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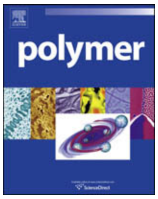

Viscometric behavior of disulfonated poly(arylene ether sulfone) random copolymers used as proton exchange membranes

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tert-Butylphenyl-terminated disulfonated poly(arylene ether sulfone) random copolymers with a sulfonation degree of 35 mol% (BPS35) and controlled molecular weights (M_n), 20–50 kg mol^{-1}, were successfully prepared by direct copolymerization of the two activated halides, 4,4′-dichlorodiphenyl sulfone (DCDPS) and 3,3′-disulfonate-4,4′-dichlorodiphenyl sulfone (SDCDPS) with 4,4′-biphenol and the endcapper, 4-*tert*-butylphenol. Dilute viscosity measurements of the BPS35 random copolymers were successfully conducted in NMP containing various concentrations of LiBr from 0.01 to 0.2 M and mostly at 0.05 M according to the measured theory. The effects of salt concentration and molecular weights of the copolymers on the viscometric behavior were studied and compared with published data for sulfonated polystyrene. The charge density parameter (ξ) for the BPS35 copolymers was determined to be smaller than 1, suggesting that no counterion condensation occurs. Studies of the effect of ionic strength (I) on the intrinsic viscosities ($[\eta]$) under theta condition were obtained by plotting $[\eta]$ vs. $I^{-1/2}$ and extrapolating to infinite ionic strength. For salt-free BPS35 solutions, the viscometric behavior was shown to fit well with the Liberti–Stivala equation, providing a way to determining intrinsic viscosity when the copolymer charge is fully screened. Intrinsic viscosity and molecular weight characterization of BPS35 copolymers by SEC and static light scattering are also presented. The results are very useful for characterizing polymeric electrolyte membrane (PEM) for fuel cells, reverse osmosis and ionic transducer membranes.

1. Introduction

Polyelectrolytes are well known to be macromolecules with ionizable groups. In polar solvents, these groups can dissociate, leaving charges on polymer chains which are a function of the counterions. Electrostatic interactions between charges lead to behavior of polyelectrolyte solutions which differ considerably from those of uncharged macromolecules. Under salt-free conditions, the reduced viscosity of polyelectrolyte solutions increases upon dilution due to repulsion between charges in the backbone, leading to an expansion of the chain. The addition of low-molar-mass salt decreases the reduced viscosity, reflecting the contraction of the polymer chains due to screening effects of the charges [1]. This characteristic behavior of polyelectrolytes has been explained by counterion condensation and chain expansion due to intramolecular repulsion [2]. However, it is to be noted that polyelectrolyte effect includes both intermolecular effects on chain conformation and intermolecular interactions. Both of these effects are important in the current study.

Physical properties of polyelectrolyte solutions are very complicated and have been studied for more than 60 years from both theoretical and experimental viewpoints [3–13]. Whereas theoretical approaches ignore the atomistic details of solvent and polymers, experimental techniques provide complementary data for each particular polyelectrolyte system. Many types of experimental techniques, such as conductance [12], viscosity [4,9–12], osmotic pressure [13] and light scattering measurements [3–5,7,8], have been used to characterize the distinctive behavior of polyelectrolyte solutions. However, experimental data are still primarily limited to several commonly encountered polyelectrolytes, such as polystyrene sulfonate, polyacrylic and polymethacrylic acids and their salts and natural polymer such as DNA. A better understanding of polyelectrolyte behavior will require further investigation by exploring additional systems.

In recent years, intensive efforts to design innovative polyelectrolytes for proton exchange membranes (PEMs) have provided new stimuli for the study of polyelectrolyte solutions [14,15]. The PEM enables proton transport from the anode to the cathode and thus directly influences fuel cell performance. PEMs must have good mechanical, thermal and chemical stabilities and still have

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high proton conductivity. Many families of polymers with different chemical structures and various strategies for incorporation of sulfonic acid groups have been explored as PEM and recently water purification reverse osmosis (RO) membrane and ionic transducer materials. Sulfonated poly(arylene ether sulfone)s are promising candidates due to their good acid and thermal-oxidative stabilities, high glass transition temperatures and excellent mechanical strength. Our group has reported many papers on the synthesis of poly(arylene ether sulfone) copolymers by the direct copolymerization of disulfonated monomers [14,16–51]. This method is preferable to post-sulfonation since it affords control over the degree of sulfonation and avoids side reactions. However, this new synthetic route brought a new challenge in determining the molecular weight of the copolymers. In the post-sulfonation method, sulfonic acid groups are formed by chemical modification of polymeric precursors. Molecular weight characterization can be determined on the non-ionic precursors. Therefore it is of great interest to develop proper techniques for the molecular weight characterization of the ion-containing PEMs. Since most molecular weight characterization techniques such as viscometry, light scattering and SEC are conducted in solution, it is important to understand the solution properties of the ion-containing PEMs in order to provide sound basis in determining molecular weight. Knowledge of the solution properties of ion-containing PEMs will also lead to improvements in membrane-casting procedures.

