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Solubility and diffusivity of sodium chloride in phase-separated block copolymers of poly(2-dimethylaminoethyl methacrylate), poly(1,1′-dihydroperfluorooctyl methacrylate) and poly(1,1,2,2-tetrahydroperfluorooctyl acrylate)

Kazukiyo Nagai[a,b,1], Satoshi Tanaka[a], Yuichi Hirata[a], Tsutomu Nakagawa[a,*], Michelle E. Arnold[b], Benny D. Freeman[b,*], Denis Leroux[c,d,2], Douglas E. Betts[c,3], Joseph M. DeSimone[c], Francis A. DiGiano[d]

[a]*Department of Industrial Chemistry, Meiji University, Higashi-Mita, Tama-Ku, Kawasaki 214-0033, Japan*
[b]*Department of Chemical Engineering, North Carolina State University, Raleigh, NC 27695-7265, USA*
[c]*Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290, USA*
[d]*Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, NC 27599-7400, USA*

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Abstract

Solubility and diffusivity of sodium chloride were determined in a series of dense films of phase-separated diblock and triblock copolymers composed of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and either poly(1,1′-dihydroperfluorooctyl methacrylate (PFOMA) or poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN). As the content of hydrophilic PDMAEMA increases in PDMAEMA-*b*-PFOMA films, total water uptake increases. The salt partition coefficient of these films increases with increasing PDMAEMA content and weight fraction of water in the PDMAEMA domains. In contrast, salt diffusivity is not monotonically correlated with PDMAEMA content and effective hydration. Triblock copolymers exhibit different values of total water uptake, total hydration, salt partition, and diffusion coefficients than those of diblock copolymers (PDMAEMA-*b*-PFOMA) at the same PDMAEMA concentration. The total water uptake of PFOMA-*b*-PDMAEMA-*b*-PFOMA copolymers is lower than that of PDMAEMA-*b*-PFOMA, while water uptake of PTAN-*b*-PDMAEMA-*b*-PTAN films is higher than that of PDMAEMA-*b*-PFOMA. Salt partition and diffusion coefficients increase monotonically with the amount of freezing water in the hydrophilic domains, suggesting that the state of water in the phase-separated block copolymers is an important factor influencing their salt uptake and transport properties. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Block copolymers; Freezing water; Salt transport

1. Introduction

The use of polymer membranes for drinking water and waste water treatment would be enhanced if lower-fouling membrane materials were available [1]. In one case, Hamza et al. [2] modified the surface of porous polyethersulfone ultrafiltration membranes with fluorotelomers and found that these modified membranes were less susceptible to fouling by oil/water mixtures than unmodified membranes. The modified membranes were more permeable than unmodified polyethersulfone ultrafiltration membranes to oil/water emulsions.

Fundamental transport properties of solutes such as sodium chloride (NaCl) were reported by Rosenbaum et al. for cellulose acetate [3] and by Yasuda et al. for various hydroxyalkyl methacrylate-based hydrogels [4,5]. On the basis of these studies, salt diffusivity decreases exponentially with decreasing reciprocal hydration, in qualitative agreement with the free volume theory of diffusion [3,4]. For highly hydrated samples, permeability coefficients also decrease exponentially with decreasing reciprocal hydration [4,5]. Salt partition coefficients are nearly equal to hydration

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[*] Corresponding authors. Tel.: +81-44-934-7211; fax: +81-44-934-7906 (T. Nakagawa). Tel.: +1-919-515-2460; fax: +1-919-515-3435 (B.D. Freeman).

E-mail addresses: nakagawa@isc.meiji.ac.jp (T. Nakagawa), benny_freeman@ncsu.edu (B.D. Freeman).

[1] Present address: CSIRO Molecular Science, Private Bag 10, Clayton South, VIC., 3169, Australia.

[2] Present address: SiPix Imaging, Milpitas, CA 95035, USA.

[3] Present address: ONDEO-Nalco Chemical Company, Naperville, IL 60563-1198, USA.

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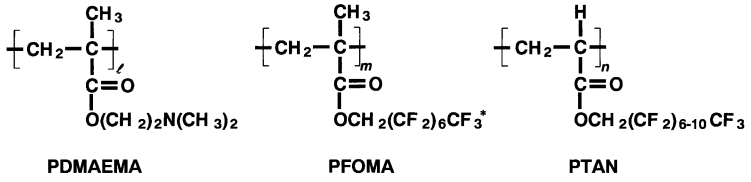

Fig. 1. Repeat units of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), poly(1,1′-dihydroperfluorooctyl methacrylate) (PFOMA), and poly(1,1,2,2-tetrahydroperfluorooctyl methacrylate) (PTAN). (* : the overall extent of branching in the PFOMA side chain is 22 ± 5%) [29].

for highly sorbing samples and are less than the hydration for low sorbing samples. In the less hydrated regions, polymer–water and polymer–ion interactions depressed salt solubility in the hydrogels. The structural state of water in polymers and its influence on the solubility, diffusivity and permeability of solutes has been widely studied [6–27]. Using a three-state model for water in polymer gels, Wisniewski and Kim suggested that inorganic chloride salts partition primarily into and are transported through bulk water regions within the polymer gels [18]. Non-freezing water, which is strongly associated with hydrophilic groups in the polymer, has selectivity for solutes such as NaCl, while the properties of freezing water are similar to those of pure bulk water [15,17,25].

