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Size-exclusion chromatography of perfluorosulfonated ionomers

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ABSTRACT

A size-exclusion chromatography (SEC) method in N,N-dimethylformamide containing 0.1 M $LiNO_3$ is shown to be suitable for the determination of molar mass distributions of three classes of perfluorosulfonated ionomers, including Nafion®. Autoclaving sample preparation is optimized to prepare molecular solutions free of aggregates, and a solvent exchange method concentrates the autoclaved samples to enable the use of molar-mass-sensitive detection. Calibration curves obtained from light scattering and viscometry detection suggest minor variation in the specific refractive index increment across the molecular size distributions, which introduces inaccuracies in the calculation of local absolute molar masses and intrinsic viscosities. Conformation plots that combine apparent molar masses from light scattering detection with apparent intrinsic viscosities from viscometry detection partially compensate for the variations in refractive index increment. The conformation plots are consistent with compact polymer conformations, and they provide Mark–Houwink–Sakurada constants that can be used to calculate molar mass distributions without molar-mass-sensitive detection. Unperturbed dimensions and characteristic ratios calculated from viscosity–molar mass relationships indicate unusually free rotation of the perfluoroalkane backbones and may suggest limitations to applying two-parameter excluded volume theories for these ionomers.

1. Introduction

Polyfluorosulfonated ionomers are copolymers of tetrafluorethylene and sulfonic acid-functionalized (SO_3H) perfluorinated vinyl ethers. DuPont™ developed and commercialized the first perfluorosulfonated ionomer, Nafion® [1], in the mid 1960s. Subsequently, other companies introduced related materials including those shown in Scheme 1. Nafion was originally used in spacecraft fuel cells, and later found applications as membrane materials for the electrolysis production of chlorine and sodium hydroxide, in the production of high purity oxygen and hydrogen, in super-acid catalysis, in the purification of precious metals, in sensors and in a variety of electrochemical applications. Studies on the structure, properties and applications of perfluorosulfonated ionomer membranes were reviewed in 1996 [2] and the state of understanding of Nafion was reviewed in 2004 [3]. In recent years the greatest interest in perfluorosulfonated ionomers has again been for use in fuel cells as a proton conducting polymer in the electrode and separator membrane layers.

The perfluorinated portion of these ionomers imparts exceptional thermal and chemical stability, while the ionic functionality, introduced by the conversion of pendant sulfonyl fluorides ($-SO_2F$) to $-SO_3H$ groups, results in solid-state morphology that provides high proton conductivity. The copolymer composition is expressed in terms of equivalent weight (EW), equal to grams of ionomer per mole of sulfonic acid groups. EW values typically range between EW = 650–1100. Depending on ionomer structure, this corresponds to 13–21 mole% (33–57 wt%) of functionalized comonomer. Ionomer dispersions are prepared at elevated temperatures and pressures at 5–28 wt% ionomer in water/alcohol or water alone. The dispersions can then be cast into membrane materials. Moore and Martin [4] discovered that membrane materials fabricated by simple air drying of Nafion dispersions were soluble in common organic solvents. If instead the dispersion was solvent-exchanged using DMSO or DMF, taken to dryness and then heated at temperatures greater than 100 °C, insoluble membranes with good mechanical properties were obtained.

Aqueous/alcohol perfluorosulfonic acid dispersions of the ionomers form rod-like [5,6] and ribbon-like [7] aggregate structures with perfluorocarbon cores and dissociated sulfonic acid ionic groups exposed to the solvent phase [8]. The influence of ionomer molar mass on the aggregate structure, which in turn influences membrane solid-state morphology, is not fully understood. This

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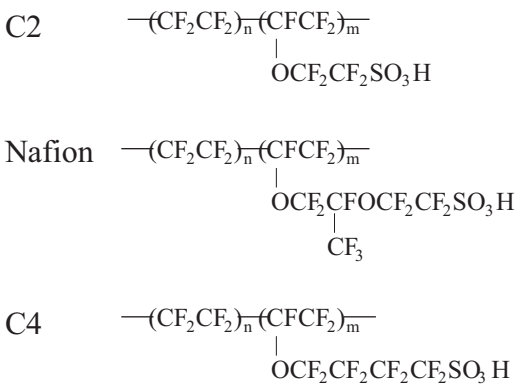

Scheme 1.

may be attributed partially to the lack of molar mass information; these ionomers do not form molecular solutions readily in solvents commonly used for SEC and other forms of polymer dilute solution characterization.

There have been only three reports of SEC of perfluorosulfonated ionomers to our knowledge. Curtin and Lousenberg examined Nafion dispersions by SEC in DMF with light scattering detection [9], and Lousenberg subsequently examined the SEC behavior of Nafion using DMSO with surfactants and an amine as eluent modifiers [10]. A pronounced shoulder was observed in SEC chromatograms at early retention volumes in both DMF and DMSO eluents for dispersion samples that were diluted directly with SEC sample solvent. The shoulder mostly disappeared only after the ionomer dispersions were subjected to autoclaving at temperatures in excess of 230 °C prior to SEC analysis, and the authors mentioned that a small persistent prepeak remained observable in light scattering chromatograms. Autoclaving is an established procedure for breaking aggregate structure and dissolving Nafion membranes that was first introduced by Martin et al. [11]. The specific refractive index increment (dn/dc) of Nafion in both DMF and DMSO is small, resulting in weak differential refractive index (DRI) and light scattering (LS) detector signals. Only one ionomer (Nafion with EW = 1000) was examined and details of the autoclaving procedure were not provided.

