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Binding of Monovalent Ions to PEO in Solution: Relevant Parameters and Structural Transitions

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ABSTRACT: We present a comparative small-angle neutron scattering and theoretical study of the charging effects of poly(ethylene oxide) (PEO) in the presence of monovalent ions as a function of the solvent characteristics and cation strength, and we demonstrate that the classical "salting-in" condition is constituted by distinct subregimes depending on salt and solvent characteristics. In solvents with moderate dielectric constant and moderate hydrogen- bonding capacity, two distinct regimes can be distinguished: (1) at low ionic strengths, the addition of salts primarily results in the formation of polymer−cation association complexes and thus in charging of the polymer chain (*binding regime*); (2) at higher salt concentrations, the binding of ions becomes increasingly unfavorable, resulting in the screening of electrostatic interactions and neutral polymer-like characteristics of PEO are observed (*screening regime*). The extent of ion-binding is compared to predictions based on mean-field theory in the thermodynamic limit, and it is shown that the pseudo-polyelectrolyte type changes in the polymer's conformation can successfully be described by the random phase approximation. In solvents of high dielectric constant or pronounced hydrogen-bonding capacity, the solvation of ions counteracts the complex formation process, and PEO effectively remains a neutral polymer in solution.

Introduction

Understanding of the consequences of ion binding to neutral amphiphilic macromolecules in solution and the associated changes in the polymer's conformation and solution properties is of fundamental relevance to many technological and biological applications. For example, the ability to control crystal shape and growth during precipitation processes has made amphiphilic polymers important additives in the controlled synthesis of various inorganic powders.[1] Electrolyte uptake and release processes are fundamental to the function of drug release systems and to the biochemical function of natural molecules.[2] Poly(ethylene oxide) (PEO) has attracted particular interest as a model system to study the effect of charging induced by ion−dipole association due to its water solubility, its chemical simplicity that nevertheless displays all features of an amphiphilic polymer, and its practical importance as bioinert implant material.[3] The latter is related to the low protein adsorption on PEO, the origin of which is thought to be in the extraordinary stabilization of PEO by hydrogen bonds in aqueous solutions.[4] Several experimental papers have been published that point out the relevance of hydrogen bonding for understanding both the solubility and reactivity of PEO. The common result of these previous studies is the observation of two distinguishable effects upon addition of salt ions to PEO in solution, depending on the valence and type of the added salt: (1) First is the "salting-out" effect that is characterized by a collapsing of the polymer coils in solution upon temperature increase or addition of salt.[5−7] This chain collapse is a gradual process in which the hydrodynamic volume of the molecule decreases as the salt concentration increases. (2) Second is the "salting-in" effect that results as a consequence of electrical repulsion between the ions that bind to the neutral polymer at low salt concentrations via a ion−dipole interaction. Previous studies of electroviscous effects in methanol demonstrated that the salt−polymer adduct exhibits typical polyelectrolyte characteristics at low salt concentrations. Measurements of the association constant between potassium iodide and PEO in the presence of methanol suggested that one salt molecule associates with about nine ethylene oxide units.[6] Despite the great effort to understand the complex properties of PEO in solution in the presence of added salts, there are still some controversies between the extensive volume of the experimental[5−10] and the few theoretical results.[11−14] The differences among the distinct phenomena that are observed in solutions of PEO in the presence of various added salts have fueled an active debate regarding which solvent and electrolyte characteristics are relevant for PEO expansion ("salting-in" or complexation, i.e., binding of salt ions) and collapse ("salting-out").

This paper presents a comparative neutron and theoretical study of the effect of added monovalent salt on PEO in solutions of solvents with varying capacity of hydrogen bonding and dielectric constant. In particular, this paper is concerned with a detailed investigation of the phenomenon of ion binding that is presumed to arise from ion−dipole interactions and that is a characteristic of the "salting-in" effect.[5,6] The association of salt ions with PEO chains is shown to transform the neutral PEO to a weakly charged polyelectrolyte in the presence of a solvent that is characterized by a moderate dielectric constant. To analyze the static properties of these association complexes, small-angle neutron scattering (SANS) studies are particularly valuable since

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the total and intrachain contributions to the scattered intensity can be decomposed via the zero-average contrast condition. The conclusions drawn from the scattering experiments and the theoretical predictions based on the mean field free energy[15] and random phase approximation (RPA)[16−19] are compared to results from concurrent nuclear magnetic resonance and conductivity measurements. The range of concentrations is significantly extended beyond the one of previous studies, revealing two distinct regimes, namely the *binding* and *screening regimes*, that can be distinguished in solutions of PEO in solvents with poor and moderate hydrogen-bonding capacity. We demonstrate that RPA as applied to weakly charged polyelectrolytes[17,18] can successfully be used to predict the observed structural changes of PEO in solutions with added monovalent salt.

The structure of the present paper is as follows. After discussing the experimental conditions as well as the data analysis procedure, we introduce the theoretical concepts that are necessary for the interpretation of the ion-binding phenomena. Next we present a detailed study of the structural changes that occur in PEO solutions as a function of the amount and ionic strength of added salts as well as solvent characteristics. We will conclude by examining molecular weight and temperature effects. We hope that our study will contribute to a better understanding of the consequences of association-complex formation on the properties of neutral polymers in solution.

Materials and Methods

Materials. Poly(ethylene oxide) (PEO) polymers of molecular weights $M_w = 9$, 58.9, 100, and 334.5 kg/mol were obtained from Polymer Source. The polydispersity coefficient was found to be between 1.05 and 1.20. The solvents (methanol, acetonitrile, *N*-methylformamide (NMF), deuterium oxide) and salts (potassium iodide, KI, potassium chloride, KCl, and lithium perchlorate, $LiClO_4$) were purchased from Aldrich Chemicals. The appropriate PEO/salt solutions were prepared in deuterated solvents in order to increase the contrast between PEO and solvents for neutron scattering measurements. To satisfy the zero-average contrast condition (ZAC condition) and to measure the form factor of PEO, a mixture of equal proportions of protonated and deuterated PEO in a suitable mixture of protonated and deuterated solvent was prepared (see section "ZAC Condition"). The concentration of PEO was chosen to be $C_{PEO} = 20$ mg/mL, which is equal to $C_{EO} = 0.45$ M, where C_{EO} denotes the concentration of ethylene oxide repeat units (note that for PEO with molecular weight $M_w = 100$ kg/mol, $C_{PEO} \approx C^*$, where C^* is the polymer overlap concentration). The salt concentration was varied from 0 to 45 mg/mL in the case of KI and $LiClO_4$ and from 0 to 5 mg/mL in the case of KCl. The molar ratio between salt and polymer C_{salt}/C_{EO} was varied from 0 to 0.6 in the case of PEO/MeOD/KI, from 0 to 0.27 in the case of PEO/MeCN/KI, from 0 to 0.93 in the case of PEO/MeOD/$LiClO_4$ and PEO/MeCN/$LiClO_4$ and from 0 to 0.15 in the case of PEO/MeOD/KCl (MeOD and MeCN represent deuterated methanol and acetonitrile, respectively). All experiments were carried out at a temperature $T = 25$ °C.