This paper reports the salt uptake and transport properties of non-porous block copolymers based on low surface energy fluoropolymers and highly hydrophilic hydrocarbon-based polymers. Incorporation of hydrophilic units into the fluoropolymer backbone leads to microphase-separated block copolymers having high water uptake and high water flux [28]. The fluorinated hydrophobic segments may provide low surface energy, minimally adhesive sites to reduce fouling, while the hydrophilic segments self-assemble to form hydrophilic channels for water permeation through the membrane. In this study, solubility and diffusivity of NaCl are reported for dense films in a systematic series of di- and triblock copolymers composed of hydrophilic poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and either poly(1,1′-dihydroperfluorooctyl methacrylate) (PFOMA) or poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN). The primary chemical structures of the homopolymer constituents of these copolymers are presented in Fig. 1. Sodium chloride is used as a marker solute to probe the effect of morphology and polymer composition on transport properties.

2. Experimental

2.1. Materials

The synthesis and characterization of diblock and triblock copolymers has been presented elsewhere [28]. PFOMA has a branched side chain structure with 22 ± 5% chain branching (i.e. approximately one out of every five side chains contains a fluorinated methyl branch), which frustrates side chain crystallization [29]. In contrast, PTAN has linear but polydisperse side chains that exhibit side chain crystallization [29,30]. The PDMAEMA content and molecular weight of the copolymers are summarized in Table 1. Dense films with uniform thicknesses of 40–180 μm were cast from 5–10% (w/v) polymer solution onto teflon plates at ambient temperature. The solvents for PFOMA- and PTAN-based copolymers were 1,1,2-trichlorotrifluoroethane (i.e. Freon 113) and α,α,α-trifluorotoluene, respectively. Ultrapure water used in this study was produced by a water purification system manufactured by Milllipore Corporation (Bedford, MA). This system consists of two prefilters (5 μ and carbon) followed by a Rios 16 reverse osmosis unit and a Milli-Q Plus TOC ultrapure water purification system in series. Sodium chloride was purchased from Fisher Scientific (Norcross, GA) and was used as received.

2.2. Water uptake measurements

The amount of water sorbed by a sample was determined

Table 1
PDMAEMA content and molecular weights of the synthesized block copolymers. Data were taken from Ref. [28]

Block copolymers	PDMAEMA content		Molecular weight, M_n	
	(wt%)	(mol%)	PDMAEMA (kg/mol)	PFOMA or PTAN (kg/mol)
PDMAEMA-*b*-PFOMA	26	52	29	111
	29	55	27	94
	40	67	32	79
	42	69	29	69
PFOMA-*b*-PDMAEMA-*b*-PFOMA	32	59	42	120 (60 for each block)
PTAN-*b*-PDMAEMA-*b*-PTAN	ca. 38	69	46	110 (55 for each block)

by immersing it in ultrapure water, blotting it between two pieces of filter paper, and weighing it. As water desorbs rapidly, the weighing process was completed within ca. 10 s to minimize experimental error. After each measurement, the film was again immersed in water, and the procedure was repeated until equilibrium water sorption was attained. The water uptake and approximate total hydration (H) were determined from:

$$\text{water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \tag{1}$$

and

$$H = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \tag{2}$$

where W_{wet} and W_{dry} are the weights of a water-swollen film at equilibrium and a dry film, respectively. Hydration is typically defined based on the volume of wet and dry films [4,5]. However, the volume fraction of water in hydrogels is frequently similar to the weight fraction, and therefore, hydration is often approximated as the weight fraction of water in the polymer. Average values of water uptake and hydration are reported for each copolymer composition.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to estimate the amounts of freezing and non-freezing water in water-swollen dense films at equilibrium [6,9,14–16,19–22,24–27], using a procedure reported previously [31]. These measurements were performed using a Perkin–Elmer DSC-7 operated at a heating rate of 10°C/min. The samples were maintained in an argon atmosphere during measurements, and the temperature range explored was from −150 to 25°C. On the basis of the results from these measurements, the masses of freezing water (W_{fw}) and non-freezing water (W_{nfw}) were determined. The mass of freezing water was calculated from:

$$W_{\text{fw}} = Q^h/\Delta H \tag{3}$$

where Q^h, the energy absorbed during melting, was calculated from the peak area of the DSC curve. The latent enthalpy of melting per unit mass of freezing water, ΔH, was assigned a value of 334 J/g, the enthalpy of melting of pure water at 0°C [31]. The mass of non-freezing water, W_{nfw}, was estimated by subtracting the weight of freezing water (W_{fw}) from the total weight of water sorbed in the sample (W_{total}):

