

Properties of Polyethylene Modified with Phosphonate Side Groups. III. Hydration Characteristics and Water Permeability

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Synopsis

The degree of hydration and the water permeability of polyethylene films were enhanced by incorporation of phosphonate pendent groups along the polymer chain. Two different phosphonate esters were considered: the dimethyl ester and an ester derived from poly(ethylene oxide) oligomers (PEO). The highest molecular weight PEO derivatives had the greatest effect on hydration and permeability. A physical change was observed during hydration for the phosphonated materials with a degree of substitution greater than 4.5. The polymers became stiff and brittle, and this was accompanied by an increase in the crystalline melting point and a remarkable change in the dynamic mechanical behavior.

INTRODUCTION

Selective diffusion of chemical species through a polymer film or membrane is one way to effect a chemical separation such as the purification of industrial process streams or the desalination of brine or sea water. For separations involving aqueous solutions, the preparation of a membrane material involves the control of the hydrophilic/hydrophobic balance of the polymer. This is most often accomplished by preparing a block copolymer from hydrophilic and hydrophobic monomers. The hydrophilic blocks increase the swelling of the material and provide the pathway for aqueous diffusion to take place, while the hydrophobic blocks prevent the complete dissolution of the copolymer as well as provide mechanical stability to the membrane. In theory, the proper selection of comonomers and block lengths can result in a permselective material with excellent mechanical properties.

An alternative approach for preparing water-permeable materials is to graft hydrophilic polymers onto a hydrophobic polymer matrix. One example of this approach involved the grafting of poly(acrylic acid) onto polypropylene.¹ The resulting graft copolymer was extremely water permeable, which was attributed to a biphasic polymer structure consisting of physically separated regions of poly(acrylic acid) in a continuous polypropylene phase.

In a previous paper we described the preparation of phosphonated polyethylene in which the phosphonate ester was a poly(ethylene oxide) oligomer.² In these materials the poly(ethylene oxide) separates into discrete microscopic domains within the hydrocarbon matrix.³ The similarity of these systems with

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TABLE I
Equilibrium Hydration of Phosphonated Polyethylenes

Sample	Deg. subst. ^a	Equilibrium hydration, g H ₂ O/100 g polymer		
		Series A	Series B	Series C
LDPE	0	0.2	—	00
1	0.09	0.5	2.4	0.3
2	0.35	—	0.9	2.2
3	0.44	0.8	—	—
4	2.7	2.2	5.0	—
5	4.5	7.3	8.1	14
6	5.8	56 ^b /43 ^c	53 ^b /48 ^c	55 ^b /50 ^c
7	9.1	62 ^b /51 ^c	80 ^b /67 ^c	—

^a Number of phosphonate groups per 100 carbon atoms.

^b Maximum hydration.

^c Final hydration.

the polypropylene-poly(acrylic acid) graft copolymers suggests that the phosphonated polyethylenes may also exhibit desirable membrane characteristics. In this paper we report the hydration behavior and the water permeability of phosphonated polyethylenes.

EXPERIMENTAL

Materials. Low-density polyethylene, LDPE, with a density of 0.923 g/cm³, a number-average molecular weight of 20,000, and a weight-average molecular weight of 80,000 was supplied by the Cities Service Research and Development Company. The phosphonated polyethylenes were prepared by an oxidative