In this paper, *tert*-butylphenyl-terminated disulfonated poly(arylene ether sulfone) random copolymers with different molecular weights were prepared by direct polymerization of the activated halides, biphenol and the endcapper, 4-*tert*-butylphenol. Number average molecular weights of the endcapped copolymers were studied by ^{1}H NMR and by end group analysis of the *tert*-butyl end groups. Dilute viscosity measurements were carried out in both salt-free and LiBr-modified conditions. The effects of salt concentration and molecular weights of the copolymers on viscometric behavior were studied. In addition, method validation for molecular weight characterization of these random copolymers by viscosity detection SEC measurements and static light scattering are presented.

2. Experimental

2.1. Materials

tert-Butylphenyl-terminated disulfonated poly(arylene ether sulfone) copolymers with specific molecular weights (20–50 kg mol^{-1}) were prepared by direct copolymerization as reported earlier [17] and shown in Fig. 1. The molecular weights determined from ^{1}H NMR spectra were consistent with the theoretical values. For all copolymers, the mole ratio of 4,4′-dichlorodiphenylsulfone (DCDPS) to 3,3′-disulfonated 4,4′-dichlorodiphenylsulfone (SDCDPS) was kept constant at 6.5/3.5, which is a good composition for both fuel cell and water purification RO membranes. The copolymers synthesized were designated as BPS35-xx, where 35 means that all copolymers contained 35% (mol%) of disulfonated repeat units, and xx represents the target molecular weight in kg mol^{-1}. A BPS35-control copolymer was also prepared under similar copolymerization conditions but without endcapping agent, in which the stoichiometry between dihalide monomers and biphenol was maintained at 1:1. SEC and intrinsic viscosity measurements showed that it has a higher molecular weight than the endcapped BPS35 copolymers, as expected.

2.2. Intrinsic viscosity measurement

Viscosity measurements were carried out with a Cannon Ubbelholde viscometer with a flow time of about 98 s for pure NMP (*N*-methyl-2-pyrrodinone) at 25 °C. The temperature was regulated at 25.0 ± 0.1 °C. Each solution for viscometry was freshly prepared and was kept at 25.0 ± 0.1 °C for 10 min prior to the measurement. All the solutions were filtered through Teflon frits in order to remove any undissolved particles before introduction into the viscometer. The polymer concentrations were chosen suitable to be large enough to ensure the reproducibility and accuracy of the measurements, but lower than the overlap concentrations. After each determination, the viscometer was flushed at least three times with distilled water before rinsing with acetone prior to drying in the oven. This procedure was important because acetone is a precipitant for the copolymer. For the same reason, acetone vapor must be thoroughly removed before the introduction of the next solution.

2.3. Size exclusion chromatography (SEC)

SEC experiments were performed on a liquid chromatograph equipped with a Waters 1515 isocratic HPLC pump, Waters Autosampler, Waters HR5-HR4-HR3 columns, Waters 2414 refractive index detector and Viscotek 270 Right Angle Laser Light Scattering (RALLS)/viscometric dual detector. NMP containing 0.05 M LiBr was used as the mobile phase. The column temperature was maintained at 60 °C to reduce the viscous nature of NMP. Both the mobile phase