$$W_{\text{nfw}} = W_{\text{total}} - W_{\text{fw}} \tag{4}$$

2.4. Kinetic salt desorption measurements

The partition and diffusion coefficients of NaCl were determined from kinetic desorption experiments. In each experiment, a dense polymer film was equilibrated in a 5 wt% aqueous NaCl solution at 25°C. The sample was then removed from the equilibrating solution, wiped to remove excess surface salt, and immersed in a fixed volume of deionized pure water maintained at 25°C. The solution was stirred vigorously to reduce boundary layer resistances to mass transfer. The optimal stirring rate was determined by performing control diffusion experiments using cellulose acetate and verifying that our values for salt partition and diffusion coefficients were in excellent agreement with the literature. As salt desorbed from the film, the conductivity was monitored as a function of time using a Fisher Scientific Model 09-326-2 conductivity meter. Conductivity was converted to mass of salt desorbed via a calibration curve. The salt solubility was determined from the total amount of salt released to the initially salt-free solution, while salt diffusion coefficients were determined from the kinetics of solution conductivity increase.

3. Results and discussion

3.1. State of water in copolymers

The glass transition temperatures (T_g) of the anhydrous homopolymers are 21°C for PDMAEMA [28] and 50°C for PFOMA [33]. The T_g for PTAN should be similar to that of poly(1,1′-dihydroperfluorooctyl acrylate) (−10°C) [33]. However, the high degree of crystallinity of the PTAN side chains makes it difficult to detect T_g. The melting point of PTAN is ca. 80°C [28]. Because the difference between the glass transition temperatures of PDMAEMA and PFOMA is only 30°C, it was difficult to determine the T_g of each phase in the di- and triblock copolymers by DSC. Transmission electron microscopy (TEM) micrographs indicate that the di- and triblock copolymers are microphase-separated [28]. The PDMAEMA-*b*-PFOMA samples (containing 55 and 67 mol% PDMAEMA) have irregular cylindrical morphologies, while the triblock copolymers (i.e. PFOMA-*b*-PDMAEMA-*b*-PFOMA and PTAN-*b*-PDMAEMA-*b*-PTAN) exhibit cylindrical and lamellar morphologies, respectively. The PTAN-*b*-PDMAEMA-*b*-PTAN copolymers are the only ones studied for which the fluoropolymer domains can crystallize.

Fig. 2 presents water uptake and hydration, H, at 25°C for the block copolymers as a function of PDMAEMA concentration. PDMAEMA is water soluble, while PFOMA and PTAN are highly hydrophobic. The water uptake of PFOMA and PTAN is very low (1–2 wt%). As the PDMAEMA content of the PDMAEMA-*b*-PFOMA samples increases, water uptake and total hydration increase. Sharp increases in water uptake and hydration were observed at PDMAEMA contents greater than 60 mol%. Interestingly, triblock copolymers had different water uptake and hydration values than diblock copolymers with similar PDMAEMA content. The PFOMA-*b*-PDMAEMA-*b*-PFOMA and PTAN-*b*-PDMAEMA-*b*-PTAN triblock copolymers sorbed approximately 50% less and 40% more

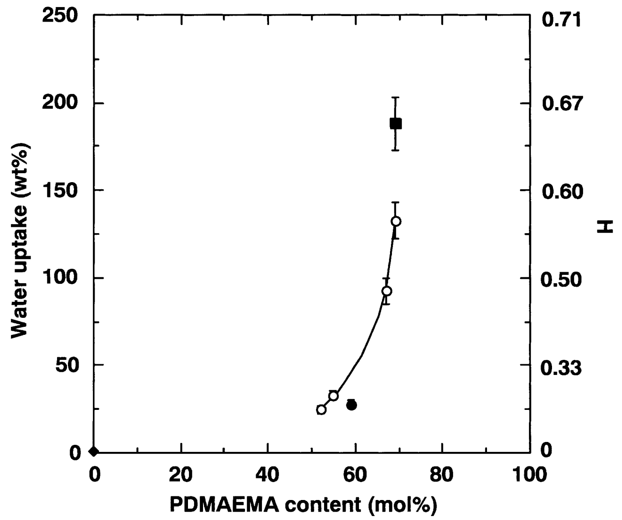

Fig. 2. Total water uptake and total hydration, *H*, of PFOMA (◆), PTAN (◆), PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●), and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of PDMAEMA content at 25°C.