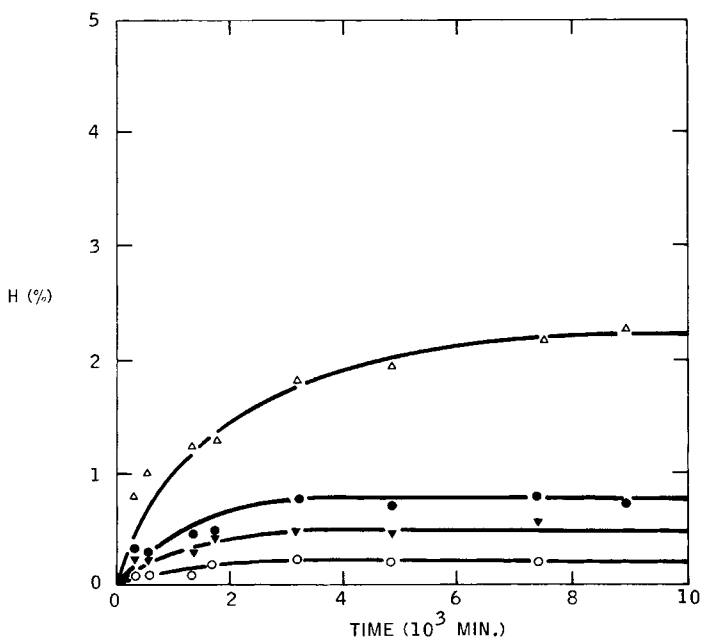


Fig. 1. Sorption isotherms for LDPE (O) and dimethyl phosphonates with degrees of substitution of 0.09 (A1) (▼), 0.44 (A3) (●), and 2.7 (A4) (Δ).

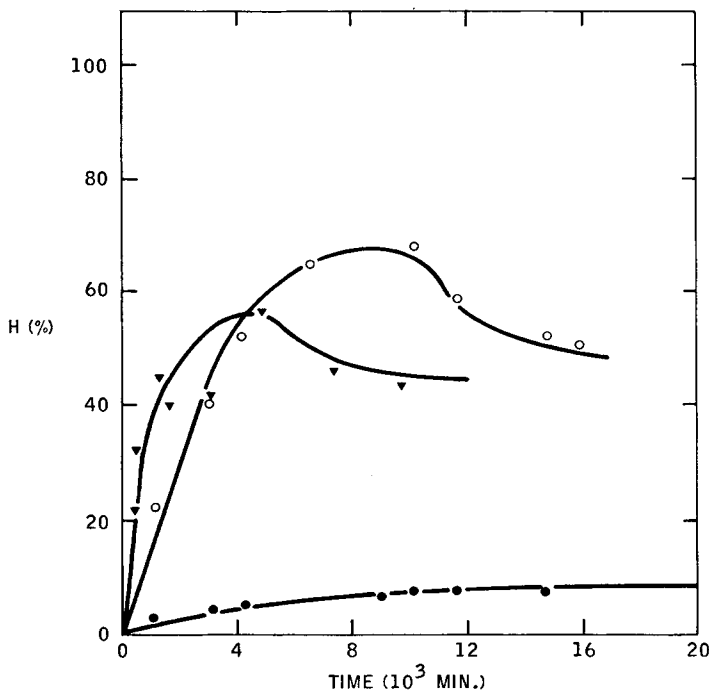


Fig. 2. Sorption isotherms for dimethyl phosphonates with degrees of substitution of 4.5 (A5) (●), 5.8 (A6) (▼), and 9.1 (A7) (○).

chlorophosphonylation reaction followed by esterification of the resulting poly(phosphonyl chloride) with either methanol or a monohydroxy-terminated poly(ethylene oxide) oligomer, PEO, with a molecular weight of either 350 or 750. Details of the preparation are described in an earlier paper.² The materials studied are summarized in Table I; the degree of phosphonate substitution, defined as the number of phosphonate pendent groups per 100 carbon atoms, varied from zero for the unmodified LDPE to 9.1 for the highest substituted polymers.

Hydration Measurements. Polymer films 0.5–1.25 mm thick were compression molded between Teflon sheets at 180°C and quenched to room temperature in ice water. The films were dried under vacuum at 40°C for 24 hr and were then immersed in a constant-temperature bath filled with distilled water at 30°C. The hydration of the sample was measured periodically by removing the film from the bath, drying the surface with a tissue, and measuring the gain in mass of the sample. The equilibrium hydration H_{eq} of the polymer was determined from the least-squares fit of the hydration data to an exponential equation of the form

$$H = H_{eq}(1 - e^{-kt}) \quad (1)$$

Water Permeability. The water permeabilities of polymer films were measured with an Amicon Model 202 ultrafiltration cell. Films approximately 150 microns thick were prepared by compression molding in the same manner as for the hydration experiments. Deionized water at 25°C was placed in the upper half of the cell which was then pressurized with nitrogen, and the permeate