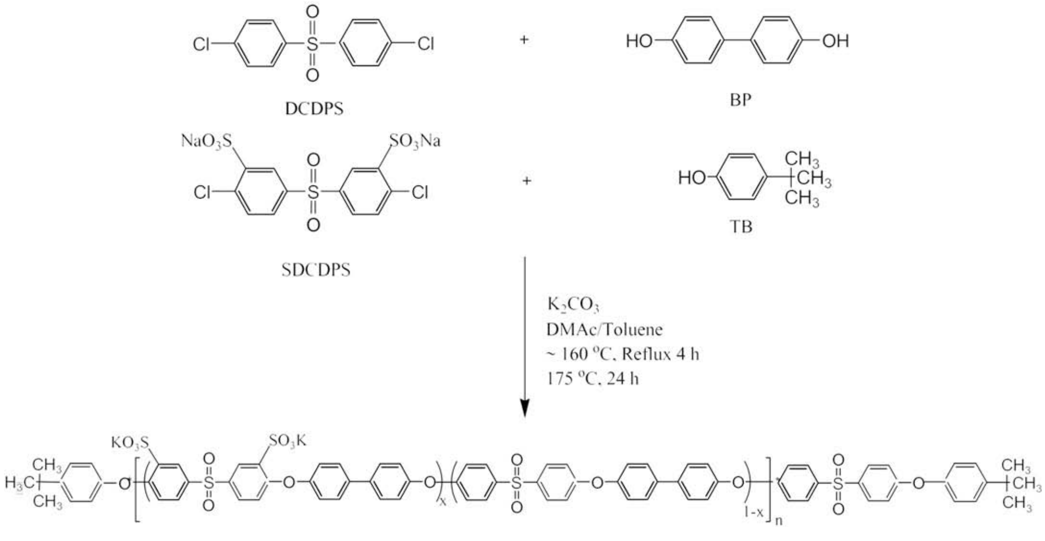

Fig. 1. Direct synthesis of *tert*-butylphenol-terminated poly(arylene ether sulfone)s containing disulfonate groups [17].

Table 1
Characterization of BPS35 random copolymers

Target M_n (kg/mol)	Experimental M_n by NMR (kg/mol)	Degree of sulfonation (%)[a]	
		Theoretical	Experimental (by NMR)
20	19.9	35	33.9
30	28.8	35	34.1
40	38.1	35	34.7
50	47.3	35	34.6
Control	–	35	34.2

[a] Mole % of sulfonated monomer.

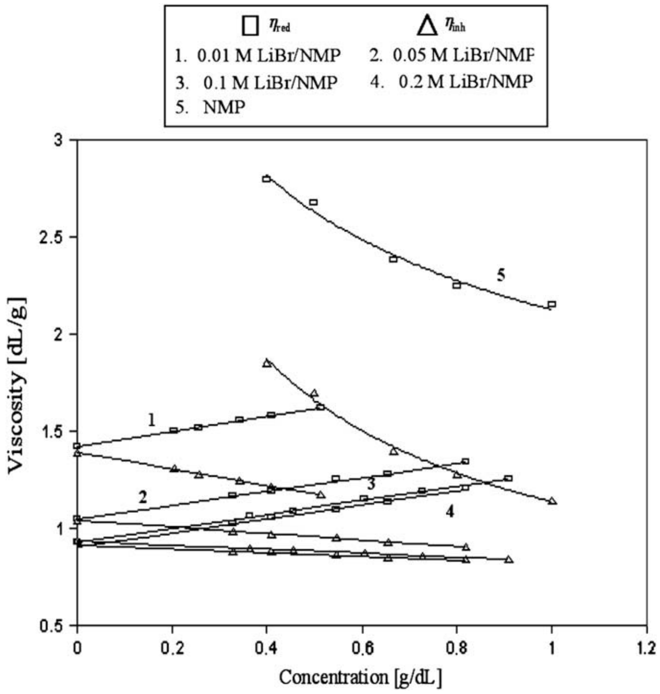

Fig. 2. Apparent viscosity–concentration behavior of a BPS35-control copolymer in NMP containing different concentrations of salt.

solvent and sample solution were filtered with Whatman PTFE 0.21 μm filters before introduction to the SEC system. Omni-SEC (Viscotek) software was used to calculate molecular weight averages based on detection data.

Viscotek 270 dual detector provided a right angle light scattering detector, which uses a 90° angle geometry for maximum signal-to-noise. In this design, angular dependence is corrected by calculating the Debye particle scattering function directly using viscometric data. An initial estimate of molecular weight (M) obtained from the Rayleigh equation is inserted, along with the measured intrinsic viscosity, into the Flory–Fox equation to obtain an estimate of R_g. Then the estimated R_g is inserted into the Debye equation to estimate the angular scattering probability function $P(\theta = 90^\circ)$. Then $P(\theta = 90^\circ)$ is used in the Rayleigh equation to calculate an improved estimate of M, which will be more close to the true value. The loop is iterated until the values of M, R_g, and $P(\theta = 90^\circ)$ converge [52].

2.4. Static light scattering measurement

Copolymer solutions were prepared by dissolving the freeze-dried samples in 0.05 M LiBr/NMP under stirring for a day at room temperature. Light scattering measurements were conducted with a CGS-3 multi-angle light scattering photometer (Malvern Instruments) at a wavelength of 633 nm at 25 °C. The sample solutions were filtered with a Whatman PTFE 0.21 μm filter for optical clarification. Due to the relatively small molecular weight of BPS35 samples involved in this study, the absolute molecular weight (M_W) can be obtained from a Debye plot by recording the scattering intensity at different sample concentrations. Measurements were done at three different points of the cell window to make sure that the effects of the roughness of the cell windows on scattering were negligible. The refractive index increment, dn/dc, was measured at 25.0 (0.1 °C using an Optilab Refractometer (Wyatt Technology)).