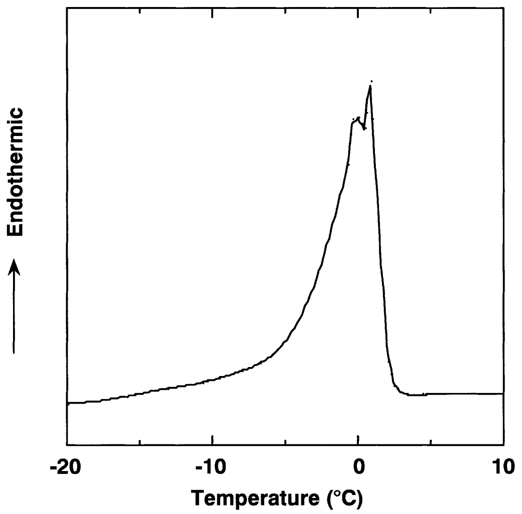

Fig. 3. DSC curve of a PDMAEMA-*b*-PFOMA film (PDMAEMA content: 67 mol%) that has been equilibrated in water. Water uptake: 93 wt% at 25°C ($H = 0.48$). Heating rate: 10°C/min.

water than PFOMA diblock copolymers of similar PDMAEMA composition, respectively. This result may be related to differences in accessibility of the hydrophilic domains of PDMAEMA in block copolymers, which possess different architectures, morphologies and abilities of the fluorinated segments to crystallize.

Fig. 3 presents a representative DSC curve for a PDMAEMA-*b*-PFOMA film (PDMAEMA: 67 mol%) that has been equilibrated in water. Two freezing water peaks were observed near 0°C. On the basis of the three state model of water in hydrophilic polymers (i.e. bulk or free water, interfacial water and bound water), the higher melting peak is ascribed to bulk water, and the lower melting peak is attributed to weakly bound interfacial water [6–27]. Differences in the two types of freezing water have been studied for random copolymers and crosslinked hydrogels [14,15,19–22,24,25]. For most polymers, the bulk free water and weakly bound interfacial water peaks overlap one another significantly, thereby compromising an accurate determination of the amount of each type of water. This problem usually becomes more severe as hydration decreases. Therefore, to compare samples with a wide range of hydration values, it is common to report overall freezing water values (i.e. bulk or free water plus interfacial water). This two state model based on DSC analyses (freezing water and non-freezing water) was used in this study. Higuchi and Iijima discuss the suitability of this model to describe transport of solutes in hydrogels [25].

The total sorbed water concentration as well as the amounts of freezing water and non-freezing water increased with increasing hydrophilic content in hydrolyzed poly(4-acetoxystyrene) [21] and in random copolymers of styrenesulfonic acid and methyl methacrylate [27]. In contrast, the amount of non-freezing water was independent of hydrophilic content in crosslinked poly(vinylalcohol-*co*-itaconic acid) [26] and in crosslinked poly(2-hydroxyethyl methacrylate) [20]. The freezing water content usually increases with increasing total water content [15,20,21,26,27]. Similar trends for bound and free water were observed by proton NMR spectroscopy of poly(2-hydroxyethyl methacrylate) hydrogels: the mole fraction of bound water decreased with increasing total water content [13].

As indicated in Fig. 2, the total amount of water sorbed increases with increasing PDMAEMA content. The fraction of freezing water is presented as a function of PDMAEMA content and total water uptake in Fig. 4a and b, respectively. The fraction of water that is present as freezing water increases with increasing hydrophilic content for PFOMA-based copolymers as shown in Fig. 4a. This behavior is similar to that observed in hydrolyzed poly(4-acetoxystyrene) [21] and in random copolymers of styrenesulfonic acid and methyl methacrylate [27]. The freezing water fraction in the PTAN-*b*-PDMAEMA-*b*-PTAN film is markedly lower than that in a PDMAEMA-*b*-PFOMA film of similar composition. The lamellar morphology of the PTAN-*b*-PDMAEMA-*b*-PTAN film may permit stronger PDMAEMA–water interactions than the irregular cylindrical morphology of the PDMAEMA-*b*-PFOMA films [28]. As indicated in Fig. 4b, the fraction of freezing water in the polymers was not strongly correlated with total water uptake. Although water uptake increases with increasing hydrophilic content for several other random copolymers and crosslinked hydrogels [21,26,27], hydrophilic content alone is not a good indicator for total water uptake for our microphase-separated block copolymers (cf. Fig. 2). Apparently, a subtle interplay between copolymer chemical content and morphology influences total water uptake and freezing water content in these block copolymers.