Another example of SEC of a perfluorosulfonated ionomer was described as part of a study of membrane degradation [12]. Membranes made from Flemion SH50 (Asahi Glass Company) were dissolved in 80/20 wt% ethanol/water with heating at 120 °C for 16 h. The SEC eluent was methanol containing 50 mM LiCl and the columns were TSK-Gel α-2500 and α-M at an unspecified temperature, and only DRI detection was used. One appealing aspect of this method is that it used a lower dissolution temperature.

This work examines more closely the sample preparation and chromatographic conditions required to obtain true size-exclusion separations of perfluorosulfonated ionomers. The result is a multi-detector SEC method that includes for the first time differential viscometry (DV) detection as well as LS detection. The method is applicable to three different perfluorosulfonated ionomer classes and it provides new information on ionomer conformation in dilute solution.

2. Experimental

2.1. Materials

Nafion perfluorosulfonic acid dispersions were obtained from E.I. du Pont de Nemours and Company (Wilmington, DE). C2 dispersions were obtained from Solvay S.A. (Brussels, Belgium). C4 dispersions were obtained from 3M Corporation (St. Paul, MN).

Table 1
Perfluorosulfonated ionomers.[a]

Ionomer	Class	EW[b]	Solids	H_2O	*n*-PrOH	EtOH	Supplier
D2020 lot#1	Nafion	950	21.6	43.5	56.5	0.0	DuPont
D2020 lot#2	Nafion	1000	21.7	42.5	57.5	0.0	DuPont
D2021	Nafion	1030	20.3	44.2	55.8	0.0	DuPont
D83-20B	C2	830(nom)	19.9	100.0	0.0	0.0	Solvay
3M low EW	C4	825(nom)	18.6	100.0	0.0	0.0	3M
3M high EW	C4	980(nom)	16.3	100.0	0.0	0.0	3M

[a] Solids and solvent fractions are listed as (w/w) %.
[b] Equivalent weight (g/mol) is measured by NaOH titration in aqueous NaCl solution; the nominal EW is reported for three dispersion samples where mineral acid was also present in solution.

Chemical structures are provided in Scheme 1, and the product names, solids content and solvent compositions are listed for these commercial dispersions in Table 1.

2.2. SEC

The SEC system is an Agilent (Santa Clara, CA) 1100 series isocratic pump, autosampler and two-wavelength spectrophotometric detector, an Agilent (formerly Precision Detectors) PD2020 two-angle LS detector, a Malvern (Worchestershire, UK, formerly Viscotek) Model 270 DV detector and a Waters Corporation (Milford, MA) Model 410 DRI detector. The DV and DRI were in a parallel configuration after the spectrophotometric and LS detectors. Three Agilent (formerly Polymer Laboratories) Olexis 7.5 mm × 300 mm columns at 35.0 °C were used with N,N-dimethylformamide (DMF, Omnisolv HPLC grade purchased from EMD Chemicals Gibbstown, NJ) containing 0.1 M $LiNO_3$. The eluent was pre-filtered using 0.22 μm Millipore (Billerica, MA) GS filters. The nominal flow rate was 1.0 mL/min and the actual flow rate was determined from the retention volume in the 270 nm UV chromatogram of 0.2% acetone added to the samples as a flow marker. The columns were calibrated with 15 PMMA narrow standards from Agilent (formerly Polymer Laboratories) with molar masses between 580 and 1,400,000. Injection volumes were 100 μL and the optimum injected sample concentration for samples not subjected to a special solvent exchange procedure discussed below was ~0.5 mg/mL.

The wavelength of the LS detector laser diode is 680 nm. The specific refractive increment (dn/dc) of PMMA at 680 nm was estimated to be 0.062 mL/g by extrapolating the dn/dc values of Mächtle and Fischer [13] for PMMA in DMF at wavelengths between 435.8 nm and 643.8 nm using the Cauchy relation [14]. The peak area response factor of the DRI detector was calculated from PMMA narrow standards and the dn/dc values of perflourosulfonated ionomers were then estimated from their integrated DRI detector responses. The estimated values of dn/dc were independent of sample concentration. The light scattering detector was calibrated with isotropically scattering PMMA standards of known molar mass assuming $dn/dc = 0.062$.

2.3. Sample dissolution

A procedure suitable for the three classes of perfluorosulfonated ionomers shown in Scheme 1 involved diluting ionomer dispersions, which are typically 5–28 wt% solids in water or water/alcohol, to a concentration of ~0.1 wt% in 80/20 *n*-propanol/water (v/v). The original dispersion percent solids and the actual concentrations of the diluted samples were determined gravimetrically. Solid ionomers have densities as high as 2 g/cm^3, so dispersions and solutions were shaken thoroughly during all dilution and transfer steps to ensure homogeneous sampling. Immediately after mixing thoroughly, 8–10 mL of each diluted solution were transferred to a poly(tetrafluorethylene) (PTFE)-lined high-strength acid diges-