Small-Angle Neutron Scattering (SANS). The scattering measurements on PEO solutions were carried out using the SAD and SAND instruments at the Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory. The momentum transfer range is $0.006 < q < 0.25$ Å^{-1}. The contribution due to incoherent scattering (isotope and nuclei-spin) was calculated as $I_{incoh} \sim \Phi b_{incoh}^2$, where Φ is the number of hydrogen atoms in the sample/cm^3 and $b_{incoh} = 2.52 \times 10^{-12}$ cm is the incoherent scattering length. I_{incoh} was determined to be equal to 0.0035 cm^{-1} which was subtracted from the measured intensity.[16]

Zero-Average Contrast Match Method (ZAC Condition). The scattering intensity $I(q)$ per unit volume (the vector $\mathbf{q}$ is characterized by the scattering angle θ and the wavelength of the incident neutrons λ and has the modulus $q = (4\pi/\lambda)\sin(\theta/2)$) from a mixture of one single polymer species in a given solvent is proportional to the sum of two contributions: the intrachain $S_{intra}(q) \propto P(q)$ (the polymer form factor) and the interchain signal $S_{inter}(q) \propto Q(q)$ (the Fourier transform of the distinct pair correlation function). The total signal $I(q)$ is derived from a single scattering measurement, using all chains either deuterated or protonated. To obtain $S_{intra}(q)$, a fraction x_D of the polymer is deuterated and the measured scattering intensity under zero-average contrast (ZAC) condition is then directly proportional to the single chain scattering function, $I_{ZAC}(q) = (\rho_D - \rho_H)^2\, x_D(1 - x_D)v\varphi NP(q)$. Here, ρ is the scattering length density of the polymer (D and H refer to the deuterated and hydrogenated polymer, respectively), with respect to the solvent, v is the volume of a monomer, φ is the polymer volume fraction (with $\varphi = C_{PEO}N_{Av}/m_0$, where N_{Av} is the Avogadro number and $m_0 = 44$ g/mol is the mass of a monomer of hydrogenated PEO), and N is the degree of polymerization. The amount of deuterated solvent fraction for ZAC condition is $x_D = 63.7\%$ for methanol, 62.2% for acetonitrile, and 59.4% for water.

Data Analysis. The background corrected intensities $I_{ZAC}(q)$ and $I(q)$ in the case of salt-free solutions were fitted to the Debye function $P_D(q) = 2(\exp(-u) + u - 1)/u^2$ where $u = q^2 R_G^2$ with one unknown parameter R_G, the radius of gyration, as well as a Lorentzian function $P_L(q) \propto (q^2 + \xi^{-2})^{-1}$, with ξ being the correlation length. Upon addition of salt to the PEO solutions, the intensity exhibits a broad peak in the scattering profile whose position q^* depends on the amount of added salt and on the polymer concentration. The characteristic length scales that determine the properties of the solutions are the electrostatic correlation length ξ_e and the screening length κ^{-1}. From the maximum position at q^*, ξ_e was determined as $2\pi/q^*$. ξ_e can be understood as a measure of the chain expansion that is a consequence of the intramolecular electrostatic repulsion that results from the binding of like-charged ions to the polymer backbone.

Nuclear Magnetic Resonance (NMR). NMR spectra were taken in a Bruker Avance DPX-400 instrument operating at 400 MHz for ^{1}H equipped with a broadband probe. All experiments were run at room-temperature $T = 25$ °C. For all experiments, tetramethylsilane (TMS) ($C_{TMS} = 0.1\%$) was used as a standard. The chemical shift is expressed in hertz.

Ionic Conductivity Measurements. Measurements of the ionic conductivity were performed using an ORION 130A conductivity meter equipped with a DuraProbe conductivity cell model 013610 (nominal cell constant: 0.55 cm^{-1}). The calibration of the cell constant was performed by measurement of aqueous KCl solutions (0.01 and 0.1 M).

Theoretical Background

Thermodynamic Limit ($q = 0$). (a) Solvent Effect. The classical solubility parameter formalism relates the Flory interaction parameter of the polymer χ, to the solubility parameters δ_i of the individual components through the Hildebrand equation, $\chi = v_{pol}(\delta_{pol} - \delta_S)^2/k_BT$ (where v_{pol} is the polymer volume and k_B is the Boltzmann constant). Indices "pol" and "s" refer to the polymer and solvent, respectively. The total van der Waals force is reflected in the solubility value δ_i often denoted as the Hildebrand or Hansen parameter for apolar or polar compounds, respectively. Hansen and Skaarup[20] assume that the cohesive energy arises from dispersive (δ_d), permanent dipole−dipole interactions (δ_p), and hydrogen-bonding forces (δ_h) where $\delta_i^2 = \delta_h^2 + \delta_d^2 + \delta_p^2$. Solubility parameters provide a means for rapidly predicting the extent of interaction between solvent and solute. Miscibility will be enhanced for components with similar solubility parameters, which are calculated based upon their cohesive energies. The literature solubility parameter for PEO is 10.5 ± 0.5

$\mathrm{cal}^{1/2}\mathrm{cm}^{-3/2}$, whereas for the solvents, $\delta_S = 23.4$ in the case of water, 16.1 for NMF, 14.5 for methanol, and 11.9 for acetonitrile.[21,22] Hence, the solubility of PEO is expected to be lower in NMF and methanol than in acetonitrile. Water has the highest value of δ_S, which is one reason for the major difficulties in applying solubility parameter theory to aqueous systems.[21]

(b) Salt Effect. Ion–dipole interactions between the cation and the ether oxygen of the polymer repeat unit can result in the formation of association-complexes upon addition of salt to PEO solutions, thus rendering the neutral polymer into a weakly charged polyelectrolyte. This formation of association-complexes was monitored in the case of PEO/KI/methanol by characteristic shifts of NMR resonances that occurred upon complexation.[23] Binding of salt ions to PEO chains induces repulsive electrostatic interactions between the repeat units of alike electrostatic charge. These long-range repulsive interactions dominate over the short-range interactions (excluded volume) and increase the polymer solubility. The specific interactions between the cation and the neutral polymer are described by the effective binding energy needed for the formation of a monocomplex. Consider, for example, a solution of neutral PEO with a monomer concentration C_{EO} in the presence of potassium iodide (KI) with a concentration C_{salt}. The concentration of available binding sites for the cation association is then C_{EO}. A concentration [complex] (with [complex] $= fC_{EO}$ where f is the charge fraction, $0 < f < 1$) of the potassium ions are bound to the PEO chains while the concentration of free potassium ions is $[K^+]_{free} = C_{KI} -$ [complex] (note that [complex] $= fC_{EO}$ refers to the concentration of $CH_2{-}CH_2{-}O{\cdot}K^+$ units; C_{EO} denotes the overall concentration of $CH_2{-}CH_2{-}O$ repeat units). Assuming a high molecular weight of the polymer, we can omit the translational entropy of the chains and focus only on the electrostatic contributions. In this case, the free energy should read as follows:[15]

$$\begin{aligned}\beta F \approx{}& [\mathrm{complex}]\log[\mathrm{complex}] + [\mathrm{EO}]_{free}\log[\mathrm{EO}]_{free} + \\ & C_I \log C_I + [K^+]_{free}\log[K^+]_{free} - \\ & E[\mathrm{complex}] - \kappa^3/(12\pi)\end{aligned} \quad (1)$$