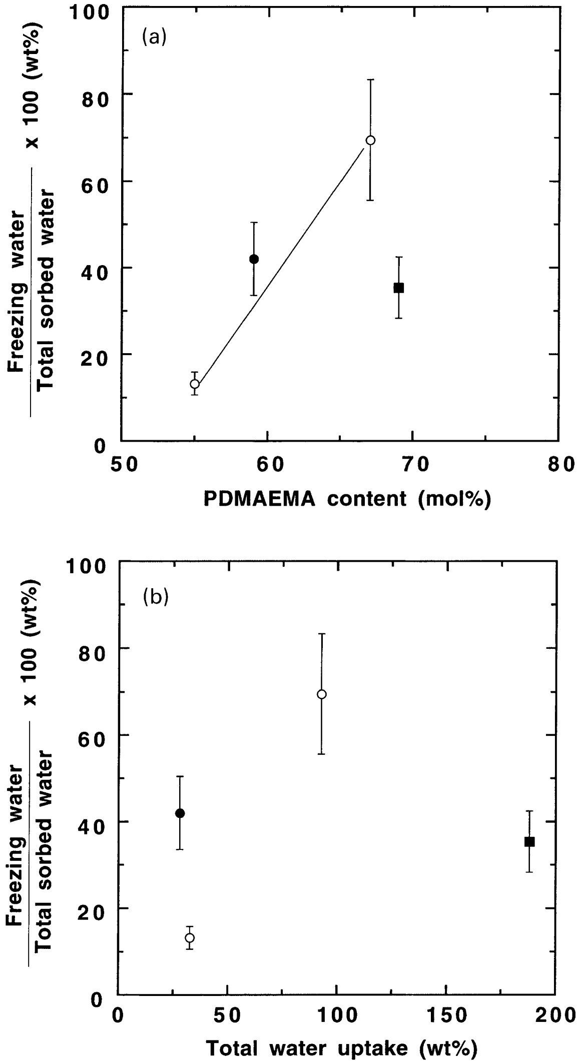

Fig. 4. (a) Percentage of freezing water in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of PDMAEMA content at 25°C. (b) Percentage of freezing water in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of total water uptake at 25°C.

3.2. Salt solubility

Fig. 5 presents the relationship between the salt partition coefficient, k, and PDMAEMA content at 25°C. The salt partition coefficient of PDMAEMA-*b*-PFOMA films increases with increasing PDMAEMA content. The salt partition coefficient of PTAN-*b*-PDMAEMA-*b*-PTAN is similar to that of PFOMA diblock copolymers with similar PDMAEMA content. The salt partition coefficient of the PFOMA-*b*-PDMAEMA-*b*-PFOMA film, however, is about half the value of a PDMAEMA-*b*-PFOMA film of similar hydrophilic (i.e. PDMAEMA) content. On the basis of these results, hydrophilic content is not the only variable influencing salt solubility. Other factors, such as morphology and amount of freezing water, may also influence salt solubility values. These issues are discussed in more detail below.

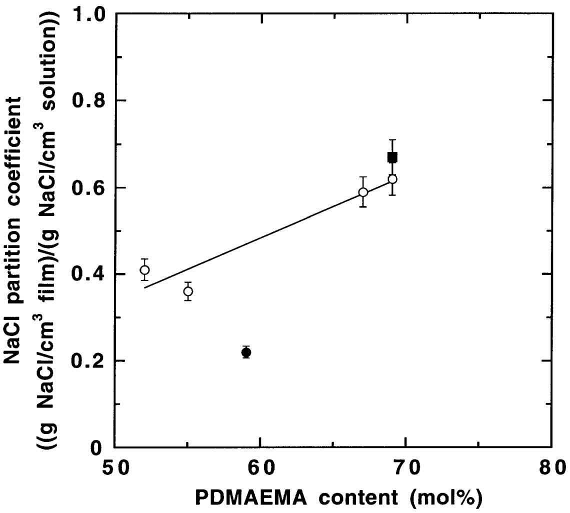

Fig. 5. Sodium chloride partition coefficients for PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of PDMAEMA content at 25°C.

Yasuda et al. reported that the salt partition coefficient should be equal to the hydration if there are no strong polymer–water interactions [4]. In this case, the concentration of the salt solution sorbed in the polymer is equal to that of the bulk salt solution. Experimentally, salt partition coefficients are nearly equal to the hydration for highly sorbing samples (e.g. hydrogels) and are often lower than the hydration for low sorbing samples. Yoon and Jhon reported that NaCl partitioned only into the water-containing regions of cross-linked poly(2-hydroxyethyl methacrylate) membranes [20]. Water uptake values for hydrophobic PFOMA and PTAN are only 1–2 wt%. Therefore, water sorbs almost exclusively into the hydrophilic PDMAEMA domains of these microphase-separated block copolymers.

