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# Electrochemical Measurements of Diffusion Coefficients of Redox-Labeled Poly(ethylene glycol) Dissolved in Poly(ethylene glycol) Melts

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Ferrocene-labeled monomethoxy–poly(ethylene glycol)s (MPEG) with molecular weights of 1900 and 750 were used as redox probe solutes in poly(ethylene glycol) melt solvents of molecular weight 750, 2000, and 20 000. Cyclic voltammetry and chronoamperometry at microdisk electrodes were employed to measure the diffusion coefficients of the redox probes, which were independent of the probe concentration and varied between  $10^{-7}$  and  $10^{-10}$  cm<sup>2</sup>/s. Diffusional activation barrier results also suggest that the ferrocene label does not significantly influence the diffusivity of the probe molecule in the host solvent. Activation barrier, viscosity, and ionic conductivity results show that the LiClO<sub>4</sub> electrolyte does not influence the diffusion barrier or viscosity as long as the ether O/Li<sup>+</sup> ratio is  $\geq 250$  (ca. 0.1 M) which is still a sufficient electrolyte concentration to allow quantitative electrochemical diffusion measurements.

Polymer electrolyte media based on poly(ether)s, like poly(ethylene oxide) (PEO), poly(ethylene glycol) (PEG), and poly(propylene glycol) (PPG), with dissolved lithium salts have been widely studied as solid or semisolid ionic conductors and as lithium ion conductors.<sup>1</sup> In recent work, we have explored the diffusive transport of redox molecules through these media using solid state voltammetry experiments.<sup>2</sup> Certain of these studies have involved the covalent attachment of PEG tails to redox molecules (such as ferrocene). Among other properties, these PEG-modified molecules have distinctive behavior, in self-diffusion<sup>3</sup> in the neat material, and in diffusion as solutes<sup>3,4</sup> in unlabeled PEG solvent. Self-diffusion in neat melts of PEG-modified redox molecules can be exceptionally slow; a diffusion coefficient as small as  $10^{-15}$  cm<sup>2</sup>/s has been measured.<sup>5</sup>

This paper describes the diffusion properties of two monomethyl–poly(ethylene glycol) (MPEG) modified ferrocenes (Fc 750, Fc 1900; see Figure 1) in several PEG polymer electrolyte solvents (MW 750, 2000 and 20 000), assessing the sensitivity of diffusion rates to the chain length of the ferrocene-attached MPEG and to that of the PEG polymer host, and to the LiClO<sub>4</sub> electrolyte concentration. Besides showing that such dependencies can be detected, the principal objective is to demonstrate that electrochemical diffusion data in polymeric media can be obtained that are unaffected by the presence of the electrolyte (LiClO<sub>4</sub>) needed to support the electrochemical experiment. In poly(ether) polymer electrolytes, dissolution of lithium salts occurs by coordinative ether oxygen solvation. The coordinating sites can lie on different PEG chains, which produces a cross-linking (albeit a transient one) between the chains and a diminution of their segmental mobility (especially significant at high electrolyte concentration), with consequent effects on the chain self-diffusion rates as well as on the polymer electrolyte's ionic conductivity, viscosity, phase behavior, and thermal stability.<sup>1</sup> Ionic conductivity and shear viscosity are measured here as well as diffusion, to establish that changes in those properties with electrolyte concentration and with poly(ether) chain length parallel those in diffusivity. Activation parameters are also described.

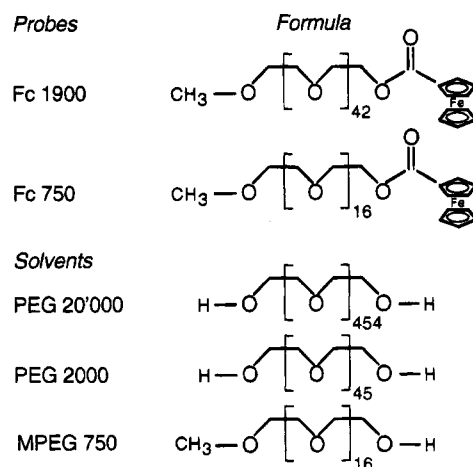


Figure 1. Chemical composition of the probe polymers and host polymers used.