3. Results and discussion

3.1. ^{1}H NMR characterization of copolymers

The ^{1}H NMR was used to determine the number average molecular weight [$\overline{M}_n$] and to confirm the degree of sulfonation of BPS35 copolymers as shown in Table 1. The degrees of disulfonation were calculated from the monomer/endcapping ratio as discussed earlier [17]. The molecular weights determined from ^{1}H NMR spectra were consistent with the theoretical values. The contents of disulfonated units in the series of copolymers were in good agreement with the ratio of feed monomers (SDCDPS/DCDPS—35/65), which suggests that all the starting monomers were successfully incorporated into the copolymer chains. Thus, all these BPS35 copolymers have similar degrees of disulfonation.

3.2. Polyelectrolyte behavior

Fig. 2 shows the effect of added salt (LiBr) on the viscosities of BPS35-control solutions. The solution properties of BPS35 in the polar medium NMP with and without added salt are radically different. A polyelectrolyte effect is clearly observed. In the case of BPS35 solutions without LiBr, both reduced and inherent viscosities increase as copolymer concentration decreases presumably due to the charge repulsion along the backbone. However, the presence of the electrolyte LiBr controls the solution ionic strength and screens out charges. This produces the viscosity (reduced and inherent)–concentration relationships of BPS35-control solutions that are now similar to a non-charged polymer solution, affording linear

Table 2
Summary of intrinsic viscosity results for BPS35 at different salt levels

Sample	$[\eta]$ (dL/g) 0.01 M LiBr	$[\eta]$ (dL/g) 0.05 M LiBr	$[\eta]$ (dL/g) 0.1 M LiBr	$[\eta]$ (dL/g) 0.2 M LiBr	$[\eta]_\infty$ (dL/g) (salt free) Liberti–Stivala equation	$[\eta]_\theta$ (dL/g) η_{red} vs. $I^{-1/2}$	$[\eta]$ by SEC 0.05 M LiBr
BPS35_20K	0.51	0.42	0.41	0.41	0.43	0.35	0.41
BPS35_30K	0.56	0.47	0.45	0.44	0.46	0.39	0.45
BPS35_40K	0.80	0.63	0.58	0.58	0.59	0.47	0.60
BPS35_50K	0.95	0.74	0.68	0.66	0.64	0.54	0.66
BPS35_control	1.41	1.04	0.93	0.91	0.91	0.72	0.95

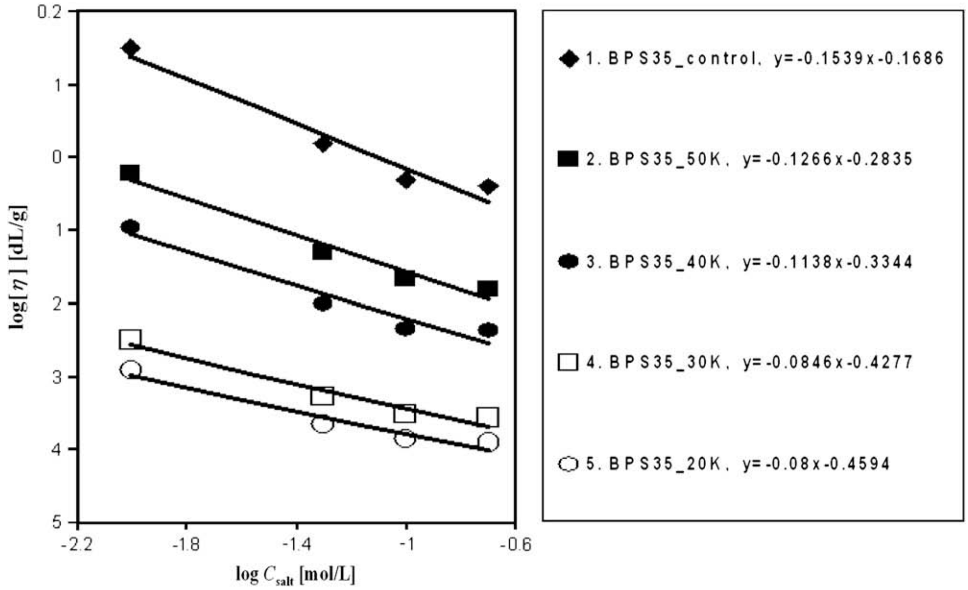

Fig. 3. Intrinsic viscosity values as a function of salt (LiBr) concentration and molecular weights for BPS35 series in the polar solvent NMP.

plots and allowing conventional extrapolations to zero concentrations.