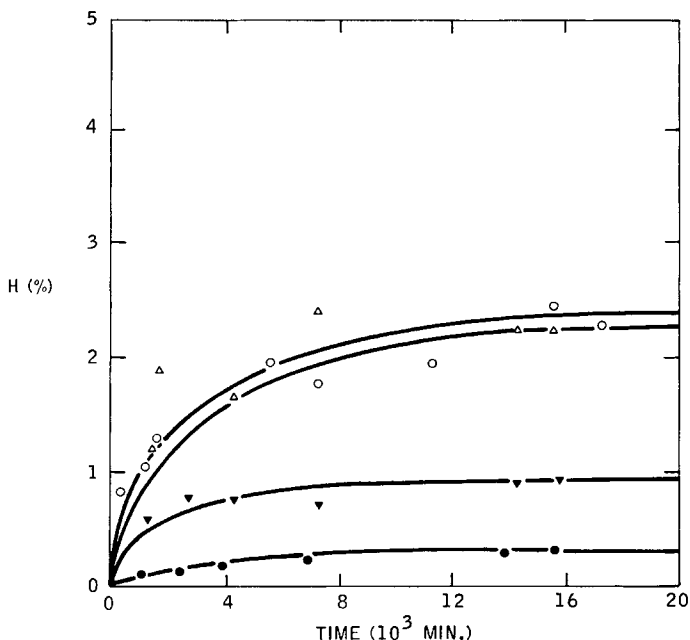


Fig. 3. Sorption isotherms for phosphonates containing poly(ethylene oxide) oligomers with degrees of substitution of 0.09 (B1, C1) (O, ●) and 0.35 (B2, C2) (▼, ▲).

collected on the low-pressure side of the cell was measured as a function of time. A solution-diffusion model was used to characterize the permeability of the polymers:

$$J = -cDv \Delta P/RT\lambda \quad (2)$$

where J is the water flux through the film, c is the concentration of water in the membrane, D is the diffusion coefficient for water in the polymer, R is the gas constant, T is the absolute temperature, v is the partial molar volume of water in the membrane, ΔP is the pressure gradient across the membrane, and λ is the film thickness. Equation (2) can be rewritten as

$$J = \beta \Delta P \quad (3)$$

where β is defined as the membrane permeation constant.

RESULTS AND DISCUSSION

Equilibrium Hydration

The extent of water sorption in a polymer film depends upon the chemical compatibility of water and the polymer and upon the nature and strength of the forces holding the polymer chains together. Polyethylene sorbs little water, and this can be attributed in part to the effect of crystallinity and in part to the nonpolar composition of the hydrocarbon structure. Therefore, it was expected that hydration of the phosphonated polymers would be enhanced by both the decrease in crystallinity accompanying phosphonation² and by the presence of polar substituents, the phosphonyl group, the methoxy groups, and the polyethylene oxide chains.

The sorption isotherms of the methyl phosphonates, series A, and of the phosphonates containing poly(ethylene oxide), series B and C, are given in Figures 1 through 5. The solid curves represent the least-squares fits of eq. (1)