We have previously proposed,<sup>3a</sup> from voltammetrically-derived diffusion coefficients of ferrocene carboxylic acid (CpFeCpCO<sub>2</sub>H) *vs* a ferrocene-labeled MPEG, (CpFeCpC(O)NH(CH<sub>2</sub>CH<sub>2</sub>O)<sub>42</sub>CH<sub>3</sub>), that the (slower) diffusion rate of the latter molecule through a host polymer of identical chain length, CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>42</sub>CH<sub>3</sub>, represented control of diffusion through the PEG host by the MPEG chain and not by the ferrocene label on the MPEG chain. This method for measuring polymer self-diffusion dynamics, i.e., of linear (redox-labeled) polymers diffusing through linear polymer hosts in a melt state, is potentially useful in assessing contemporary theory for such phenomena. Prominent among existing models of linear polymer self-diffusion is the "reptation" theory developed by De Gennes,<sup>6</sup> which considers the polymer chains to be highly entangled, with motion of each chain restricted to one-dimensional diffusion within an imaginary tube defined by chain entanglement points. This model applies to chains larger than a critical (entanglement) molecular weight ( $M_c$ ), which for PEG has been reported as 6400<sup>7</sup> and as 3600.<sup>8</sup> One prediction of the model is that, for chains above  $M_c$ , the chain self-diffusion coefficient is proportional to (MW)<sup>-2</sup>. Experimental tests<sup>9</sup> of reptation theory involve some labeling of the polymer chain whose diffusivity is to be measured. For poly(propylene glycol)

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self-diffusion measurements by photopattern bleaching, Smith et al.<sup>10</sup> labeled PPG with a fluorescent dye.

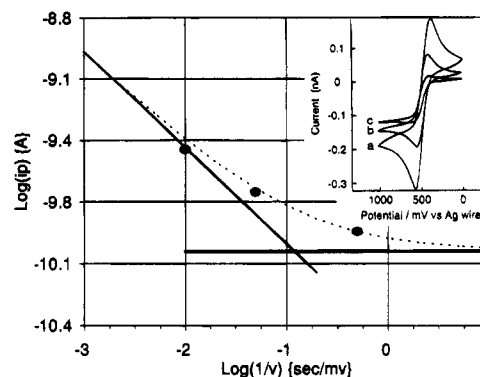
In application of solid state voltammetry to polymer self-diffusion measurements, the redox group attached to the polymer chain (either at its terminus, as here, or as a unit in the chain's interior) is the label that tracks the chain's diffusion. The previous study<sup>3a</sup> showed that influences of the label on the chain self-diffusivity could be assessed by comparison to the diffusivity of the free redox molecule (i.e., lacking an attached polymer chain). The previous study<sup>3a</sup> did not, however, address the potential liability of the voltammetric method caused by the required presence of a supporting electrolyte, which might affect the polymer dynamics. As noted above, for LiClO<sub>4</sub> electrolyte, transient cross-linking and effects on polymer segmental mobility, and presumably thereby on chain diffusivity, can be substantial. This motivated the present study, to ascertain whether the electrolyte concentration (LiClO<sub>4</sub>) can be lowered to values sufficiently small that diffusion rates become insensitive to electrolyte concentration and yet retain an ionic conductivity adequate to support the voltammetric measurement. We present evidence that this indeed is possible, both for host PEG molecular weights that lie below the critical entanglement value (i.e., 750 and 2000) and above it (i.e., 20 000).

## Experimental Section

**Chemicals.** Poly(ethylene glycol) host solvents (Fluka) were dissolved in distilled water and purified over acidic and alkaline ion exchanger, which were prewashed with distilled water. The water was removed by evaporation and the polymers dried at 110 °C under vacuum (10<sup>-3</sup> Torr). LiClO<sub>4</sub> (Aldrich) was dried at 100 °C under vacuum (10<sup>-3</sup> Torr). Solutions of ferrocene-labeled MPEG's in the host PEG solvents were prepared in a glovebox. The proper amounts of the components were weighed into a glass tube which had a vacuum outlet and which was fitted with a Schott screw-cap through which the electrode could be inserted. A few drops of distilled acetonitrile were added to dissolve the electrolyte and mix the components; the acetonitrile was removed by evacuation at elevated temperature (100 °C, 10<sup>-3</sup> Torr).

Ferrocene-labeled monomethyl poly(ethylene glycol) (Fc 750) was prepared<sup>11</sup> by deprotonation of monomethyl poly(ethylene glycol) (Aldrich, nominal MW = 750, 3.0 mmole) in THF (20 mL) using NaH (60% oil dispersion, 3.1 mmol) at room temperature under nitrogen, stirring for 2 h. A slight excess of ferrocenoyl chloride in THF (10 mL) was added to this solution and reacted for 1 h. The solution was rotary evaporated to a reddish-brown oil, and the residue was purified by column chromatography on silica (230–400 mesh) using CH<sub>2</sub>Cl/CH<sub>3</sub>CN as the eluent. The major orange fraction was collected and taken to dryness and dried in vacuo at 100 °C overnight.