Here, $\beta = 1/k_BT$, $[\mathrm{EO}]_{free} = C_{EO} -$ [complex], C_I is the iodide concentration, and E is the binding energy. The first two lines in eq 1 describe the entropy of interchange between the charged and neutral repeat units along the chain as well as the entropy of the small ions which do not contribute to the formation of monocomplexes. The third line includes the effective binding free energy and the electrostatic polarization energy of the solution similar to that of a simple electrolyte solution where all the charges contribute to the screening.[24,25] The screening length is given by $\kappa^2 = 4\pi l_B \sum_i C_i z_i^2$ where C_i is the concentration of the ionic species i and z_i is the valence of ion i. The Bjerrum length $l_B = \beta e^2/(\epsilon_0\epsilon_r)$, where e denotes the elementary charge, is the distance where the thermal energy compensates the Coulombic interaction. The average concentration of monocomplexes [complex] is the one that minimizes the free energy and thus the classical chemical equilibrium law[5,6,23] is recovered:

$$K_{eq} = [\mathrm{complex}]/([\mathrm{EO}]_{free}[K^+]_{free}) \quad (2a)$$

Here, the equilibrium constant can be written as[15]

$$K_{eq} = k_0 \exp[-\kappa l_B/2] \quad (2b)$$

k_0 is the bare equilibrium constant that is defined as $k_0 = \exp[1 + E]$. Note that following eq 2b, two distinct regimes can be distinguished. In the *binding regime* ($\kappa l_B/2 \ll 1$), one can expand eq 2b as $K_{eq} \approx k_0(1 - \kappa l_B/2)$. Consequently, the equilibrium constant K_{eq} is expected to be nearly independent of the salt concentration (at very low C_{salt}) and corresponds to k_0 at vanishing ionic strength. However, at high ionic strength, i.e., in the *screening regime* ($\kappa l_B/2 \gg 1$), K_{eq} decreases exponentially. For PEO chains consisting of N repeat units of size a, each chain then carries $Z = fN$ elementary charges where the degree of ionization of the monomers f is much smaller than unity, or more explicitly, $f \ll (a/l_B)^2$.

Scattering at Finite q from a Single Polyion in Solution. Here we qualitatively estimate the effect of the electrostatic interactions on the scattered intensity $I(q)$. A model which properly describes the scattering intensity of charged systems has to take into account all the interactions between different segments: short-range (excluded volume interactions) and long-range repulsive interactions (electrostatic interactions). The general formalism is based on a straightforward extension of the classical Zimm formula to charged mixtures, written in matrix form as[16–19]

$$\mathbf{S}^{-1}(q) = \mathbf{S}_0^{-1}(q) + \mathbf{U}(q) \quad (3)$$

where $\mathbf{S}(q)$ and $\mathbf{S}_0(q)$ are the total and the bare structure matrices, $\mathbf{U}(q)$ is the interaction matrix, and q is the magnitude of the wave vector. $\mathbf{U}(q)$ is the sum of the classical excluded volume matrix and the electrostatic interaction matrix:

$$\mathbf{U}(q) = \mathbf{V} + \alpha(q)\, f f^{T} \quad (4)$$

The elements of the excluded volume matrix $\mathbf{V}$ are the parameters v_{ij}, with $v_{ij} = 1/\varphi_s - \chi_{is} - \chi_{js} + \chi_{ij}$, where φ_s is the solvent concentration (number of solvent molecules per unit volume) and χ_{is} and χ_{ij} are the polymer i/solvent and polymer i/polymer j Flory interaction parameters, respectively. The second term in eq 4 describes the electrostatic interaction, which can be written for an isotropic system as

$$\alpha(q) = \frac{4\pi l_B}{q^2 + \kappa^2} \quad (5)$$

The Bjerrum length l_B and the Debye–Hückel screening length κ^{-1} are defined above. $\boldsymbol{f}$ is a column vector whose elements f_i represent the apparent valences of monomers i (charge fraction $0 < f_i < 1$), and $\boldsymbol{f}^{\mathbf{T}}$ is its transpose. For a single polyion in solution, the matrix equation becomes scalar and reduces to

$$S^{-1}(q) = S_0^{-1}(q) + U(q) \quad \text{or} \quad S(q) = \frac{S_0(q)}{1 + U(q)S_0(q)} \quad (6)$$

with

$$U(q) = v + \alpha(q) f^2 \quad \text{and} \quad S_0(q) = \varphi N P(q) \quad (7)$$

Next, we assume that the weakly charged polyion is a flexible polymer and that its form factor $P(q)$ can be represented by the Debye function. Substitution of eq 7 into eq 6 in its reciprocal form leads to

$$\varphi N S^{-1}(q) = \varphi N S^{-1}(q)|_{\text{neutral}} + \alpha(q) f^2 \varphi N \qquad (8)$$

with

$$\varphi N S^{-1}(q)|_{\text{neutral}} = 1/P_{\text{D}}(q) + v\varphi N \qquad (9)$$

The excluded volume parameter v is related to the experimental second virial coefficient A_2 by, $v = 2A_2 m_0^2/N_{\text{Av}}$. In the low q range, it is sufficient to expand the form factor $P_{\text{D}}(q)$ in terms of q and to keep only the first-order contributions. This allows us to write eq 9 in terms of the correlation length ξ

$$\varphi N S^{-1}(q)|_{\text{neutral}} = \varphi N S^{-1}(q = 0)(1 + q^2\xi^2) \qquad (10)$$

where the structure factor at zero q and the correlation length are given by

$$\varphi N \text{S}^{-1}(q = 0) = 1 + v\varphi N \quad \text{and} \quad \xi^2 = \frac{R_{\text{G}}^{\,2}}{3}\frac{1}{1 + v\varphi N} \qquad (11)$$

The scattered intensity for one polymer in solution is known as $I(q) = (b_{\text{pol}} - b_{\text{S}})^2 S(q)$, where the structure factor $S(q)$ is given by eqs 6−9 and b_{pol} and b_{S} are the coherent scattering lengths per monomer and solvent molecule, respectively. The important property connected to $S(q)$ is that it has a peak at the wave vector q^* in the presence of electrostatic interactions. This can be seen directly by differentiating $S(q)$ with respect to q^2. This calculation is simplified if we use the Pade approximation for the bare structure factor $S_0(q)$, $S_0(q) \approx \varphi N/(1 + q^2R_{\text{G}}^2/2)$ which fits quite well the Debye function in the whole q range. R_{G}^2 is the unperturbed radius of gyration, i.e., $R_{\text{G}}^2 = Na^2/6$, where a is the monomeric size of the polyelectrolyte. The structure factor has a peak at the finite value of q^*

$$q^{*2} = \left(\frac{48\pi l_{\text{B}} f^2 \varphi}{a^2}\right)^{1/2} - \kappa^2 \qquad (12)$$

Addition of a large amount of salt increases the ionic strength of the solution and shifts the peak of the intensity to lower q^* values until it eventually reaches $q^* = 0$. All electrostatic interactions are screened, and the solution characteristics of a neutral polymer are obtained.

Results and Discussion

The effects of the addition of monovalent salt to solutions of PEO can be distinguished depending on the solvent's capacity to form hydrogen bonds and to screen the long-range electrostatic interactions. To compare the experimental data with theoretical predictions we evaluate eqs 3−12 using the following numerical values that are valid for the rest of the paper unless explicitly noted otherwise: $N = M_{\text{w}}/m_0 \approx 2272$ (for $M_{\text{w}} = 100$ kg/mol), $C_{\text{PEO}} = 20$ mg/mL equal to $C_{\text{EO}} = 0.45$ M, and the salt concentration C_{salt} is varied between 0 and 45 mg/mL.