3.3. Viscosity behavior in solutions with added salts

Dilution solution viscosity measurements of different molecular weight BPS35 samples in NMP containing various concentrations of LiBr from 0.01 M to 0.2 M were performed to assess concentration dependence. Linear plots were obtained in all cases. Dilute viscosity measurements with higher salt concentrations were not employed for two reasons. Firstly, LiBr is highly hygroscopic. Water absorption from the air due to too much LiBr will greatly influence the flow times, and therefore reliable data cannot be obtained. Secondly, although it was expected that higher salt concentrations would further suppress polyelectrolyte effects, this also decreases solvent quality (e.g. LiBr insolubility). This is especially problematic for high molecular weight copolymers. Intrinsic viscosity data obtained for different concentrations of salt are presented in Table 2. One observed trend is that increasing the salt concentration decreases intrinsic viscosities. It is clearly shown that the intrinsic viscosity drops significantly from the salt level of 0.01–0.05 M for all the samples. Obviously, 0.01 M LiBr is not sufficient to screen the charges of BPS35. Furthermore, for copolymers with molecular weights lower than $M_n = 40{,}000$ g/mol, only a small decrease of intrinsic viscosity was observed from 0.05 to 0.1 M. For the copolymers with molecular weights equal or higher than 40,000 g/mol, intrinsic viscosities decrease with salt concentration from 0.05 to 0.1 M. The intrinsic viscosities in solutions containing 0.1–0.2 M salt show negligible change. Thus it was concluded that 0.1 M LiBr is sufficient to screen the charges for all the BPS35 copolymer solutions, including the highest molecular weight BPS35-control.

The intrinsic viscosities, [η], are plotted as a function of salt concentration (C_s) in Fig. 3. Linear relationships were observed between log[η] and log C_s. Similar relationships between log[η] and log C_s have been reported for various polyelectrolyte systems, although the slope of the line varies [4]. The slopes of the lines reflect the significance of the polyelectrolyte effect. The absolute values of the slope (S) for the BPS35 copolymers and several other polyelectrolytes are listed in Table 3. The values of S for all the BPS35 copolymers are lower than those of the other polyelectrolyte systems with higher ion content up to 100%. It is also shown that S increases slightly with the molecular weight of BPS35. Furthermore, S for the lightly sulfonated polystyrene ionomer with a molecular weight of 400,000 g/mol is 0.12, and this is similar to the BPS35 copolymers (0.08–0.15). It seems that both of these factors, i.e. ion content and molecular weight, may influence the slope. S increases with ion content and molecular weight, implying a more significant polyelectrolyte effect.

3.4. The charge density parameter, ξ

According to the Manning counterion condensation theory, the effective charge (in units of charge per monomer unit) of a polyion has an upper bound, since a fraction, x, of the counterions condense, and the effective charge is $1 - x$ [53]. The viscosity behavior of a polyelectrolyte solution depends on the effective charge of the polyion. Therefore, the viscosity behavior is influenced by the fraction of condensed counterions. The effect of the ionic groups on the viscosity behavior can be quantified through the charge density parameter (ξ), as defined by [54]

$$\zeta = \frac{l_B}{d} \tag{1}$$

where l_B is the distance between effective charges on the polyion (Bjerrum length), and d is the distance between two elementary charges. The Bjerrum length (Eq. (2)) is a natural length scale for

Table 3
Dependence of slope of log[η] vs. log $C_{\rm salt}$ on ion content and molecular weight

Sample	Ion content (%)	Slope of log[η] vs. log $C_{\rm salt}$
BPS35_20K	35	−0.08
BPS35_30K	35	−0.08
BPS35_40K	35	−0.11
BPS35_50K	35	−0.13
BPS35_control	35	−0.15
PS03_400K[a]	3[b]	−0.12[b]
Various polyelectrolytes	Varies up to 100%	−0.2 to −0.5[b]

[a] Lightly sulfonated polystyrene with molecular weight about 400 K.
[b] Data taken from Ref. [4].