The labeled polymer was characterized by UV–vis and NMR as follows: The optical spectra of two pure ferrocene esters (FcCO<sub>2</sub>(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>CH<sub>3</sub> and FcCO<sub>2</sub>(CH(CH<sub>3</sub>)CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>) were identical in dimethoxyethane solution [ $\lambda_{\max}(\epsilon)$ : 264 (4600), 306 (1055), 340 (280), 456 (193)]. A weighed sample of Fc 750 was analyzed by its optical spectrum from which the weight average molecular weight  $M_w$  was determined to be 962 g/mol (equivalent to an MPEG chain on  $M_w$  = 750). Peak areas in the <sup>1</sup>H NMR of Fc 750 [ $\delta$  4.77t (2 H, Fc), 4.44 t (2 H, Fc), 4.32 t (2 H, CH<sub>2</sub>  $\alpha$  to CO<sub>2</sub><sup>-</sup>), 4.23 s (5 H, Fc), 3.77 t (2 H, CH<sub>2</sub>  $\beta$  to CO<sub>2</sub><sup>-</sup>), 3.7–3.45 m (~71 H, –OCH<sub>2</sub>CH<sub>2</sub>O–), 3.28 s (3 H, terminal CH<sub>3</sub>)] correspond to an MPEG MW = 841 and overall MW = 1053. We consider the UV–vis determination the more reliable as to MW. Fc 1900 was prepared and



**Figure 2.** Diagram of log(peak current) vs log(inverse scan rate) based on the cyclic voltammetry (inset) of a PEG 3350 melt containing 50 mM Fc 1900 and LiClO<sub>4</sub>, O/Li = 16, measured with a microdisk electrode of radius 5  $\mu$ m at 65 °C. Open circles: experimental current maxima at 2, 20, and 100 mV/s scan rates. Solid lines: theoretical behavior for pure linear diffusion (calculated from  $i_p = 2.69 \times 10^5 n^{1.5} r^2 \pi D^{1/2} \nu^{1/2} C$ ) or radial diffusion (calculated from eq 1) with  $D = 1.1 \times 10^{-8}$  cm<sup>2</sup>/s. Dotted line: mixed diffusion according to Aoki<sup>13</sup> (eq 2) using  $D = 1.0 \times 10^{-8}$  cm<sup>2</sup>/s.

analyzed in an analogous manner. No attempt was made to measure or control MW polydispersity in the present measurements.

**Voltammetry.** Pt microdisk electrodes<sup>12</sup> constructed from 10  $\mu$ m Pt wire sealed in a glass capillary were used in all the measurements. A silver wire was used as a pseudoreference electrode and a thick Pt wire as the auxiliary electrode. All three electrodes were embedded in an Epon 825 epoxy rod as described before<sup>2</sup> and polished with alumina polishing powders (Buehler) through the finest grade (0.05  $\mu$ m). Cyclic voltammetry and chronoamperometry were performed on a BAS 100B electrochemical analyzer or with a locally built potentiostat and voltage programmer.

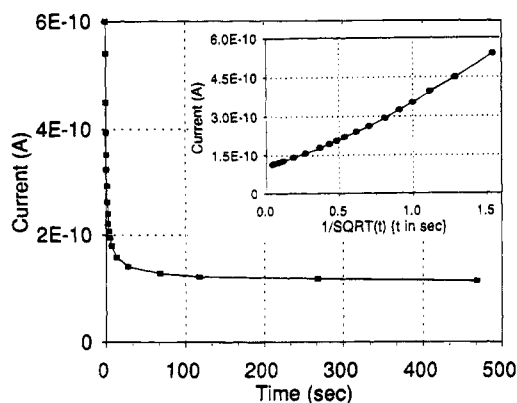
**Conductivity Measurements.** A cell with two parallel Pt disk electrodes was constructed in the following way: A Pt wire (8 mm long, 0.76 mm thick) with leads wires attached at each end, was embedded in Epon 825 epoxy resin in a PTFE tube. A notch 1 mm wide and perpendicular to the Pt rod was cut in the resin tube so as to sever the wire and create two parallel, equal area, Pt surfaces. The cell constant ( $k = 8.78$  cm<sup>-1</sup>) was measured by ac impedance in 0.5 mM and 5 mM KCl solutions. The  $R_{\text{soln}}$  values were obtained by extrapolation of the semicircle generated by measurements at a series of frequencies to the  $Z'$  (resistance) axis of the Nyquist plots. Solution conductivity was calculated as  $\sigma = k/R_{\text{soln}}$ . Ac impedance measurements were performed with a Solartron 1286 electrochemical analyzer interfaced with a 1255HF frequency response analyzer; data were analyzed using ZPLOT and ZFIT programs.

**Viscosity Measurements.** A Wells-Brookfield cone-plate viscometer Model DV-1 was used, with temperature controlled with a Brookfield EX-100 circulating water/ethylene glycol bath.

All measurements were done at temperatures (70–110 °C) at which the PEG polymer electrolyte solutions are in the molten, isotropic state.

## Results

**Diffusion Coefficient Methods.** The diffusion coefficients of the ferrocene-labeled polyethers Fc 750 and Fc 1900 (Figure 1) in host PEG/LiClO<sub>4</sub> polymer electrolytes were measured with previously described procedures.<sup>2c,e</sup> Typical cyclic voltammetry of Fc 1900 dissolved in PEG 3350 is shown in Figure 2 (inset). (The PEG 3350 MW host polymer is used here only



**Figure 3.** Potential step chronoamperometry of a PEG 3350 melt containing 50 mM Fc 1900 and LiClO<sub>4</sub> at O/Li = 16, measured with a microdisk electrode at 65 °C. Inset: Cottrell plot of the same experimental data.

to illustrate the voltammetry; the data shown typify the other MW hosts.) Potential scan rates ( $\nu$ ), 100 mV/s in this example, produce peak-shaped voltammograms (curve a) with peak current approaching proportionality to  $\nu^{1/2}$ , indicative of linear diffusion conditions around the electrode.