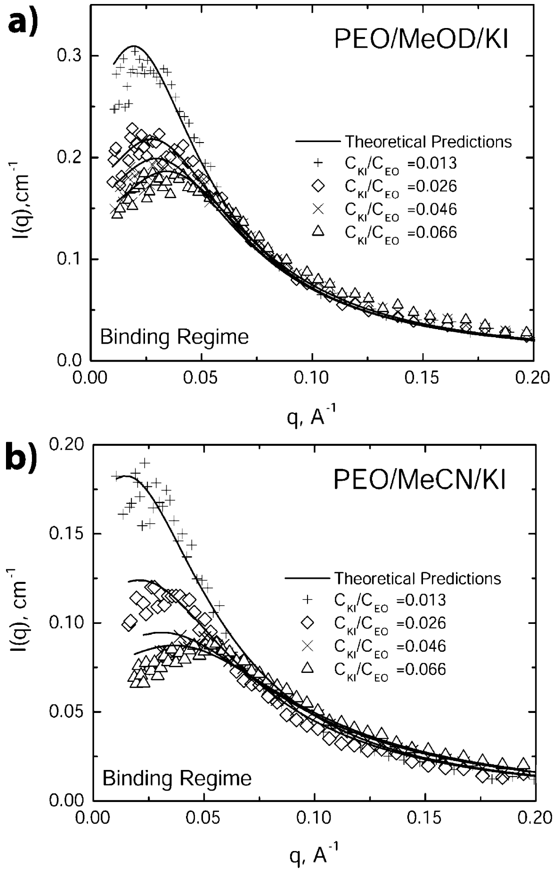

Figure 1. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{\text{EO}} = 0.45$ M. $M_{\text{w}} = 100$ kg/mol (*binding regime*). The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. The continuous lines are obtained for an adjustable charge fraction f and correspond to the fixed ratio $C_{\text{KI}}/C_{\text{EO}} = 0.013$ (+), 0.026 (◇), 0.046 (×), and 0.066 (Δ). Panel a: $f = 0.00585$, 0.012, 0.014, and 0.018 (case of PEO/MeOD/KI). Panel b: $f = 0.00585$, 0.012, 0.021, and 0.0295 (case of PEO/MeCN/KI).

(A) Solvents with Moderate Dielectric Constant and Moderate or Poor H Bonding: Methanol and Acetonitrile. Here we report a comparative study of the consequences of the addition of different added monovalent salts (KI, $LiClO_4$, and KCl) to solutions of PEO in methanol and acetonitrile. Note that both solvents are characterized by a moderate dielectric constant ($\epsilon_{\text{MeOD}} = 32.5$ and $\epsilon_{\text{MeCN}} = 36$) and moderate or poor hydrogen-bonding capacity. Figures 1−5 depict the variation of $I(q)$ as a function of q, for various values of the ionic strength for different mixtures, that is PEO/KI/MeOD, PEO/KI/MeCN, PEO/$LiClO_4$/MeOD, PEO/$LiClO_4$/MeCN, and PEO/KCl/MeOD where different symbols represent the SANS measurements and the continuous curves correspond to the theoretical predictions based on RPA (see eqs 3−12).

Effect of Salt (KI) Concentration. Two distinct concentration regimes can be distinguished depending on the salt concentration. Parts a and b of Figure 1 reveal a pronounced decrease of the scattered intensity in the low q range upon addition of potassium iodide to the salt-free solutions (PEO/MeOD or PEO/MeCN), indicative of the *binding regime* ($\kappa l_{\text{B}}/2 < 1$). Within the range $q\xi < 1$, the introduction of increasing amounts of KI progressively lowers the scattered intensity, indicating the lower osmotic compressibility generated by the salt ions and the increased entropy of the system. These

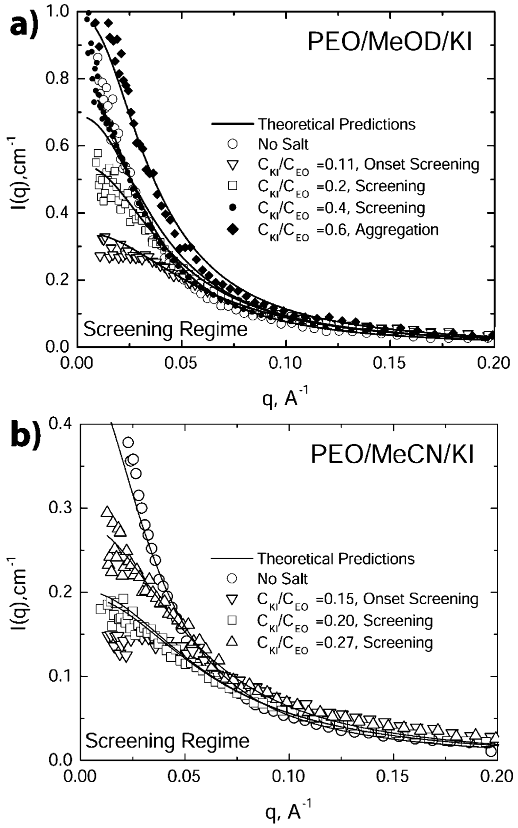

Figure 2. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{\mathrm{EO}} = 0.45$ M. $M_w = 100$ kg/mol (*screening regime*). The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. Panel a: PEO/MeOD/KI, (○, ▽, □, ●, ◆) refer to: no salt and $C_{\mathrm{KI}}/C_{\mathrm{EO}} = 0.11$ (*onset of screening*), 0.2, 0.4 (*screening*), and 0.6 (aggregation). Panel b: PEO/MeCN/KI, (○, ▽, □, Δ) refer to the following: no salt; $C_{\mathrm{KI}}/C_{\mathrm{EO}} = 0.153$ (*onset of screening*), 0.2, and 0.27 (*screening*).

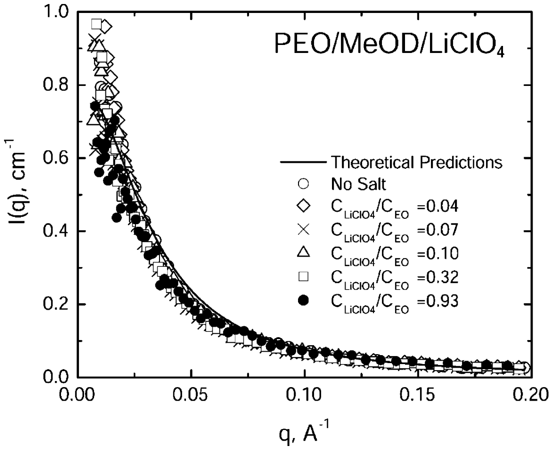

Figure 3. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{\mathrm{EO}} = 0.45$ M. $M_w = 100$ kg/mol for PEO/MeOD/LiClO$_4$. The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively (○, ◇, ×, Δ, □, ●) refer to the following: no salt and $C_{\mathrm{LiClO_4}}/C_{\mathrm{EO}} = 0.04$, 0.07, 0.10, 0.32, and 0.93.

