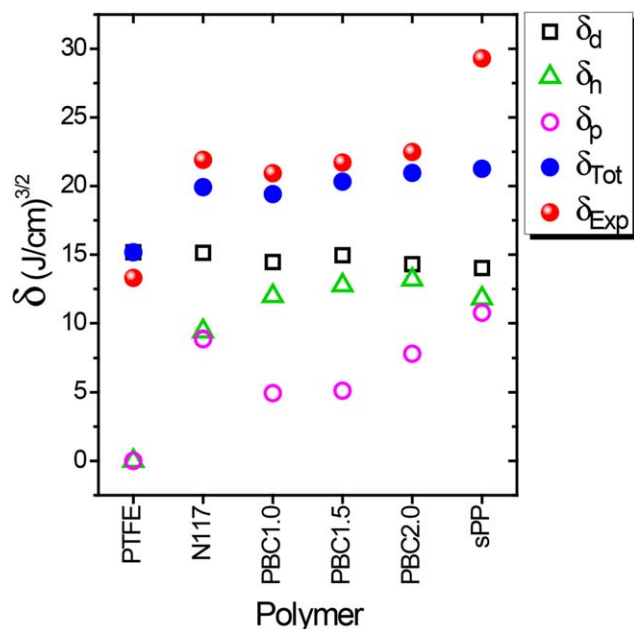

FIGURE 6 Predicted δ_d, δ_p, δ_H, and δ_{Tot} for the following polymers. [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 4 Ionomer water swelling, n, ϕ_2, and χ_{12}

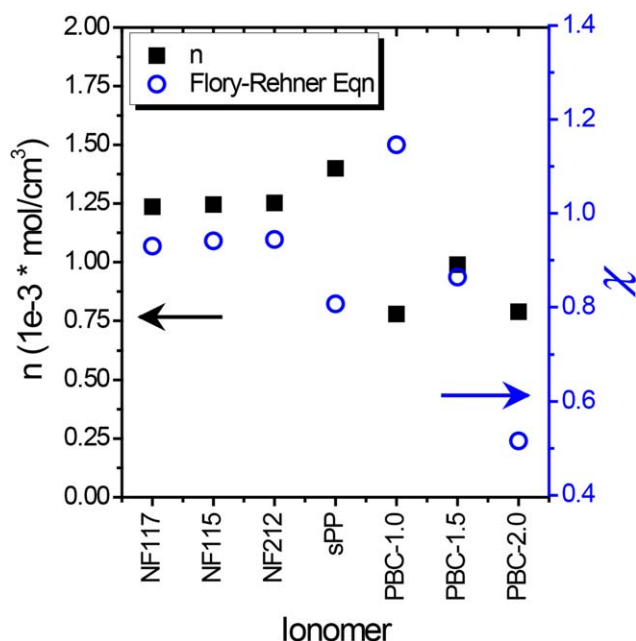| Ionomer	WU wt (%)	ϕ_2 vol. frac.	n (wet) mol/cm^3	χ_{12}
NF117	23.1	0.686	1.24e-03	0.930
NF115	22.5	0.691	1.25e-03	0.941
NF212	22.1	0.695	1.25e-03	0.944
sPP	48.6	0.622	1.40e-03	0.807
PBC-1.0	29.4	0.771	7.79e-04	1.146
PBC-1.5	54.4	0.640	9.89e-04	0.864
PBC-2.0	159	0.372	7.89e-04	0.516

WU = water uptake.

FIGURE 7 Ionomer n and χ_{12} properties due to swelling in water. [Color figure can be viewed at wileyonlinelibrary.com]

processing method that relies upon solution-casting it. This method is known to alter the arrangement of polymer chains and clustering of ionic groups. Consequently, while this film should have much greater swelling, it is approximately the same as these lower IEC PSFA ionomers. The general relationship between n and χ_{12} are shown in Figure 7.