At much slower potential scan rates (2 mV/s, Figure 2 (inset) curve c), the voltammetry becomes scan rate-independent and sigmoidal-shaped with limiting currents, indicative of radial diffusion conditions. The solid lines in the figure, drawn for  $D = 1.0 \times 10^{-8}$  cm<sup>2</sup>/s for linear diffusion and for the same  $D$  under radial diffusion control at a microdisk electrode of radius  $r = 5 \mu\text{m}$ <sup>12</sup>

$$i_{\text{LIM}} = 4nFrDC^* \quad (1)$$

are consistent with the experimental currents (●) at very high and very slow potential scan rates, respectively.

At intermediate potential scan rates, peak currents (Figure 2) indicate diffusion conditions intermediate between the linear and radial diffusion limiting cases, i.e., mixed diffusion. This proved common throughout this study. Determination of diffusion coefficients from cyclic voltammograms taken under mixed linear–radial diffusion control can be accomplished from peak currents measurements using the Aoki expression<sup>13</sup>

$$i_{\text{PEAK}} = 4nFCDr[0.34 \exp[-0.66p] + 0.66 - 0.13 \exp[-11/p] + 0.351p] \quad (2)$$

where

$$p = [nFr^2\nu/RTD]^{1/2}$$

Figure 2 (dotted line) shows a fit of experimental peak currents to a plot of eq 2 based on  $D = 1.0 \times 10^{-8}$  cm<sup>2</sup>/s, as a  $\log[i]$  vs  $\log(1/\nu)$  plot, which is in good agreement with the results above.

Well-formed cyclic voltammetry could still be obtained at electrolyte concentrations lower than in Figure 2, but  $\Delta E_p$  values are larger owing to the lower ionic conductivities. For quantitative diffusion measurements, potential step chronoamperometry is more tolerant of resistive conditions. A chronoamperometric current–time transient is illustrated in Figure 3 for the same polymer solution discussed in Figure 2, together with the corresponding  $i$  vs  $t^{-1/2}$  plot (inset) of the Cottrell equation.<sup>14</sup>

$$i = nF\pi^{1/2}r^2D^{1/2}C/t^{1/2} \quad (3)$$

The linear, zero-intercept short-time portion of the plotted currents corresponds to a linear diffusion condition; the slope of this line gives  $D = 1.1 \times 10^{-8}$  cm<sup>2</sup>/s, in good agreement

with the above results. The curvature in the Cottrell plot at longer times (lower left-hand corner, Figure 3, inset) reflects the onset of radial diffusion conditions, which often obscured the linear region, in which case the diffusion coefficients were obtained by fitting the appropriate mixed diffusion equation to the Shoup–Szabo expression<sup>15</sup>

$$i = 4nFDrC[0.7854 + 0.8862\tau^{-1/2} + 0.2146 \exp(-0.7823\tau^{-1/2})]$$

where  $\tau = 4Dt/r^2$ .

All of the diffusion coefficients reported below were measured by the chronoamperometric procedure, using  $r = 5 \mu\text{m}$  Pt microdisk electrodes. The diffusion coefficient measurements were normally reproducible to within  $\pm 10\%$ , with stringent precautions at avoiding trace water and pumping away organic solvents both of which act to plasticize the polymer electrolyte and enhance the diffusion values.<sup>16</sup>

**Diffusion Coefficient Results.** Table 1 gives results for diffusion coefficients ( $D$ ) of the two ferrocene-labeled MPEG's (Fc 750 and Fc 1900) over a range of temperatures, host PEG MW, and electrolyte concentrations (which are stated as the ratio of polymer ether oxygens to dissolved LiClO<sub>4</sub> electrolyte). The temperature dependencies are shown in Figure 4 as activation plots, which are linear over the temperature range investigated. The apparent diffusional activation barriers obtained from the slopes of these plots are given in Table 1 and are indicated in Figure 4.