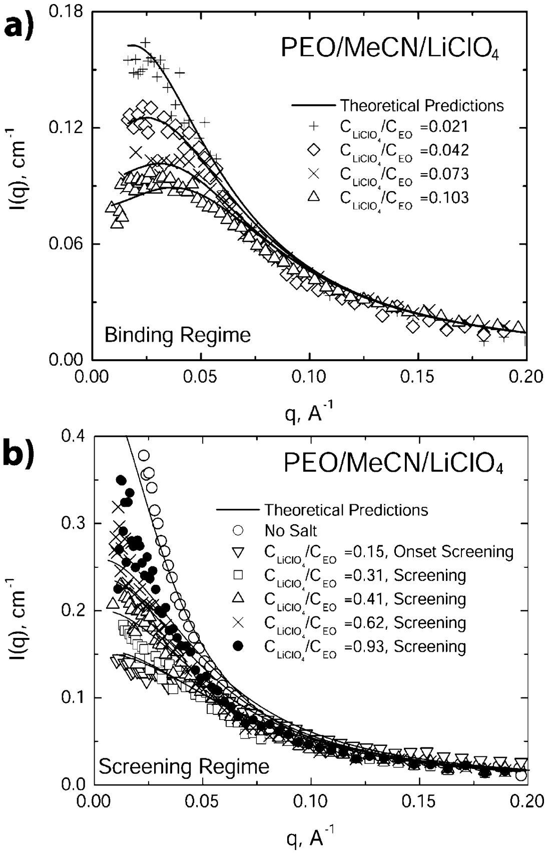

Figure 4. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{\mathrm{EO}} = 0.45$ M. $M_w = 100$ kg/mol for PEO/MeCN/LiClO$_4$. The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. Panel a: *binding regime*. The continuous lines are obtained for an adjustable charge fraction $f = 0.0091$, 0.018, 0.027, and 0.038 and correspond to the following: $C_{\mathrm{LiClO_4}}/C_{\mathrm{EO}} = 0.021$ (+), 0.042 (◇), 0.073 (×) and 0.103 (Δ). Panel b. The continuous lines are obtained for an adjustable charge fraction $f = 0$, 0.065 and correspond to: $C_{\mathrm{LiClO_4}}/C_{\mathrm{EO}} = 0$ (○), 0.15 (▽, *onset of screening*), 0.31 (□), 0.41 (Δ), 0.62 (×), and 0.93 (●) (*screening regime*).

results are interpreted in terms of a transformation of the neutral polymer molecules into polyelectrolyte-type association complexes through ion–dipole interactions between cations (K$^+$) and the ether oxygens of the PEO chains. The charge–charge repulsions between PEO/KI complexes swell the PEO coils and result in repulsive interactions between the coils ("salting-in" effect) and thus in improved solubility. The peak appearing at a finite wave vector q^* is signature of polyelectrolyte behavior. The decrease of the scattered intensity is more pronounced in the case of acetonitrile than in methanol. We reason that this more pronounced effect is due to the poor ability of acetonitrile to form hydrogen bonds and to its lower Bjerrum length ($l_{\mathrm{B-MeCN}} = 15.61$ Å) in comparison to methanol ($l_{\mathrm{B-MeOD}} = 17.56$ Å). Consequently, the solvation energies in acetonitrile are lower than in methanol, resulting in increased ion-binding and a more significant polyelectrolyte effect. If we assume charging of the PEO chains, then the intensity $I(q)$ can be calculated using RPA (eqs 3–9). The calculated scattering curves are presented as continuous lines in Figure 1, parts a and b. The good agreement between the theoretical predictions and the SANS results confirms that PEO in the presence of potassium iodide in solvents with moderate dielectric constants and poor or moderate hydrogen bonding exhibits the characteristics of a weakly charged polyelectrolyte. Note that in the high q regime, the intensity profiles reveal a decrease in the slope of $I(q)$, indicating a local extension of the segments due to the unscreened electrostatic repulsion between ions that bind to the PEO backbone (e.g., $I(q) \propto q^{-1.34\pm0.05}$ at $C_{\mathrm{KI}}/C_{\mathrm{EO}} = 0.066$). This compares favor-

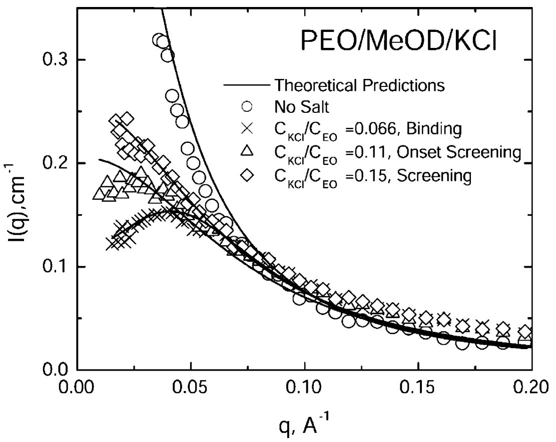

Figure 5. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{EO} = 0.45$ M. $M_w = 100$ kg/mol for PEO/MeOD/KCl. The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. The continuous lines are obtained for an adjustable charge fraction $f = 0$, 0.025, 0.047, 0.047 and correspond to the following: no salt (○), *binding regime* with, $C_{KCl}/C_{EO} = 0.066$ (×), *onset of screening regime* with, $C_{KCl}/C_{EO} = 0.11$ (Δ), and the *screening regime* with, $C_{KCl}/C_{EO} = 0.15$ (◊).

ably with the increase in the radius of gyration that was determined by using the ZAC condition in the case of PEO/MeOD and PEO/MeCN for a salt concentration of potassium iodide equal to 0.03 M (see Supporting Information and Figure 2 in ref 15).

In Figure 2, parts a and b, the *screening regime* ($\kappa l_B/2 > 1$) is shown. At high salt concentrations, the binding of ions becomes inefficient, and thereby the number of free ions within the solution increases, resulting in the disappearance of the peak of the scattered intensity. The onset of the screening is expected to occur when the Debye screening length equals half the Bjerrum length, that is $\kappa^{-1} = l_B/2$, corresponding to a fixed ratio C_{KI}/C_{EO} equal to 0.107 in the case of methanol and 0.153 in acetonitrile. Next to the disappearance of the electrostatic peak at high salt concentrations, the intensity was found to scale like $I(q) \propto q^{-1.56\pm0.05}$ at large q. Thus, at salt concentrations above the *binding*-to-*screening* transition, PEO exhibits the characteristics of a neutral flexible polymer with excluded volume. Note that, in methanol, at $C_{KI}/C_{EO} = 0.6$ (corresponding to symbol ♦ in Figure 2a), aggregation of PEO is observed ($C_{KI} = 20$ mg/mL is the maximum amount of KI that could be dissolved in PEO/MeCN).

Effect of Cation Charge/Radius. A better understanding of the characteristics of PEO in the presence of solvents and added monovalent salt is obtained by studying the effect of the charge/radius ratio (ion strength) of the added cations on PEO in solution, for example, by replacing K^+ with Li^+. The lithium ion is of special interest because it is the smallest monovalent cation ($r(Li^+) = 71$ pm as compared to $r(K^+) = 151$ pm). Figure 3 reveals that the addition of $LiClO_4$ to PEO/MeOD does not change the behavior of the polymer indicating that no cations are bound to the polymer backbone. This can be understood as a consequence of the dominating solvation of Li^+ ions in methanol. In contrast, as presented in Figure 4, PEO exhibits a weakly charged polyelectrolyte behavior in acetonitrile (where no hydrogen bonds are formed) upon addition of $LiClO_4$. Note the good agreement between experimental and calculated results (using RPA eqs 3−9) supporting the proposed complex formation. These results are in accordance with prior studies where it was shown that in methanol Li^+ binds less to PEO than Na^+ or K^+.[5,9,26] Whereas these previous studies could not clarify the binding of Li^+ at low concentrations, our experiments confirm that in methanol solution lithium ions do not bind to PEO even at very low ion concentrations.