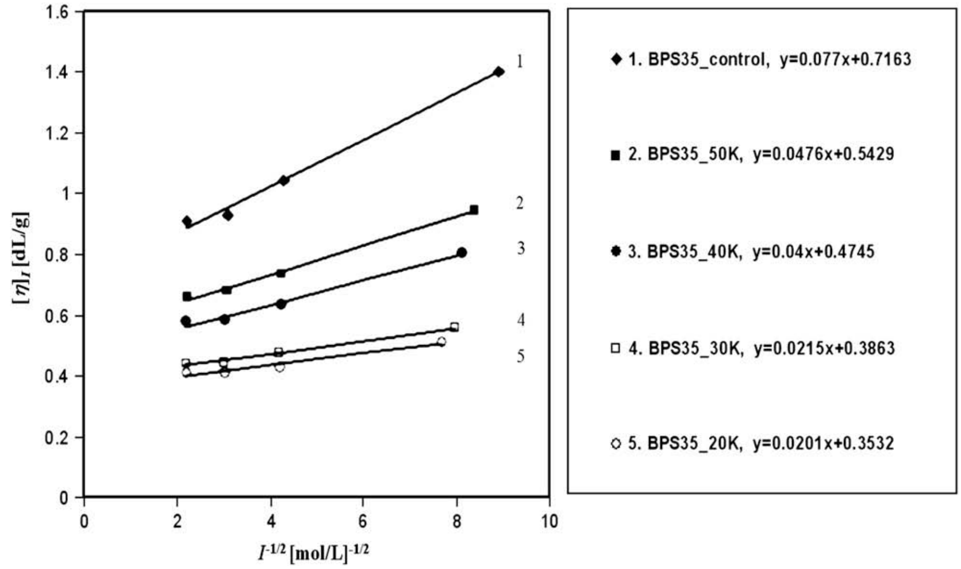

Fig. 4. Dependence of $[\eta]$ on the ionic strength.

polyelectrolytes in solution and has been defined as the distance between two elementary charges when the electrostatic energy equals the thermal energy, k_BT.

$$l_B = \frac{e^2}{4\pi\varepsilon\varepsilon_0 k_B T}. \tag{2}$$

where e is the charge of an electron, ε is the dielectric constant of the solvent, ε_0 is the vacuum permittivity, k_B is the Boltzmann constant and T is the absolute temperature in Kelvin.

The charge density parameter, ξ, is a structural parameter. For $\xi > 1$, there is a fraction $(1 - 1/\xi)$ of condensed counterions on the polyelectrolyte chain. For $\xi < 1$, no counterion condensation occurs [53]. Condensation of counterions occurs in polyelectrolyte solutions until the free energy of charge repulsion balances that arising from the entropy of a free counterion so that the distance between effective charges on the polyion is the Bjerrum length.

Using the dielectric constant of NMP ($\varepsilon = 32$), the value of Bjerrum length for BPS35 copolymers was calculated to be 1.75 nm. The average distance between ionic groups (d) was determined to be 6.3 nm. Therefore, ξ was determined to be 0.28, which is smaller than 1, suggesting that no counterion condensation occurs.

3.5. Dependence of the intrinsic viscosity on the ionic strength

The dependence of the intrinsic viscosity on the ionic strength has been expressed, for a series of polyelectrolytes, by the empirical equation [53]

$$[\eta]_I = [\eta]_\theta + S[I]^{-1/2} \tag{3}$$

where $[\eta]_I$ is the intrinsic viscosity at an ionic strength I, and $[\eta]_\theta$ is the intrinsic viscosity extrapolated to infinite ionic strength. Ionic strength is a measure of the total ion concentration in the solution. A plot of $[\eta]_I$ vs. $I^{-1/2}$ for BPS35 copolymers is shown in Fig. 4 and the values of $[\eta]_\theta$ are presented in Table 2. The $[\eta]_\theta$ may be interpreted as the viscosity under theta conditions. It was observed that the intrinsic viscosity at a salt concentration of 0.2 M for all the BPS35 copolymers was significantly higher than those under theta conditions. Although 0.2 M LiBr is sufficient to screen the charges on the copolymer chain, theta conditions are not reached.

3.6. Comparison of intrinsic viscosity measured by SEC and Ubbelohde viscometer

SEC equipped with a viscosity detector can be used to determine intrinsic viscosities in addition to Ubbelohde viscosity measurements. As it is well known, the intrinsic viscosity is defined as the limiting value as $c \to 0$ of the ratio of specific viscosity ($\eta_{sp} = (\eta - \eta_0)/\eta_0$) and concentration c.

$$\left[\eta\right] = \lim_{c \to 0} \frac{\eta - \eta_0}{\eta_0 c} = \lim_{c \to 0} \frac{\eta_{sp}}{c} \tag{4}$$

In SEC, concentrations of solutions are very low, therefore $[\eta]_i$ can be approximated by $[\eta]_{sp}/c$ at each elution volume and these values can be averaged to obtain $[\eta]$.