The effect of LiClO<sub>4</sub> electrolyte concentration on the MPEG-labeled ferrocene diffusion rate was investigated with Fc 1900 in the host polymer PEG 20,000 containing four different O/Li ratios: 8, 16, 250, and 500 (corresponding to entries I, H, F, and E, Table 1, and to 3.1, 1.6, 0.1, and 0.05 M LiClO<sub>4</sub>, respectively). We see that  $D(\text{Fc 1900})$  is substantially depressed, and  $E_A$  elevated, at the higher LiClO<sub>4</sub> concentrations (O/Li = 8 and 16). (The same trend is seen in  $D(\text{Fc 1900})$  measurements in PEG 2000 with O/Li ratios of 250 and 16, entries D vs G.) For the lower LiClO<sub>4</sub> concentrations corresponding to O/Li = 250 and 500 (entries F and E), on the other hand, both diffusivity  $D(\text{Fc 1900})$  and  $E_A$  in PEG 20 000 appear to be essentially independent of electrolyte concentration. We also see an independence of  $D(\text{Fc 750})$  and of  $E_A$  on electrolyte concentration in the comparison of entries B vs C (the differences lie within experimental uncertainty). This is a key observation (*vide supra*) since application of the voltammetric method to self-diffusion dynamics of polymer electrolytes requires that the influence of the cross-linking effect of the required electrolyte be reduced to a negligible level.

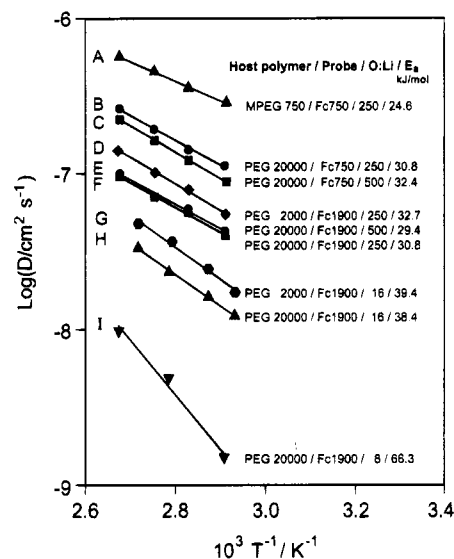
It is worth alternatively figuring the LiClO<sub>4</sub> electrolyte concentrations as Li<sup>+</sup> per polymer molecule as opposed to per ether oxygen, since this is a better measure of the actual degree of coordinative cross-linking (by Li<sup>+</sup>) that a diffusing MPEG-labeled ferrocene molecule (and its PEG host polymer surroundings) would experience. For a 10 mM Fc1900 solution in PEG 20 000 with O/Li = 250 (i.e., entry F, Table 1), there are *ca.* 1.8 Li<sup>+</sup> for each PEG 20 000 molecule, but only 0.2 Li<sup>+</sup> for each Fc 1900 molecule. From this, the extent of coordinative interaction experienced by a diffusing Fc 1900 should be essentially negligible, and that experienced by the PEG 20 000 host polymer chain nearly so. The analysis is similar for 10 mM Fc 750 in PEG 20 000 at O/Li = 250 (entry C). This is fully consistent with the lack of any noticeable change in  $D(\text{Fc 750})$  or  $D(\text{Fc 1900})$  when the electrolyte concentration is lowered further, to O/Li = 500 (entries C and E).

**TABLE 1: Summary of Diffusion, Conductivity, and Viscosity Results**

host polymer salt concn	T (°C)	D(Fc 750) × 10 <sup>8</sup> (cm <sup>2</sup> /s)	D(Fc 1900) × 10 <sup>8</sup> (cm <sup>2</sup> /s)	σ × 10 <sup>5</sup> (Ω <sup>-1</sup> cm <sup>-1</sup> )	η (cP)
(A) PEG 750 (O/Li = 250)	70	28		17.3	24.6
	80	35		21.3	19.1
	90	45		25.3	15.1
	100	56		29.8	12.0
	110			33.9	
<i>E<sub>a</sub></i> (kJ/mol) =		25		18	27
(D) PEG 2000 (O/Li = 250)	70		5.4	7.9	131.4
	80		7.8	9.6	101.4
	90		10	11.5	78.8
	100		14	13.3	63.5
	110			15.3	
<i>E<sub>a</sub></i> (kJ/mol) =			33	18	26
PEG 20000 (no LiClO <sub>4</sub> )	70				21600
	80				15600
	90				10400
	100				8490
					33
<i>E<sub>a</sub></i> (kJ/mol) =					
(B, E) PEG 20000 (O/Li = 500)	70	8.7	4.2		
	80	12	5.9		
	90	16	7.0		
	100	22	9.9		
		32	29		
<i>E<sub>a</sub></i> (kJ/mol) =					
(C, F) PEG 20000 (O/Li = 250)	70	10	3.9	6.8	22700
	80	14	5.5	8.4	16300
	90	19	7.0	10.2	11500
	100	26	9.4	12.1	8500
	110			14.1	
<i>E<sub>a</sub></i> (kJ/mol) =		31	31	20	35
PEG 20000 (O/Li = 25)	70			59	
	80			82	
	90			111	
	100			140	
	110			177	
<i>E<sub>a</sub></i> (kJ/mol) =				30	
(H) PEG 20000 (O/Li = 16)	68		1.2		
	70		1.3		33600
	75		1.6		
	80				21900
	85		2.3		
<i>E<sub>a</sub></i> (kJ/mol) =	90				14300
	95		3.3		
	100				9790
			38		44
(I) PEG 20000 (O/Li = 8)	70		0.15		
	86		0.48		
	101		0.97		
<i>E<sub>a</sub></i> (kJ/mol) =			66		
(G) PEG 2000 (O/Li = 16)	68		1.7		
	75		2.4		
	85		3.6		
	95		4.7		
<i>E<sub>a</sub></i> (kJ/mol) =			39		