Fig. 6 presents the salt partition coefficient as a function of the effective hydration, H_{eff}, which is estimated as the weight fraction of water sorbed into the hydrophilic PDMAEMA domains of the copolymers. The effective hydration is estimated by assuming that all of the sorbed water is confined to the hydrophilic PDMAEMA regions of the copolymers and has units of mass of water sorbed per mass of PDMAEMA in the copolymer. As the effective hydration increases, the salt partition coefficient increases in PDMAEMA-*b*-PFOMA films. All salt partition coefficients lie below the line $k = H_{\mathrm{eff}}$, suggesting that polymer–salt interactions influence the overall salt solubility in the copolymer. The ratio of the partition coefficient to effective hydration is plotted as a function of effective hydration in Fig. 7. This ratio is approximately constant for PDMAEMA-*b*-PFOMA samples, suggesting that water–salt–polymer interactions in PFOMA diblock copolymers are similar to each other. The value of k/H_{eff} for PTAN-*b*-PDMAEMA-*b*-PTAN is similar to that of the PFOMA diblock copolymers. However, the k/H_{eff} value shown in Fig. 7 for PFOMA-*b*-PDMAEMA-*b*-PFOMA is about half that of PDMAEMA-*b*-PFOMA of

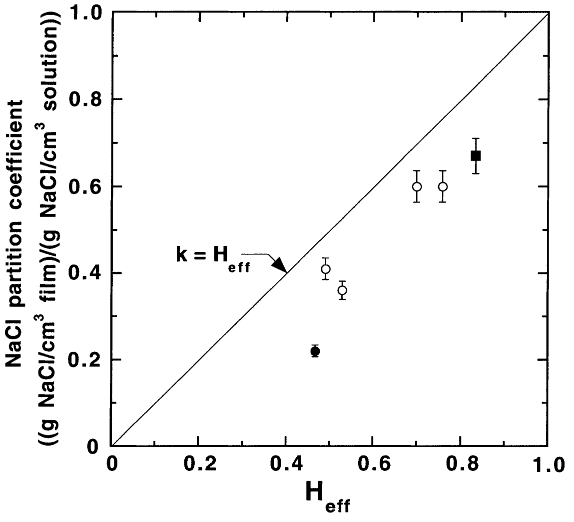

Fig. 6. Sodium chloride partition coefficients for PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of effective hydration, H_{eff}, at 25°C. Effective hydration is calculated by assuming that all sorbed water is confined to the hydrophilic domains of the polymer.

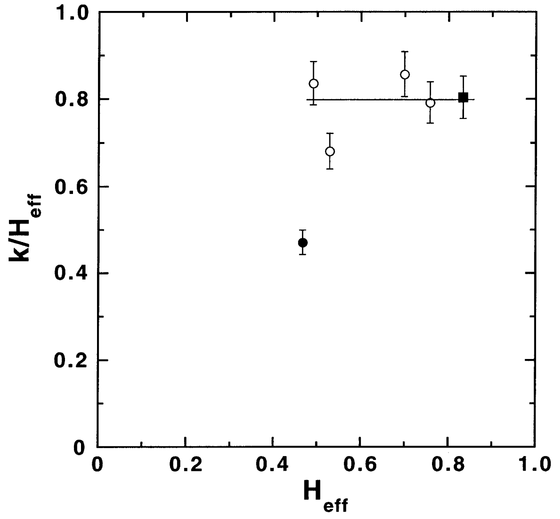

Fig. 7. Ratio of sodium chloride partition coefficient, *k*, to effective hydration, H_{eff}, in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of effective hydration at 25°C. Effective hydration is calculated by assuming that all sorbed water is confined to hydrophilic domains.

similar composition. Yasuda et al. reported k/H values of 0.44–1.12 for various hydroxyalkyl methacrylate based hydrogels [4]. The values in Fig. 7 are consistent with their results.

Wisniewski and Kim proposed that inorganic chloride salts partition primarily into the bulk water regions of crosslinked poly(2-hydroxyethyl methacrylate), suggesting that ion partitioning and transport occur primarily in regions rich in bulk water [18]. In this regard, Fig. 8 presents k as a function of corrected hydration, H^*, which is estimated as the weight fraction of *freezing* water sorbed in PDMAEMA domains. The salt partition coefficients for the highly sorbing copolymers are in excellent agreement with the relationship $k = H^*$, suggesting that the amount of freezing water (i.e. water which has no strong interactions with polymer segments) strongly influences the salt solubility in highly hydrated samples of these copolymers. The sample with the lowest corrected hydration, a PDMAEMA-*b*-PFOMA sample containing 55 mol% PDMAEMA, deviates from this relation, implying that salt sorption in relatively weakly hydrated samples may be influenced by polymer–water and polymer–ion interactions. Like conventional crosslinked hydrogels, the partition coefficient of NaCl for these heterophase materials depends primarily on the freezing water content of the hydrophilic PDMAEMA domains in the phase-separated block copolymers.

3.3. Salt diffusivity

Salt diffusion coefficients, D, for the block copolymers were determined using a Fickian analysis for desorption from a plane sheet [32]. The volume of initially pure water into which the salt is desorbing is finite. However, the volume of water is sufficiently large and the amount of salt desorbing is sufficiently small that the salt concentration in the desorption cell does not influence the results. Values of D were estimated from the kinetic desorption data in the region where the fractional desorption, M_t/M_∞, is a linear function of $t^{1/2}$. The following equation was used to calculate diffusion coefficients:

$$\frac{\mathrm{d}(M_t/M_\infty)}{\mathrm{d}(t^{1/2})} = \frac{4}{\ell}\left(\frac{D}{\pi}\right)^{1/2} \tag{5}$$

where ℓ is polymer film thickness, t is time, and M_t and M_∞ are the masses of penetrant in the polymer at time t, and at the beginning of the experiment, respectively. Values of D were estimated for short times, corresponding to values of $M_t/M_\infty < 0.6$. The uncertainties in the diffusion coefficients were estimated using a propagation of error analysis and were found to be ca. 10% [34].