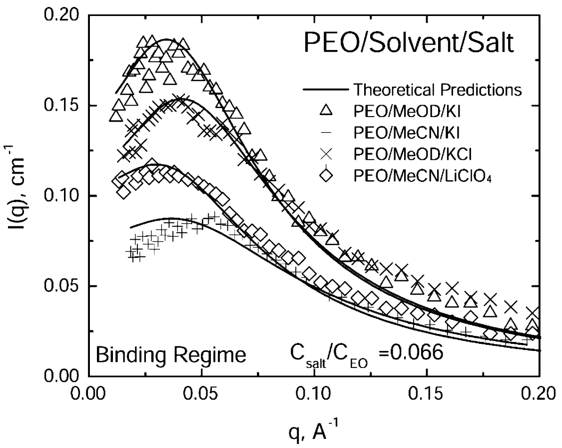

Figure 6. Plot of the total intensity $I(q)$ vs the wavevector q for different solvents and salts at fixed molar ratio $C_{salt}/C_{EO} = 0.066$. The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. The symbols (Δ, +, ×, ◊) refer to the following: PEO/MeOD/KI, PEO/MeCN/KI, PEO/MeOD/KCl, and PEO/MeCN/$LiClO_4$.

Effect of Anions. The effect of anions on the ion-binding was studied by replacing potassium iodide (KI) with potassium chloride (KCl) in the solution PEO/MeOD. The interesting case of PEO/MeCN/KCl was not studied because the chloride was not effective in dissolving the poly(ethylene oxide) in acetonitrile. Figure 5 displays the SANS results and the theoretical predictions for PEO/MeOD/KCl where the scattered intensity $I(q)$ is shown in both the *binding* and the *screening* regimes. Figure 5 demonstrates that for potassium chloride the polyelectrolyte effect is more pronounced as compared to the (PEO/MeOD/KI) system (see Figure 1a). Already at small amounts of added KCl, the polymer is transformed into a weakly charged polyelectrolyte. The continuous lines correspond to the theoretical predictions (eqs 3−12), and the results show a good agreement with the experimental data.

Comparison of Salt and Solvent Effects at Fixed Concentration. Figure 6 displays the scattered intensity against the wavevector at a fixed ratio $C_{salt}/C_{EO} = 0.066$ for different solvents and salts. The results clearly reveal that, in the case of potassium iodide, the polyelectrolyte effect is stronger in acetonitrile than in methanol (see symbols +, Δ). We reason that, in contrast to the PEO/MeOD solution (methanol forms strong hydrogen bonds), the binding of potassium ions to the ether oxygen of PEO in acetonitrile dominates over solvation. Furthermore, in the presence of the same solvent, i.e., methanol, the polyelectrolyte effect is stronger for KCl than for KI. This is in good agreement with previous results of Bailey et al., who found a progressive increase in the reduced viscosity of methanol solutions of PEO for the halide series KI < KBr < KCl < KF, indicating increased ion-association.[5,6]

Effect of Polymer Concentration at Fixed Ratio C_{salt}/C_{EO}. Figure 7a depicts the variation of q^* vs

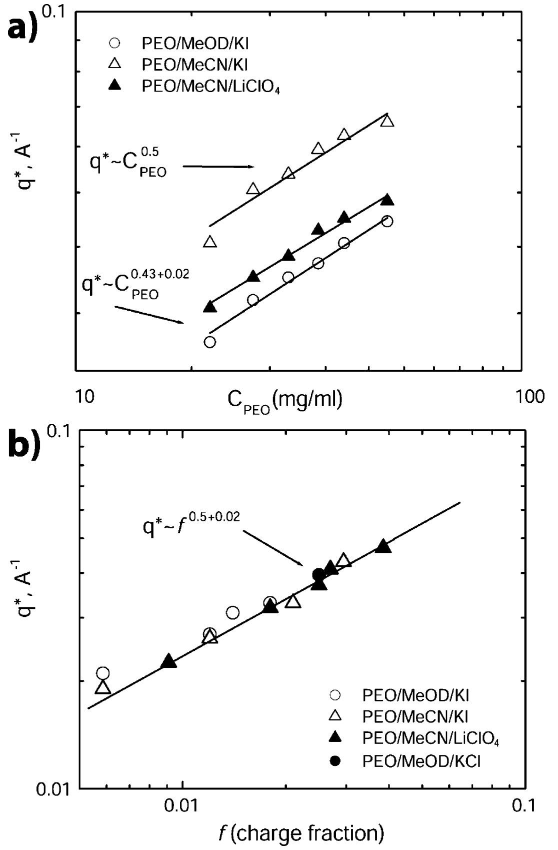

Figure 7. Plot of the characteristic peak-wavevector q^* vs the polymer concentration (panel a) and charge fraction (panel b) for different mixtures. The continuous lines and the symbols represent a power fit and the experimental SANS data, respectively. The symbols (○, △, ▲, ●) refer to the following: PEO/MeOD/KI, PEO/MeCN/KI, PEO/MeCN/LiClO$_4$, and PEO/MeOD/KCl.

the polymer concentration, at fixed ratio $C_{\mathrm{salt}}/C_{\mathrm{EO}}$ for different cations and solvents. The peak position is found to scale with the polymer concentration as $q^* \propto C_{\mathrm{PEO}}^{0.45\pm0.05}$. This result is in a good agreement with theoretical predictions where q^* has been shown to scale with the polymer concentration as, $q^* \propto C^{1/2}$.[19] Figure 7b displays the dependence of q^* as a function of the charge fraction f for all the systems in our study within the *binding regime*. A power law fit reveals that $q^* \propto f^{\,0.5\pm0.02}$. This is in excellent agreement with eq 12, and the behavior of $I(q)$ and q^* as shown by Figures 1−7 is similar to the results that have been reported for hydrophilic polyelectrolyte solutions, both by theory and by experiment.[16−19] Note that at salt concentrations above the *binding*-to-*screening* transition that is determined by $\kappa^{-1} \cong l_{\mathrm{B}}/2$ the binding of ions becomes less favorable, and further increase in the salt concentration merely increases the number of free ions in the solution and hence the electrostatic screening. In this *screening regime*, the PEO characteristics are the one of a neutral polymer with excluded volume and can be well described by eq 9.

Effect of Salt and Solvent on the Equilibrium Constant. Figure 8 summarizes the dependence of the calculated normalized equilibrium constant for the ion *binding* and *screening regime* as a function of the molar ratio $C_{\mathrm{salt}}/C_{\mathrm{EO}}$ for all the mixtures used in our studies. As the concentration of added salt increases above a crossover value, the binding of ions becomes increasingly unfavorable, resulting in a drop of the binding constant by an order of magnitude as compared to the low concentration. We note that the predicted decrease of K_{eq}/k_0 with increasing salt concentration within the *screening regime* confirms previous experimental results that have been reported by Bailey et al. and Liu,[5,6,23] who studied the properties of PEO solutions at high salt concentrations. Moreover, our study demonstrates that at very low salt concentrations the ion binding to PEO is significantly enhanced, rendering PEO a weakly charged polyelectrolyte, and that the binding constant within this *binding regime* is nearly independent of the amount of added salt.