The diffusion data also reveal chain length effects. That of the ferrocene probe's MPEG label on its diffusion coefficient can be considered from results for Fc 750 and Fc 1900 in a given PEG polymer host solvent. This is seen by comparison of data in entries C and F (Table 1) where  $D(\text{Fc 750})$  and  $D(\text{Fc 1900})$  were both measured in PEG 20 000. The shorter-tailed Fc 750 diffuses about 2.5-fold faster. In entries B and E,  $D(\text{Fc 750})$  and  $D(\text{Fc 1900})$  were again both measured in PEG 20 000, at a smaller electrolyte concentration (O/Li = 500), with a nearly identical difference. There is a small but consistent difference between the diffusivity of Fc 750 and Fc 1900 which can be attributed to the differing MPEG chain lengths of these probes. The activation barriers for entries B, C, E, and F are, on the other hand, all the same within experimental uncertainty ( $\pm 2$  kJ/mol).

The chain length effect of the PEG polymer host solvent on

**Figure 4.** Activation plots of the diffusion coefficients for the indicated polymer melt solutions.  $E_a^*$  is the apparent activation energy in kJ/mol. See also Table 1.**TABLE 2: Dependency on the Diffusion Coefficient on the Probe Concentration**

Fc 750, mM (70 °C)	$D_{\text{Fc}} \times 10^7$ , cm <sup>2</sup> /s	
	O/Li = 250	O/Li = 25
10	2.8	0.97
40	2.9	1.03
100	2.2	1.60

the ferrocene probe diffusivities is seen, at constant electrolyte concentration, by comparison of entries A *vs* B, D *vs* F, and G *vs* H. In each case, diffusion is slower in the higher MW host polymer (PEG 20 000). The difference, in diffusion coefficient and in the activation barrier, is largest for the entry A *vs* B comparison for diffusion of Fc 750 in PEG 750 *vs* in PEG 20 000. The difference for Fc 1900 diffusion in PEG 2000 *vs* PEG 20 000 is reproducible but small, only about 1.5-fold in  $D(\text{Fc 1900})$ ; the  $E_a$  values for entries D *vs* F and G *vs* H are again indistinguishable. We also note that a smaller probe (Fc 750) in a host polymer of high MW (PEG 20 000, entry B) can show a larger diffusivity than a larger probe (Fc 1900) in a polymer of lower MW (PEG 2000, entry B). This latter observation emphasizes that the consequences of the MPEG label chain length can be cleanly detected with the voltammetric diffusion measurements.

The validity of voltammetric diffusion measurements in polymer solutions additionally depends on whether the measured  $D$  parameter reflects solely physical diffusion effects or includes a contribution from electron self-exchanges<sup>17</sup> in the mixed-valent diffusion layer around the electrode. The latter contribution should be proportional to the redox-diffusant concentration, so experiments at differing concentrations (10, 40, 100 mM) of Fc 750 were conducted in PEG 750 solutions containing O/Li ratios of 25 and 250. The results, given in Table 2, show that over a 10-fold Fc 750 concentration range there is at O/Li = 250 no discernible concentration dependence of  $D$ , and only a slight one at O/Li = 25. We conclude that electron self-exchanges are unimportant in these data, particularly at the lower ferrocene concentrations. For diffusivities much smaller than those in Table 1, on the other hand, it is possible that avoiding electron self-exchange could require the use of lower probe concentrations.

**Ionic Conductivity.** The ionic conductivities ( $\sigma$ ) of three PEG solutions (MW 750, 2000, 20 000) with O/Li = 250 (0.1

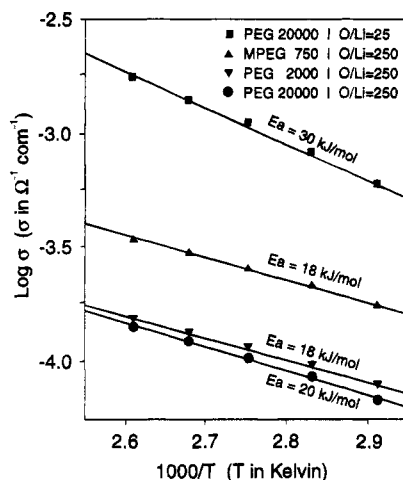


Figure 5. Activation plots of conductivity data.