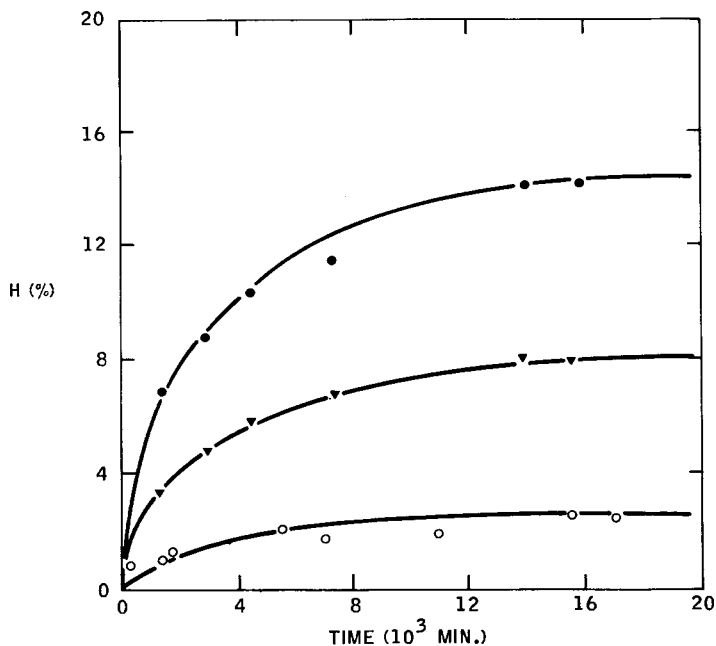


Fig. 4. Sorption isotherms for phosphonates containing poly(ethylene oxide) oligomers with degrees of substitution of 2.7 (B4) (○) and 4.5 (B5, C5) (▼, ●).

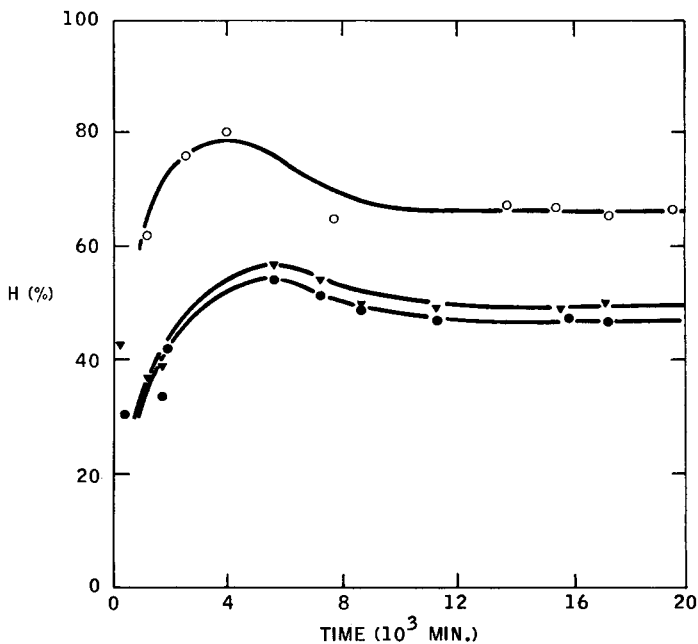


Fig. 5. Sorption isotherms for phosphonates containing poly(ethylene oxide) oligomers with degrees of substitution of 5.8 (B6, C6) (●, ▼) and 9.1 (B7) (○).

to the data, and the equilibrium hydration values determined by the curve fitting analysis are listed in Table I. For the samples which exhibited a maximum in their sorption isotherms, the maximum hydration was taken as the equilibrium hydration. The reason for this will become clear in the discussion that follows.

The equilibrium hydrations of the phosphonated polymers are plotted against phosphonate concentration in Figure 6. The hydration of polyethylene is increased by phosphonation, and for a given degree of substitution the hydrations of the phosphonate derivatives follow the sequence series C > series B > series A. This result indicates that the solubility of water in these polymers is dependent not only on the extent of phosphonation but also on the chain length of the phosphonate ester. This result is reasonable, because for these polymers the number of polar groups, i.e., the ether linkages, increases with the molecular weight of the phosphonate ester.