The PBC series had increasing water uptake with –SO_3H concentration (IEC) that ranged from 29.4% (PBC-1.0) to 159% (PBC-2.0). This dramatic change led to an equivalent decrease in χ_{12} for PBC-1.0 (1.146), PBC-1.5 (0.864), and PBC-2.0 (0.516) that is attributed to the sulfonated group that improved its affinity for water. The change in IEC caused significant swelling that caused n to decrease between PBC-1.5 (9.91e-4 mol/cm^3) and PBC-2.0 (7.89e-4 mol/cm^3). This is attributed to excessive volumetric changes within PBC-2.0 that alters the sulfonated concentration density within the swollen matrix. The sPP film had the highest swelling and greatest number of network chains n involved in the swollen material, which is attributed to its high IEC (1.8 mmol/g). Its χ_{12} value was 0.807, which is close to PBC-1.5 (0.864). This similarity in χ_{12} value was also accompanied by similar water uptakes for PBC-1.5 (54.4 wt %) and sPP (48.6 wt %). These results support that polymer processing and composition had a larger role in its swelling properties.

Swelling and Chemical Potential

ΔG_{Tot} and $\Delta \mu_{Tot}$ can be used study ionomer swelling in water or other solvent. Polymer swelling involves a molecule overcoming the cohesive energy density of polymer chains with the release of energy. This is typically characterized by ΔG_{mix} that is balanced with ΔG_{elas} and ΔG_{ion} forces. This total event must provide sufficient energy for polymer chain reptation, stretching, and dissociation that accompanies swelling. This process was characterized for N117, NF115, NF212, sPP, PBC-1.0, PBC-

1.5, and PBC-2.0 shown in Figure 8. The dominant part of ΔG_{Tot} associated with swelling is ΔG_{mix}. While the terms for ΔG_{el} and ΔG_{ion} were all positive, their magnitudes were more than an order of magnitude smaller than ΔG_{mix}. These were forces ranged between 0.4 and 1.7 J for ΔG_{ion}, and 0.9 and 4.9 J for ΔG_{elas}. The ΔG_{mix} for NF117 (−16.5 J), NF115 (−16.3 J), and NF212 (−16.2 J) were nearly identical and varied by less than 2%. The PBC series had an increasingly negative ΔG_{mix} with IEC concentration for PBC-1.0 (−23.9 J), PBC-1.5 (−35.1 J), and PBC-2.0 (−59.8 J). This result clearly shows that increasing sulfonic acid group concentration enhances its compatibility with water. sPP had a ΔG_{mix} of −31.5 J, which is similar to PBC-1.5 that was found for water swelling and predicted χ_{12}.

At equilibrium, $\Delta \mu_{Tot}$ for ionomer swelling is zero for all these ionomers. Their individual contributions $\Delta \mu_{mix}$, $\Delta \mu_{elas}$, and $\Delta \mu_{ion}$ are shown in Figure 9 as a function of n. The change in $\Delta \mu_{mix}$ is the dominant part of this equilibrium process, which is balanced with $\Delta \mu_{elas}$ and $\Delta \mu_{ion}$. A linear $\Delta \mu_{elas}$ and $\Delta \mu_{ion}$ versus n was found for this ionomer series that had the following trend: PBC-1.0 > PBC-2.0 > PBC-1.5 > NF117 > NF115 > NF212 > sPP. In a similar fashion, became more negative in reverse order in order to balance these changes and system maintain equilibrium (PBC-1.0 < PBC-2.0 < PBC-1.5 < NF117 < NF115 < NF212 < sPP). This reveals that the concentration of n, which is a function of the sulfonic acid group concentration, is incredibly important in these ionomer systems. In general, the ionomer's elastic forces limit the extent of swelling. These forces are entropic in nature and reduce the number of available chain conformations. sPP has the largest value for n, which creates the greatest elastic restraining forces. In contrast to sPP, PBC is too flexible. Overall, the PBC series had slightly lower values for $\Delta \mu_{mix}$, $\Delta \mu_{elas}$, and $\Delta \mu_{ion}$ as compared to
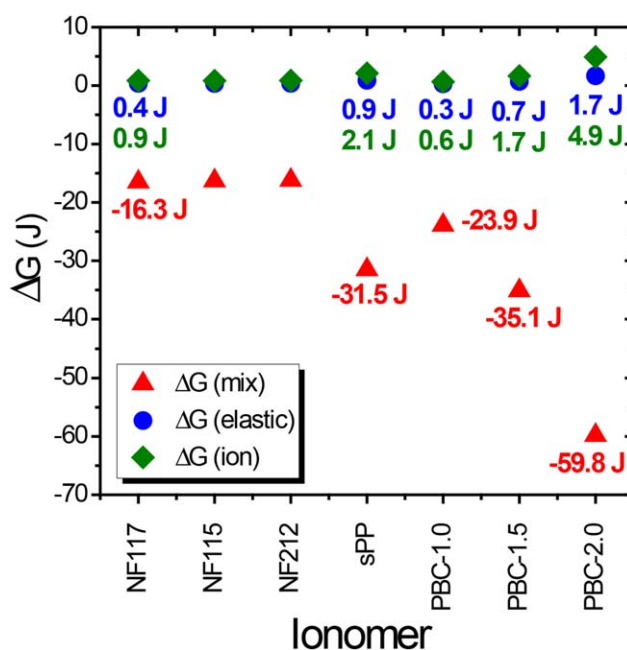