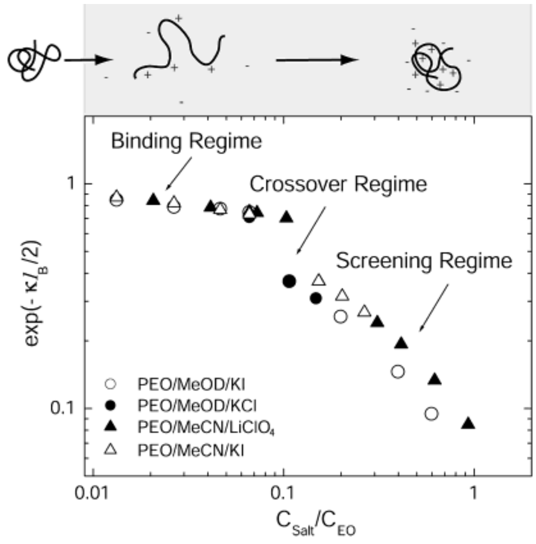

Figure 8. Plot of the normalized equilibrium constant ($K_{\mathrm{eq}}/k_0 = \exp(-\kappa l_{\mathrm{B}}/2)$) vs the molar ratio $C_{\mathrm{salt}}/C_{\mathrm{EO}}$ for different mixtures, PEO/MeOD/KI (○), PEO/MeOD/KCl (●), PEO/MeCN/LiClO$_4$ (▲), and PEO/MeCN/KI (△), calculated using eq 2. Top scheme: schematic of the chain transformation upon salt addition.

Limiting Coordination of Cations by Ether Oxygens at the Binding/Screening Crossover . The crossover concentration from the *binding* to the *screening regime* marks the onset at which the association of cations to the ether oxygens becomes ineffective and allows one to estimate the number of available ether oxygens that can coordinate to a bound cation. Using the mean field approach in eq 2b, the crossover concentration is determined by the condition $\kappa^{-1} = l_{\mathrm{B}}/2$ which is confirmed by the disappearance of the electrostatic peak $I(q^*)$ in the scattering profile as well as by the order of magnitude increase of the conductivity of the respective solution. The theoretically predicted and experimentally determined amounts of bound ions are compared in Table 1 (the deviation for the PEO/KI/MeCN system is due to the limited solubility of KI in acetonitrile). By determining the *binding-to-screening* crossover, we find in our experiments for the PEO/KI system a maximum number of possible binding sites for potassium ions of $C_{\mathrm{EO}}/C_{\mathrm{KI}} = 9.3$ and 6.5 for methanol and acetonitrile solution, respectively. This is in good agreement with earlier investigations by Bailey et al., who suggested that in methanol solution potassium ions do not bind to PEO in molar ratios $C_{\mathrm{EO}}/C_{\mathrm{KI}} > 9.1$.[5,6] We note that, in a recent neutron scattering study of the structure of a PEO/Li salt (solid) polymer electrolyte with a molar ratio of $C_{\mathrm{EO}}/\mathrm{Li}^+ = 7.5$, Mao et al. developed a structural model in which each Li$^+$ ion is coordinated by five ether oxygen atoms of PEO.[27] This indicates that only a fraction of the available ether oxygens actually

Table 1. Number of Available Ether−Oxygen Binding Sites for Cation Coordination Determined at the Crossover *Binding*−to−*Screening Regime*, Using the Mean Field Approach in Eq 2, i.e., $\kappa^{-1} = l_B/2$ and the Experimental (SANS) Data for All Systems with C_{EO} = 0.45 M

system	$\kappa^{-1} = l_B/2$ (Å)	$C_{salt,bound}$ theory (M)	$C_{salt,bound}$ theory (mg/mL)	C_{salt}/C_{EO} theory	C_{EO}/C_{salt} theory	$f_{estimated}$ (SANS/RPA)	$C_{salt,bound}$ (SANS/RPA) (M)
PEO/KI/MeOD	8.78	0.0488	8.1	0.107	9.34	0.04	0.041
PEO/KCl/MeOD	8.78	0.0488	3.63	0.107	9.34	0.047	0.0485
PEO/KI/MeCN	7.81	0.0695	11.5	0.153	6.53	0.03	0.031
PEO/LiClO$_4$/MeCN	7.81	0.0695	7.4	0.153	6.53	0.065	0.067

constitute the coordination sphere of a bound cation in solution. With decreasing ability of the solvent to compete with the ether oxygens for binding to the cation (e.g., by substituting methanol with acetonitrile) the probability for binding of an individual ether oxygen increases; therefore, the number of available ether oxygen binding sites per cation (i.e., C_{EO}/C_{KI} at the crossover point) approaches the actual coordination number of the cation that could be expected in the solvent free (solid) state.

NMR and Ionic Conductivity Studies. The interaction of monovalent salt with PEO was studied in MeOD and MeCN by high resolution nuclear magnetic resonance (NMR) as a function of cation strength and salt concentration in order to validate the ion-binding assumption and thereby to justify the application of polyelectrolyte theory. Because of the high molecular weight of the PEO in our studies, only one resonance peak could be observed that is attributed to the ethylene protons of the polymer repeat units: ($\delta(C-CH_2-O) =$ 1452 Hz in MeOD and $\delta(C-CH_2-O) = 1419$ Hz in MeCN). In salt solutions, the exchange between ethylene protons in the neighborhood of bound or free ether oxygens occurs fast compared to the time scale of the measurement, thus resulting in one resonance peak for the ethylene protons in PEO/salt solutions at a frequency $\delta = X_f\delta_f + X_b\delta_b$ with X_f, X_b representing the molar ratios of free and bound ether oxygens and δ_f, δ_b representing the chemical shifts of the ethylene protons in the neighborhood of free and bound ether oxygen, respectively. Because of the electron-pulling effect of the positively charged potassium ions, the resonance of ethylene protons in the presence of salt is shifted to lower fields, resulting in positive values for δ. Figure 9 shows the difference in chemical shift between PEO/MeCN/KI and PEO/MeCN at different salt concentrations. The data mark a distinct increase in the chemical shift of ethylene protons in the PEO/MeCN/KI system, indicative for binding of potassium ions to PEO. The preferential binding of potassium ions to the PEO ether oxygens as opposed to the solvation by MeCN molecules is demonstrated by the constant chemical shift of MeCN protons in the presence of KI and PEO as presented in the inset of Figure 9. Note that in the absence of PEO, the protons of acetonitrile show a distinct shift upon addition of potassium ions. Similar results were obtained for lithium perchlorate and the respective methanol solutions.

Measurements of the ionic conductivity (Λ) of PEO/MeCN/KI solutions further support the ion-binding argument. Table 2 lists the values obtained for the ionic conductivity for different salt concentrations. The decrease in Λ of the PEO-containing salt solutions with respect to the polymer-free salt solutions indicates an association of ions to the polymer accompanied by a decrease of the mobility of free charge carriers in solution. Note that at a relative concentration of KI of $C_{KI}/C_{EO} = 0.2$ the ionic conductivity of the polymer-free salt solution equals the one of the polymer containing solution indicative for the *screening regime*, that is the saturation of ion binding to the polymer backbone.