The equilibrium hydration curves in Figure 6 exhibit an inflection between a phosphonate concentration of 4%–5%. Above this concentration the sorption

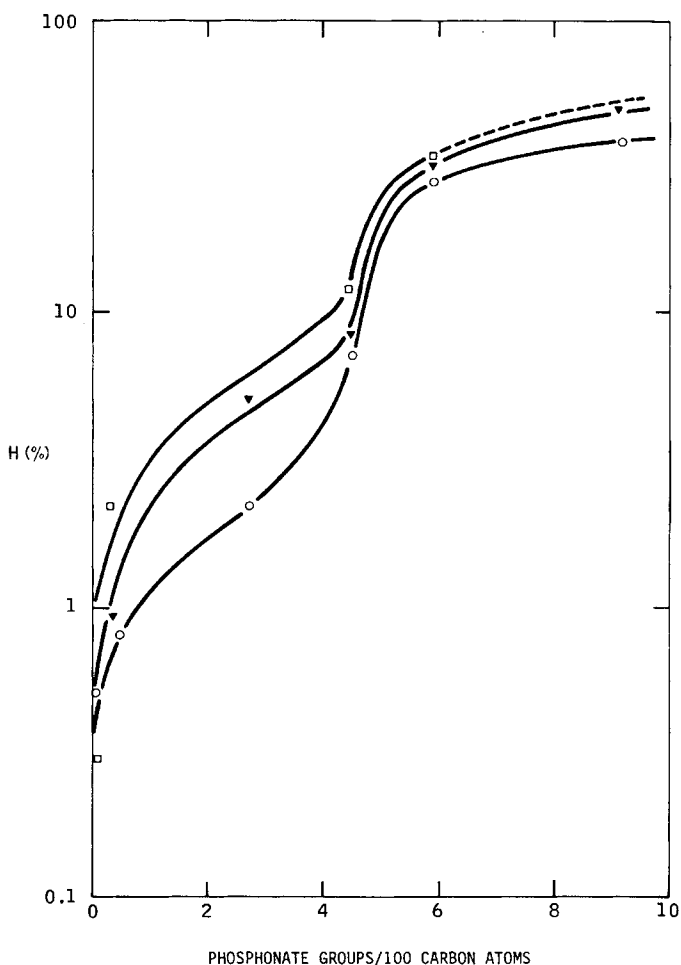


Fig. 6. Equilibrium hydration of phosphonated polyethylene vs. degree of substitution: (\square) Series C; (\blacktriangledown) Series B; (\circ) Series A.

isotherms exhibit a maximum (cf. Figs. 2 and 5). It was also noted that the polymers became stiff and brittle during the hydration experiment, and the onset of this physical change coincided with the sorption maximum. Furthermore, this phenomenon was not reversible upon dehydration. It is not known whether the change in the physical characteristics of these polymers is due to a chemical or a morphological change.

Although the physical change that takes place in the highly phosphonated materials during hydration has not been studied in detail, several observations are noted here. The melting thermograms determined by differential scanning calorimetry for polymer B6 before and after hydration are shown in Figure 7. Both samples were dried and annealed for 24 hr at 40°C. The sample which had been hydrated exhibited a maximum in the melting endotherm approximately 15°C higher than for the unhydrated polymer, which suggests that one effect of hydration may be to further anneal the polymer. Such a mechanism might explain the maximum in the sorption isotherms, but it cannot account for other differences observed between the unhydrated and hydrated polymers.

In a previous paper the dynamic mechanical behavior of the phosphonated polyethylenes was reported. In Figure 8 the dynamic and loss tensile moduli as determined with a Toyo Vibron Dynamic Viscoelastometer Model DDV-II (Rheovibron) are given as a function of temperature for Polymer B6 before and after hydration. The hydrated sample was dried to constant weight, and both samples were annealed for 24 hr at 40°C. The unhydrated sample exhibits three loss dispersion regions: (1) a relaxation at -122°C which corresponds to the γ -loss mechanism of polyethylene; (2) a broad dispersion region, β' , between -50 and -30°C, which is due to discrete domains of poly(ethylene oxide)³; and (3)