FIGURE 8 ΔG changes due to water swelling versus NF117, NF115, NF212, sPP, PBC-1.0, PBC-1.5, and PBC-2.0. [Color figure can be viewed at wileyonlinelibrary.com]
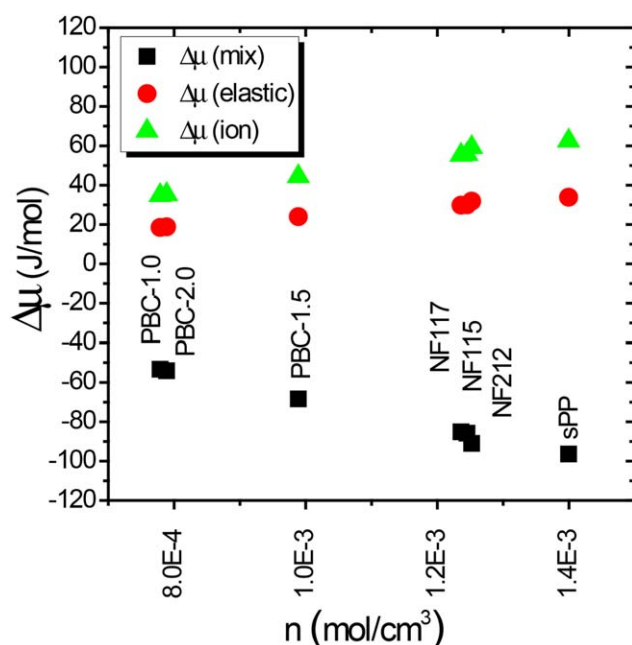
FIGURE 9 $\Delta\mu$ changes due to water swelling versus n for NF117, NF115, NF212, sPP, PBC-1.0, PBC-1.5, and PBC-2.0. [Color figure can be viewed at wileyonlinelibrary.com]

the Nafion series and sPP. These differences are attributed enhanced mixing due to the composition of the PBC chain that contains a flexible hydrogenated isoprene group (HI) that has a T_g below room temperature (-40 °C). This would reduce the polymer chain elastic forces needed to resist swelling by their recoiling forces attempting to increase configurational entropy. Finally, it is apparent that n, IEC, ionomer composition, and film processing has a large impact upon its swelling properties.

CONCLUSIONS

Numerous research efforts have focused on creating correlations describing a material's solubility parameter, and its physical properties. The ionomer properties of PTFE, NF117, NF115, NF212, sPP, PBC-1.0, PBC-1.5, and PBC-2.0 were studied with regard to swelling. Several predictive methods were found to predict their solubility parameter δ using HSP and solvent swelling. The Flory-Huggins and Flory-Rehner relationships were used to predict their χ parameter in order to determine δ_d, δ_p, δ_h, ΔG_{mix}, ΔG_{el}, ΔG_{ion}, $\Delta\mu_{mix}$, $\Delta\mu_{elas}$, and $\Delta\mu_{ion}$. The results revealed that swelling is highly dependent upon the concentration of elastically active chains n within an ionomer network. This relationship scaled linearly with changes in $\Delta\mu_{mix}$, $\Delta\mu_{el}$, and $\Delta\mu_{ion}$. This result reveals that n and its relationship to swelling within an ionomer is incredibly important. Furthermore, the Gibb's free energy of mixing ΔG_{mix} was the most significant factor associated with water swelling, which becomes increasingly negative with $-SO_3H$ concentration (IEC) within an ionomer. Finally, the individual contributions of δ_d, δ_p, and δ_h were predicted using HSP and compared to

experiment. The results revealed that δ_p and δ_h are dependent on sulfonated acid group concentration, but the dispersive component δ_d was nearly constant for this series of materials. While not investigated in this work, ionomer morphology and the spatial distribution of functional groups is anticipated to impact the interactions between solvent and polymer.

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