Fig. 9 is a representative salt kinetic desorption curve for a PTAN-*b*-PDMAEMA-*b*-PTAN film (69 mol% PDMAEMA). A short induction period is observed for $t^{1/2} < 5\ \mathrm{s}^{1/2}$. This phenomenon is ascribed to delays associated with conductivity meter response and the time required to establish a zero-concentration boundary condition at the film surface when the film is introduced into the water and the experiment is started. On the basis of control experiments, in which an initially salt-free solution is spiked suddenly with a small aliquot of salt solution, these factors are expected to last approximately 10 s or less. Another possible source of delay in the beginning of diffusion-controlled release of salt from the polymer film is the unique morphological structure of these materials. The hydrophilic PDMAEMA microdomains are sandwiched in a matrix of

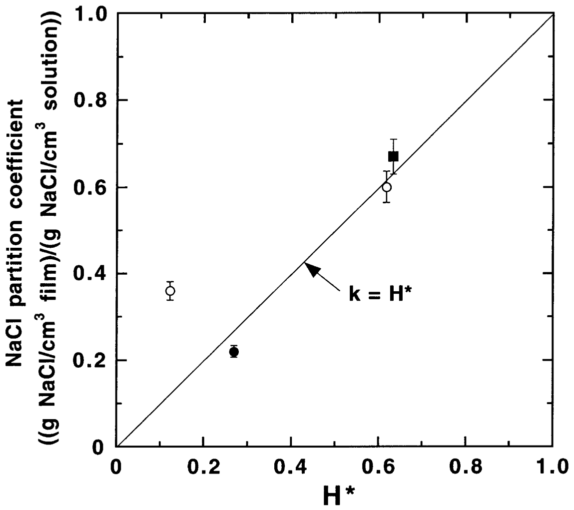

Fig. 8. Sodium chloride partition coefficient in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of corrected hydration, H^*, at 25°C. Hydration was corrected to include only the amount of freezing water present in hydrophilic domains.

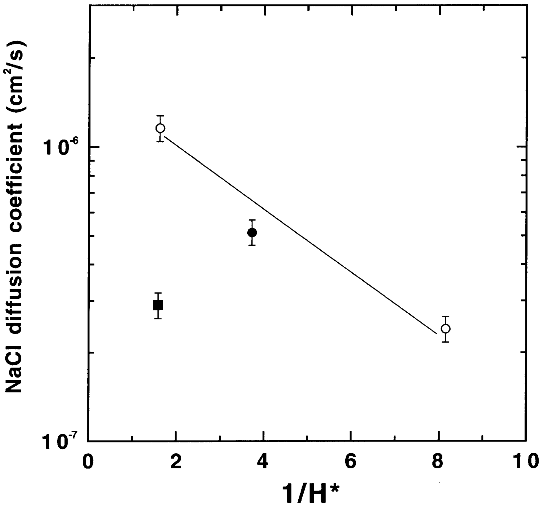

Fig. 10. Sodium chloride diffusion coefficient in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of corrected hydration, H^*, at 25°C.

hydrophobic PTAN microdomains. This structure may lead to some induction period as the concentration gradients inside the film for Fickian-dominated mass transport are established.

Systematic correlations between salt diffusivity and hydrophilic content of the polymers are not observed. Previous studies report, in qualitative agreement with free volume theory, that salt diffusivity decreases exponentially with decreasing reciprocal hydration in cellulose acetate [3] and in a variety of hydroxyalkyl methacrylate (e.g. hydroxyethyl methacrylate, HEMA)-based hydrogels [4,5]. However, our data do not exhibit a simple, systematic change in salt diffusion coefficients with either reciprocal hydration or reciprocal effective hydration. However, when the hydration is corrected to include only the weight fraction of freezing water in the hydrophilic domains, then the salt diffusivity of PFOMA-based copolymers decreases linearly with increasing $1/H^*$ as shown in Fig. 10. Presumably, freezing water is more mobile than non-freezing water and can more effectively assist in salt transport. Salt diffusion coefficients vary by a factor of approximately 50 among the various copolymers considered in this study. The PTAN-*b*-PDMAEMA-*b*-PTAN film has a much lower salt diffusion coefficient than PFOMA-based copolymer films with similar values of $1/H^*$, suggesting that other factors, such as morphology, also influence salt diffusion. All of the PFOMA-based copolymers exhibit some form of cylindrical morphology, and the morphology of PTAN-*b*-PDMAEMA-*b*-PTAN is lamellar [28]. This change in morphology may result in a different tortuosity factor for PTAN-*b*-PDMAEMA-*b*-PTAN than for the other copolymers.