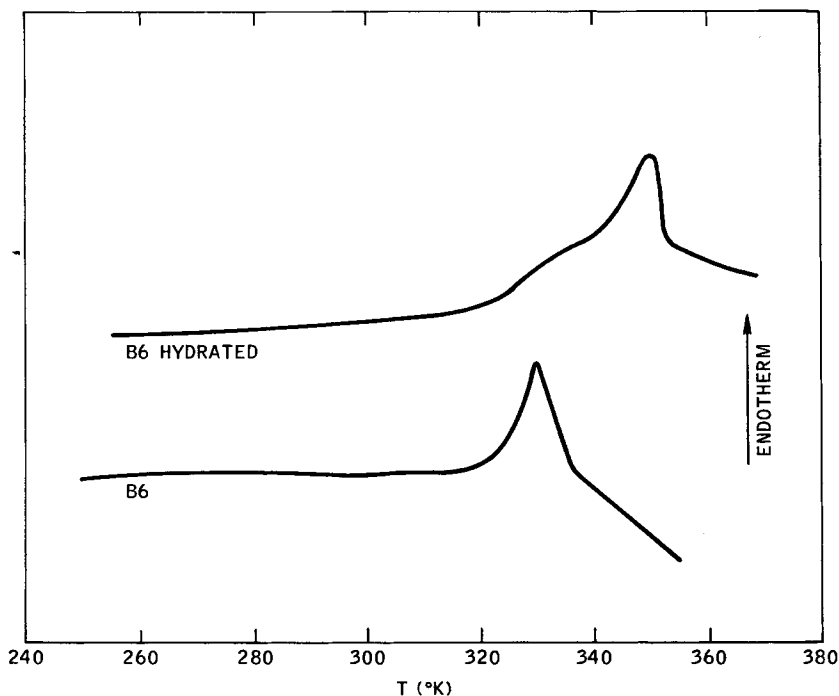


Fig. 7. DSC thermograms of sample B6 before and after hydration.

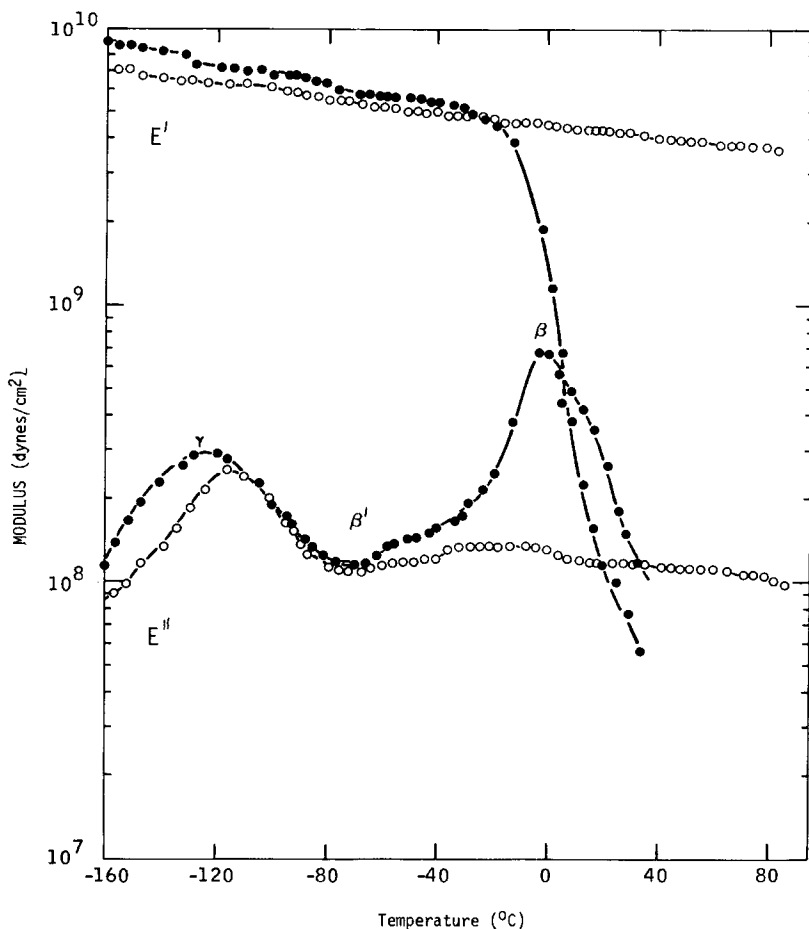


Fig. 8. Dynamic mechanical moduli at 110 Hz versus temperature for sample B6 before (●) and after hydration (○).

the β relaxation of low-density polyethylene near 0°C. The β relaxation is accompanied by a reduction of the dynamic modulus of two orders of magnitude.