The intrinsic viscosities of BPS35 copolymers measured by SEC at the salt level of 0.05 M LiBr are included in Table 2. At the

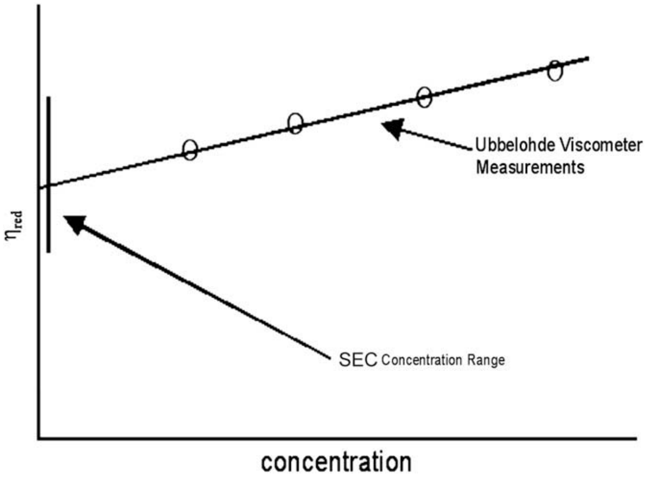

Fig. 5. Comparison of intrinsic viscosity determination by Ubbelohde viscometer and GPC.

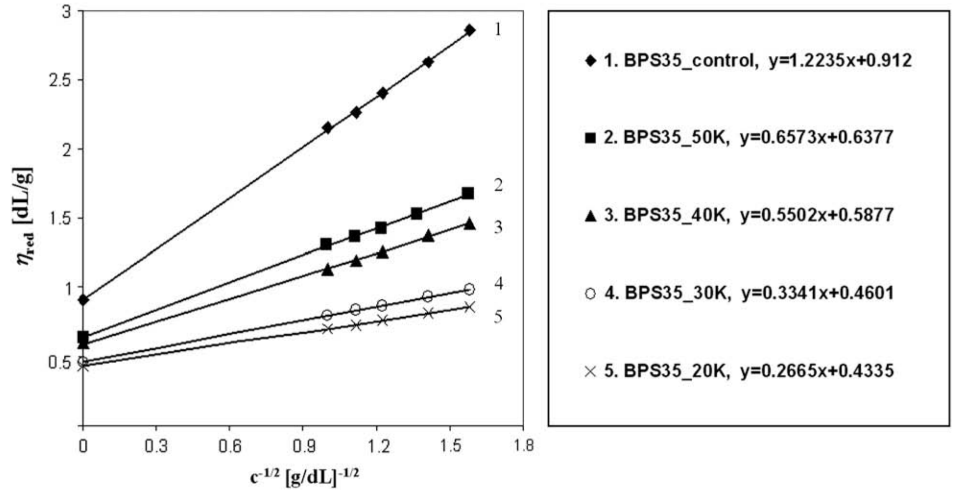

Fig. 6. Determination of $[\eta]_\infty$ under salt-free condition for the BPS35 series.

same salt concentration, $[\eta]$ from SEC is slightly lower than $[\eta]$ from Ubbelohde viscometry. One explanation could be the polyelectrolyte effect in SEC can be more effectively suppressed than that in Ubbelohde measurement at the same salt concentration level, since SEC measurements are made one order of magnitude lower in concentration than Ubbelohde measurements (Fig. 5).

3.7. Viscosity behavior of salt-free BPS35 copolymers

For salt-free polyelectrolyte solutions, an empirical analysis was also performed to extract the intrinsic viscosities by extrapolation to infinite concentration using the Liberti–Stivala equation [55,56]

$$\eta_{\text{red}} = [\eta]_\infty + k\frac{[\eta]_\infty}{\sqrt{c}} \tag{5}$$

where $[\eta]_\infty$ represents the intrinsic viscosity when the charges are shielded to the extent that the macromolecule behaves as a noncharged. η_{red} is the reduced viscosity. The equation is limited to the range of conditions for which η_{red} decreases with increasing c. The plot of η_{red} vs. $c^{-1/2}$ is presented in Fig. 6. The viscosity of BPS35 solutions is well represented by the Liberti–Stivala equation since a linear behavior is obtained. $[\eta]_\infty$ values of BPS35 copolymers with different molecular weights obtained by linear extrapolation are listed in Table 2. It is observed that $[\eta]_\infty$ is comparable to intrinsic viscosities at the salt concentrations of 0.1 and 0.2 M for all the BPS35 copolymers. This illustrates another elegant approach to determining intrinsic viscosity when the polymer charge is fully screened.