Table 2. Ionic Conductivity of PEO/MeCN/KI System at *T* = 25 °C

C_{KI}/C_{PEO}	ionic conductivity (mS/cm) in the absence of PEO	ionic conductivity (mS/cm) in the presence of PEO	regime
0	4.2×10^{-3}	17.7×10^{-3}	no salt
0.013	0.947	0.730	binding
0.026	1.652	0.929	binding
0.046	2.86	1.725	binding
0.066	3.21	2.33	binding
0.15	6.25	5.05	onset screening
0.20	6.25	6.22	screening

Effect of Molecular Weight and Temperature. Within the range of molecular weights covered in our experiments (M_w = 9−334.5 kg/mol), identical results were obtained for the ion binding on PEO at T = 25 °C in methanol. This is in accordance with the theoretical prediction in eqs 1 and 2 that relate the ion binding and concurrent polyelectrolyte transition to the Bjerrum and Debye screening lengths that do not depend on the molecular weight of the polymer.

Temperatures were varied from 9 to 30 °C. In salt-free methanol solutions of PEO, a phase separation was observed at 18 °C. The addition of salt was found to increase the solubility of PEO. At a salt concentration of C_{LiClO_4} = 1 M, no phase separation could be observed. The increased solubility can be understood as a consequence of repulsive interactions between the bound cations and the associated swelling of the coils.

(B) Solvents with High Dielectric Constant and Strong or Poor H Bonding. Water and NMF. Light scattering studies of PEO in water reveal an unusually large second virial coefficient A_2, indicating that water is a good solvent for PEO (for example A_2 was determined by Selser et al. to be on the order of 10^{-3} and 10^{-4} cm^3/g^2 in aqueous and organic solutions, respectively[8,10]). These results were confirmed by our previous studies,[15] where the q-dependence of the scattered intensity $I(q) \propto q^{-1.44}$ reveals the local extension of the polymer chains. Following Selser et al., this behavior can be understood as a consequence of the ability of water molecules to “pack” into and swell coils along with a general structuring of water in the PEO/H$_2$O system. Figure 10 shows the coinciding scattered intensities of aqueous solutions of PEO with varying salt concentrations, indicating that there is no effect of salt ions on the PEO/water system. This is in agreement with previous studies by Bailey et al. and more recently by Annis et al., who demonstrated that the addition of potassium iodide or lithium salts to aqueous solutions of PEO had essentially no effect on the solutions’ properties.[5,6,28] These results can be understood as a consequence of the high capacity of water to form hydrogen bonds combined with a large dielectric constant (ϵ_{water} = 78.13), resulting in the stabilization of

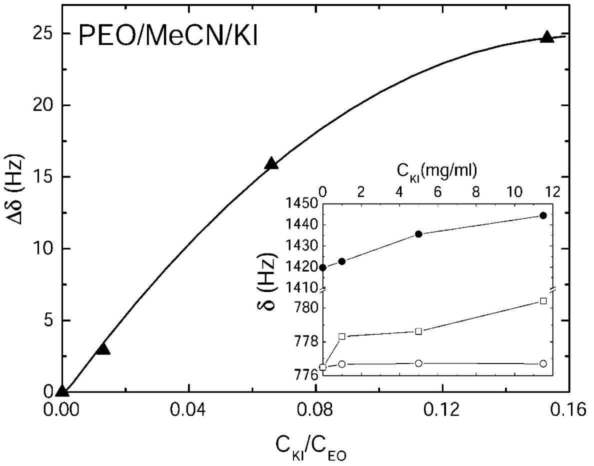

Figure 9. Plot of the difference in chemical shift $\Delta\delta = \delta$(PEO, salt)$-\delta$(PEO, no salt) of PEO ($C_{EO} = 0.45$ M, $M_w = 100$ kg/mol) in MeCN solution. Inset: Chemical shift of PEO (●) in MeCN solution. Open symbols represent the respective chemical shift of MeCN with (●) and without (○) PEO.

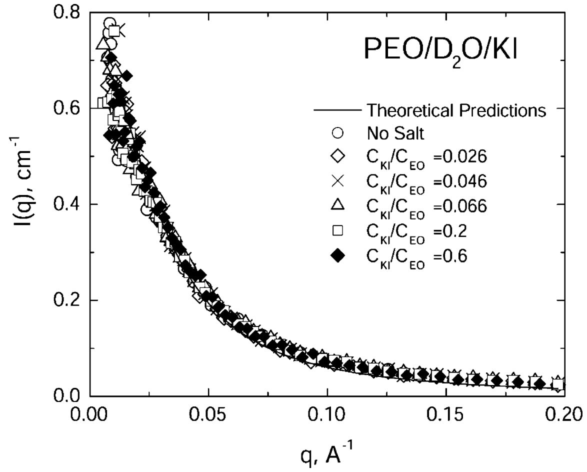

Figure 10. Plot of the total intensity $I(q)$ vs the wavevector q as a function of ionic strength at $C_{EO} = 0.45$ M. $M_w = 100$ kg/mol, $T = 25$ °C for PEO/D$_2$O/KI. The continuous lines and the symbols represent the theoretical predictions (RPA) and the experimental SANS data, respectively. The symbols (○, ◇, ×, △, □, ◆) refer to the following: $C_{KI}/C_{EO} = 0$, 0.026, 0.046, 0.066, 0.2, and 0.6.

the hydrated ions in solution. The hydration of K^+ or Li^+ ions counteracts the association of the cations to the ether oxygens in the polymer backbone. The importance of dielectric screening for the solution behavior of PEO is confirmed by comparing the results obtained in aqueous solution to the results obtained in NMF solution. Note that NMF is characterized by a high dielectric constant ($\epsilon = 109$), thereby effectively screening electrostatic interactions similar to water; however, NMF cannot form hydrogen bonds as opposed to water. The absence of the polyelectrolyte peak in $I(q)$ indicates that monovalent ions do not bind to the polymer in significant amounts in the PEO/NMF system.

Conclusion

Monovalent cations bind to PEO in solvents of moderate dielectric constant and moderate capacity of hydrogen bonding and increase the solubility of the polymer ("salting-in"). Two distinct concentration regimes can be distinguished: At low concentrations ($\kappa^{-1} \gg l_B/2$), the addition of ions primarily results in charging of the polymer chains (*binding regime*). The associated weak-polyelectrolyte type characteristics are well accounted for by the random phase approximation in the mean field limit. At high salt concentrations ($\kappa^{-1} \ll l_B/2$), the binding constant decreases, resulting in screening of the electrostatic interactions and the chain characteristics equal those of a neutral polymer with excluded volume (*screening regime*). In solvents with high dielectric constant and high capacity of hydrogen bonding, no charging effects can be detected, indicating that the solvation of cations outweighs the complex formation. The pronounced solvation of ions thus explains the absence of a "salting-in" effect in solvents that are characterized by strong hydrogen- bonding capacity and a high dielectric constant.

The ability to use mean field theory in order to effectively predict the structural changes of PEO induced by ion-binding for a given solvent/salt condition could provide a useful tool for designing solvent/polymer/salt compositions that are optimized with respect to desirable properties. The relevance of the cation valence for ion-binding, especially in aqueous systems that are of particular technological relevance, remains to be understood and will be the subject of future study.

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Supporting Information Available: Figure 1S, plot of the total scattered intensity and of the intra-chain structure factor vs q in the case of salt free and added salt solution HPEO/KI/CD$_3$CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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