The moduli-temperature relationships of the hydrated polymer are significantly different from those of the unhydrated sample. Although the γ relaxation was unchanged, the β and β' loss regions were greatly reduced in magnitude. Similarly, the dynamic modulus did not exhibit any substantial change between -160 and 100°C. It is doubtful that increased crystallinity could alone account for these dynamic mechanical results, however, no satisfactory explanation has been found for these observations.

Water Permeability.

Due to a lack of sufficient quantities of material, only a limited number of flux experiments were made and only with the unmodified polyethylene and with the highest phosphonated materials. The experimental results are given in Table II. In the last column of Table II are listed the membrane permeation constants

TABLE II
Permeation Data for Phosphonated Polyethylenes

Sample	D.S. ^a	ΔP , psi	A , cm ²	λ , μm	J , g-cm ⁻² sec ⁻¹	β , g-cm ⁻² sec ⁻¹ atm ⁻¹
LDPE	0	50	30.1	160	4.2×10^{-7}	9.5×10^{-8}
A7	9.1	20	30.1	146	6.4×10^{-7}	2.2×10^{-7}
		50	30.1	146	1.7×10^{-6}	3.9×10^{-7}
B6	5.8	50	30.1	165	2.0×10^{-5}	4.5×10^{-6}
C6	5.8	20	30.1	147	1.7×10^{-6}	7.0×10^{-6}
		50	30.1	147	8.6×10^{-5}	1.9×10^{-5}

^a Number of phosphonates per 100 carbon atoms.

for the polymer films, and it can be seen that the permeability of polyethylene is improved significantly as a result of phosphonation. Permeability is also increased by substitution of a PEO chain for the methyl group in the phosphonate ester as is evidenced by the relative values of β for samples A7 (methyl phosphonate) and B6 and C6 (PEO phosphonate). Similarly, the constants for samples B6 and C6 indicate that increasing the molecular weight of the poly(ethylene oxide) ester increases the permeability.

The characterizations of these membranes were made by assuming a solution-diffusion model as the mechanism of water transport. This model is not completely justified as is evidenced by the effect of pressure on the membrane permeability constant. A solution-diffusion mechanism dictates that β be independent of pressure, while the data for samples A7 and C6 show that β increased as the hydrostatic pressure was increased from 20 to 50 psi. The probable explanation for the discrepancy between the model and the experimental observations is that some transport took place by bulk flow through imperfections in the films. That imperfections exist in the films studied is not at all improbable considering their thickness. Nevertheless, the analysis outlined above is most likely valid for qualitative comparisons within the context of these experiments and these systems.

A major limitation of the use of these polymers as membrane materials is the fact that the water flux could not be sustained for more than several hours. This can most likely be attributed to compaction of the polymers. Another limitation is the preparation of thin membranes (ca. 20 μm). Attempts at compression molding films less than 150 μm were unsuccessful due to the tendency of the materials to relax upon removal of the molding pressure. Because of the lack of a suitable solvent for these materials we were unable to cast membranes from solution. Due to the differences in the solubility parameters of the hydrocarbon backbone and the polar sidechains, a single solvent is not sufficient for dissolution of the entire polymer. Dilute solutions (< 1%) were achieved with a mixed solvent system of tetralin/diglyme/DMSO (70/20/10); however, no attempt was made to cast membranes from this solution.

CONCLUSIONS

This investigation has demonstrated that phosphonated polyethylenes do have potential as membrane materials for aqueous separations. Work is needed, however, to improve the resistance of these polymers to compaction and to de-

velop a suitable solvent system so that thin membranes can be prepared. At relatively high degrees of substitution (> 4.5 phosphonate groups per 100 carbon atoms) it was observed that hydration of the polymers had an irreversible effect on the thermal and the viscoelastic behavior of these polymers. Additional studies are needed to determine the origins of these effects.

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