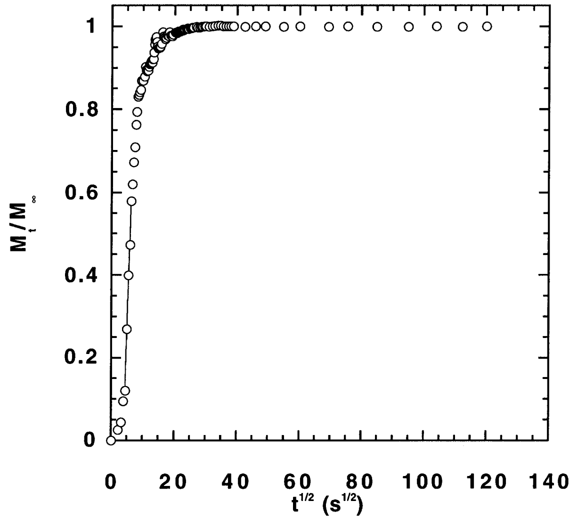

Fig. 9. Kinetic desorption of sodium chloride from PTAN-*b*-PDMAEMA-*b*-PTAN film (PDMAEMA content: 69 mol%) at 25°C. The film thickness is 50 μm, and the straight line through the experimental data is the best fit of Eq. (5) to the data from $0.1 < M_t/M_\infty < 0.6$, which yields a salt diffusivity of 2.9×10^{-7} cm^2/s.

To underscore the impact of freezing water content on salt diffusivity, Fig. 11 presents a correlation of salt diffusivity and the fraction of freezing water in the sample. Interestingly, for the PFOMA-based copolymers, salt diffusivity increases as the amount of freezing water increases. The freezing water presumably has weaker interactions with the hydrophilic sites in the polymer backbone and is readily accessible to assist in salt transport. In contrast to the results reported previously for hydroxyalkyl methacrylate-based hydrogels [4], the salt diffusion coefficients of PDMAEMA copolymers do not depend simply on the total hydration. Instead, they are correlated with the freezing water content of the hydrophilic domains. Hence, the state of water in the

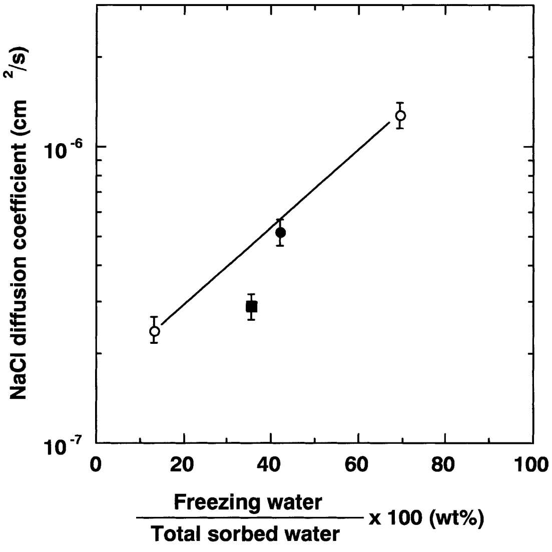

Fig. 11. Sodium chloride diffusion coefficient in PDMAEMA-*b*-PFOMA (○), PFOMA-*b*-PDMAEMA-*b*-PFOMA (●) and PTAN-*b*-PDMAEMA-*b*-PTAN (■) as a function of the percentage of freezing water at 25°C.

phase-separated block copolymers is an important factor influencing salt transport.

4. Conclusions

Solubility and diffusivity of NaCl were determined in dense films of microphase-separated block copolymers composed of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) and either poly(1,1′-dihydroperfluorooctyl methacrylate) (PFOMA) or poly(1,1,2,2-tetrahydroperfluorooctyl acrylate) (PTAN). PDMAEMA is water soluble, while PFOMA and PTAN are highly hydrophobic. As PDMAEMA content (i.e. hydrophilic content) of PDMAEMA-*b*-PFOMA diblock copolymers increases, total water uptake and hydration increase. The salt partition coefficients also increase with increasing PDMAEMA content and effective hydration. In contrast, salt diffusivity does not correlate well with increasing PDMAEMA content and effective hydration.

Triblock copolymers (i.e. PTAN-*b*-PDMAEMA-*b*-PTAN and PFOMA-*b*-PDMAEMA-*b*-PFOMA) have different values of total water uptake, hydration, salt partition, and diffusion coefficients than those of PFOMA diblock copolymers with the same mole percent of hydrophilic PDMAEMA in the chain backbone. However, regardless of polymer morphology, salt partition and diffusion coefficients of these phase-separated block copolymers are well correlated with the percentage of freezing water in the sample.

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