Colby et al. reported an extensive experimental study on the dependency of the salt-free solutions of certain polyelectrolyte (2-vinyl pyridine and *N*-methyl-2-vinyl pyridinium chloride random copolymers) on the polymer concentration [57]. The reduced viscosity plotted as a function of concentration revealed no local maxima and was independent of concentrations in dilute solutions. It is believed that Eq. (5) is also expected to give a fit to the data.

3.8. Molecular weight characterization of BPS35 copolymers by SEC and static light scattering

SEC was also used to characterize the BPS35 copolymers in 0.05 M LiBr/NMP. Salt was added to suppress the polyelectrolyte effect. The salt concentration of 0.05 M was used instead of 0.1 M because high salt concentrations also tend to damage the pump seals.

For the SEC measurements, both universal calibration and SEC-RALLS-viscometry methods were used to analyze the chromatograms. It is well known that each of these methods has advantages and disadvantages. Universal calibration demands that the retention mechanism in the column be pure size exclusion, which is a very strict requirement for the characterization of charged polymers. In addition to size exclusion, some additional non-size exclusion effects might be involved such as electrostatic and hydrophobic interactions. Thus it was of interest to demonstrate the feasibility of characterizing ion-containing BPS35 copolymers by each of the SEC methods. The molecular weights obtained from the different methods including static light scattering are provided in Table 4. The molecular weights obtained from universal calibration and SEC-RALLS-viscometry agreed well, especially for M_w, and this indicates that the salt concentration of 0.05 M is sufficient to maintain good column separation without significant electronic interactions. Static light scattering measurements further confirmed the SEC results. However, M_n values obtained from SEC are lower than NMR results. It appears that higher molecular weights afford larger discrepancies by the reasons not well understood at this point.

Berry et al. reported the effects of non-isorefractive index mixed solvents on the apparent molecular weight determined by light

Table 4
Molecular weight determination of BPS35 series by static light scattering and GPC methods (solvent: 0.05 M LiBr/NMP)

Sample	Static light scattering method M_w (g/mol)	SEC (universal calibration)			SEC (RALLS-viscometry)			IV (dL/g) by SEC 0.05 M LiBr/NMP
		M_n (g/mol)	M_w (g/mol)	PDI	M_n (g/mol)	M_w (g/mol)	PDI	
BPS35_20K	32,000	20,100	32,100	1.6	19,200	30,200	1.6	0.40
BPS35_30K	38,000	23,400	36,300	1.6	27,000	37,900	1.4	0.45
BPS35_40K	48,000	20,100	44,800	2.2	26,800	47,000	1.8	0.61
BPS35_50K	58,000	35,000	61,000	1.7	34,400	58,900	1.7	0.66
BPS35_control	91,000	47,100	93,500	2.0	56,900	92,900	1.6	0.95

scattering technique [58]. Especially for multi-component solvents, there is a possibility generation of experimental error due to difficulty in polymer dissolution, evaporation of solvent, polymer adsorption or in the Δn determination. These can affect the contrast factor for the scattering and could be involved in the unexplained deviation of M_n estimated from the SEC and NMR results.

4. Conclusions

Dilute viscosity measurements of the BPS35 random copolymers were performed in NMP containing various concentrations of LiBr from 0.01 to 0.2 M. The salt (LiBr) was used to shield the polyions from intramolecular expansion. Linear plots were obtained for all of the solutions. Increasing the salt concentration decreases intrinsic viscosities, particularly at higher molecular weights. It was found that 0.1 M LiBr is sufficient to screen the charges for all the BPS35 copolymer solutions, including the highest molecular weight BPS35-control. The effects of salt concentration and molecular weights of the copolymers on viscometric behavior were also studied. Linear relationships were observed between $\log[\eta]$ and $\log C_s$. The slopes of the lines reflect the significance of the polyelectrolyte effect. Study of the effect of ionic strength on the intrinsic viscosity could yield the viscosity under theta condition, $[\eta]_\theta$. It was observed that the intrinsic viscosity at a salt concentration of 0.2 M for all the BPS35 copolymers was significantly higher than that under theta conditions. For salt-free BPS35 solutions, the viscometric behavior was shown to fit well with the Liberti–Stivala equation, providing an elegant way to determining intrinsic viscosity when the polymer charge is fully screened. The molecular weights of BPS35 copolymers obtained from universal calibration and SEC-RALLS-viscometry agreed well, especially for M_w. Static light scattering measurements further confirmed the SEC results. The results are important to correlate structure–property relations in fuel cell and related membranes, e.g. reverse osmosis water purification membranes.

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