M LiClO<sub>4</sub>) were measured using ac impedance and a cell with parallel Pt wire tip electrodes as described in the Experimental Section. These solutions contain no electroactive species, so the Pt electrodes act as "blocking" electrodes and the conductivity results reflect ionic transport in the electrolyte alone. The results (Table 1) show that at the lower LiClO<sub>4</sub> concentration (O/Li = 250), the conductivities fall in the order PEG 750 solutions > PEG 2000 > PEG 20 000, at all temperatures. These changes parallel those (*vide supra*) in  $D(\text{Fc } 750)$  and  $D(\text{Fc } 1900)$ . Activation plots of these data (Figure 5) are slightly curved in the manner common to polymer electrolyte solution conductivities;<sup>18</sup> the average activation energies  $E_\sigma$  taken from their slopes are given in Table 1. We see that there are only slight differences in the apparent activation barriers (*ca.* 20 kJ/mol) for ionic transport in these three O/Li = 250 solutions and that the thermal barrier for ionic transport in all cases is lower than that for the ferrocene probe. The ionic conductivity of a solution of PEG 20 000 with a higher electrolyte concentration O/Li = 25 (1 M LiClO<sub>4</sub>) was also measured (Figure 5); this displayed a higher conductivity, and a larger apparent  $E_\sigma$  (*ca.* 30 kJ/mol).

**Viscosity.** Diffusivity and ionic conductivity in polymer electrolytes are both affected by the short-range segmental motion of the polymer chains (microscopic viscosity). Longer range chain motions influence the macroscopic melt viscosity, which is a function of the temperature, the molecular weight of the polymer, and the electrolyte cross-linking effect. It is therefore important to include the melt viscosity of a polymer electrolyte in a study of its electrochemical properties. The viscosities of PEG solutions were measured as a function of the molecular weight of the polymer and the concentration of the electrolyte. The results are presented in Table 1 and in Figure 6 as  $\log [1/\eta]$  plots which are linear over the temperature range and from which apparent activation energies were taken (Table 1).

Inspection of the results leads to the following observations. (a) The apparent activation energies for viscometric flow increase somewhat with the molecular weight of the PEG host solvent and are similar to those for diffusion of the ferrocene-labeled MPEG's varying between 27 and 35 kJ/mol. (b) The viscosities vary strongly with the PEG solvent MW; PEG 750 < PEG 2000 < PEG 20 000, at O/Li = 250 (Table 1). Unlike the ionic conductivity results where a large change occurred between PEG 750 and 2000 and little between 2000 and 20 000, a considerable viscosity difference is seen between PEG 2000 and 20 000. (c) Most significantly, addition of electrolyte at the O/Li = 250 concentration has almost no effect at all on

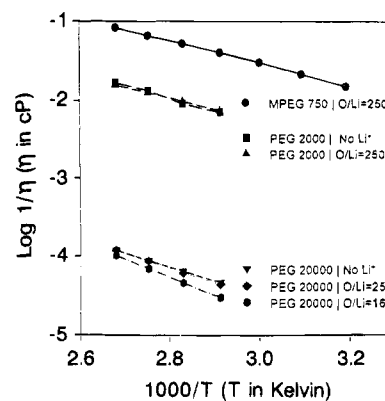


Figure 6. Activation plots of viscosity data.

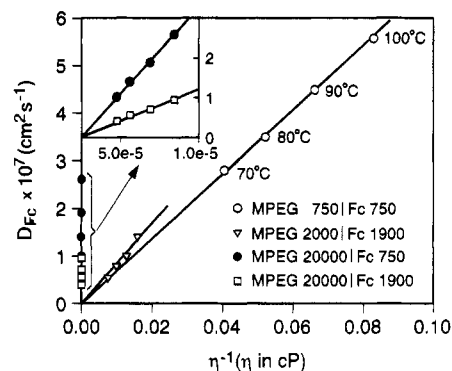


Figure 7. Inverse relation between the diffusion coefficient of the ferrocene-labeled MPEG and the viscosity of the host solvent polymer. The four data points on each line correspond to 70, 80, 90, and 100 °C.

viscosity; see the comparison between PEG 20 000 with no LiClO<sub>4</sub> and with O/Li = 250 (entry C, F) in Table 1, and the analogous one for PEG 2000 in Figure 6. This result is consistent with the observations above regarding the O/Li = 250 concentration range as exerting minimal effects on polymer chain dynamics. Addition of higher electrolyte concentrations does noticeably elevate viscosity, and apparent activation energy, as would be expected. Table 1 shows that at O/Li = 16, the apparent activation energies for viscosity and diffusion are both elevated to 44 and 38 kJ/mol, respectively.

## Discussion

Diffusion and viscosity evidence has been presented above that at LiClO<sub>4</sub> electrolyte concentrations as low as O/Li = 250, there is little if any effect of the presence of the electrolyte on the dynamical properties of the polymer chain. The central conclusion of the study is then that voltammetric measurements at low electrolyte concentrations are possible and, given attention to polymer probe MW monodispersity<sup>10</sup> (which was not done here), should be suitable for polymer self-diffusion investigations.

The chain length and viscosity data allow some additional comparisons to the diffusion results. The Figure 7 plot of Table 1 data shows that each different ferrocene-labeled PEG solution displays an inverse relation between the diffusion coefficient of ferrocene-labeled MPEG and the viscosity of the PEG host solvent. The Stokes-Einstein relation predicts an inverse proportionality between diffusion coefficient and viscosity but is not expected to apply to the present case, where the diffusing solute is smaller than the solvent. Artificially small values of the hydrodynamic radius  $R_H$  result in fact from applying the Stokes-Einstein equation to Figure 7. The classical Rouse model<sup>19</sup> for viscoelastic properties of polymers predicts that the

viscosity of a polymer melt should be proportional to the product of the host polymer molecular weight  $M_{\text{host}}$  and the monomer friction coefficient  $\zeta_0$ , and that the diffusion coefficient of a diffusant in the polymer should be inversely proportional to the product of  $\zeta_0$  and the diffusant molecular weight  $M_{\text{probe}}$ . Thus, through  $\zeta_0$  the Rouse model also anticipates an inverse  $D$  vs  $1/\eta$  relation and Figure 7 thus portrays Rouse-like behavior in which the  $D$  vs  $1/\eta$  proportionality constant contains  $\zeta_0$ ,  $M_{\text{host}}$ , and  $M_{\text{probe}}$ .

Examining the slopes of Figure 7 (inset), those for Fc 750 and Fc 1900 in PEG 20 000 fall in a 2.5 ratio, meaning that for this case of a probe diffusing in a much larger host, the  $D$  vs  $1/\eta$  slope varies approximately linearly with  $M_{\text{probe}}$ . For Fc 750 diffusing in PEG 750 and Fc 1900 diffusing in PEG 2000, the  $D$  vs  $1/\eta$  slopes on the other hand are much smaller, by ca.  $10^2$ -fold as compared to those in PEG 20 000. Thus, Figure 7 describes the approximate<sup>20</sup> relation  $D_{\text{probe}} \propto M_{\text{probe}} M_{\text{HOST}}^2 / \eta$  and draws together the experimental interrelations of diffusivity, chain length, and viscosity described above. The stronger dependency on  $M_{\text{host}}$  obviously originates in the steep dependence of  $\eta$  on the host polymer MW, noted earlier. It is well known<sup>21</sup> that polymer  $\eta$  values often exhibit stronger than linear dependence on polymer MW, and our observation is another example of this phenomenon.

Stated in alternative terms, the diffusion coefficient of the ferrocene-labeled polyether is expected to reflect the microscopic viscosity of the host polymer and relatively short-range motions, whereas the measured polymer viscosity is a macroscopic property and reflects relatively long range displacements. Figure 7 shows that the microscopic  $D$  and macroscopic  $\eta$  retains an inverse proportionality even though the proportionality constant is MW-dependent.

The diffusion of polymer chains in poly(ether) melts with molecular weights below the so-called critical entanglement molecular weight ( $M_c$ ), or close to it, has seen relatively little investigation, and the study by Smith et al.,<sup>10</sup> on poly(propylene oxide) self-diffusion, is the only study of which we are aware. We finish then with a brief examination of the small body of probe and polymer host chain length data at  $O/\text{Li} = 250$  in terms of a power law<sup>6</sup>  $D \propto M^{-x}$ . For dependency of diffusion on the host MW, we find

$$D(\text{Fc 750/PEG 20000})/D(\text{Fc 750/PEG 750}) = 0.41 = (20000/750)^{-x}; \quad x = 0.27$$

$$D(\text{Fc 1900/PEG 20000})/D(\text{Fc 1900/PEG 750}) = 0.70 = (20000/750)^{-x}; \quad x = 0.11$$

and on the ferrocene-labeled MPEG MW,

$$D(\text{Fc 1900/PEG 20000})/D(\text{Fc 750/PEG 20000}) = 0.38 = (1900/750)^{-x}; \quad x = 1.04$$

and on the ferrocene-labeled MPEG MW when diffusing in a host of the same MW:

$$D(\text{Fc 1900/PEG 2000})/D(\text{Fc 750/PEG 750}) = 0.22 = (1900/750)^{-x}; \quad x = 1.6$$

These comparisons show that the host MW ( $x = 0.27, 0.11$ ) influences diffusivity much less than does that of the MPEG probe ( $x = 1.04$ ), even though the host MW changes from below to above the critical entanglement  $M_c$  and the viscosity changes by about  $10^3$  in the comparison.

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- (20) Dividing the Figure 7 slopes,  $6.7 \times 10^{-6}$  (○),  $9.2 \times 10^{-6}$  (▽),  $2.2 \times 10^{-3}$  (●), and  $0.8 \times 10^{-3}$  (□) by  $M_{\text{probe}} M_{\text{HOST}}^2$  gives  $1.2 \times 10^{-15}$ ,  $1.6 \times 10^{-14}$ ,  $7 \times 10^{-15}$ , and  $1 \times 10^{-15}$ , respectively.
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