
Ralph Ruffolo,† Christopher E. B. Evans,† Xiao-Hua Liu,† Yizeng Ni,† Zhen Pang,† Peter Park,† Andrew R. McWilliams,† Xijia Gu,‡ Xin Lu,¶ Ahmad Yekta,¶§ Mitchell A. Winnik,*,‡ and Ian Manners*,‡

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, M5S 3H6, Ontario, Canada, and Photonics Research Ontario, University of Toronto, 60 St. George Street, Toronto, M5S 1A7, Ontario, Canada

We examine the use of thionylphosphazene-based block copolymers as matrices for oxygen sensor applications. Poly(aminothionylphosphazene)-b-poly(tetrahydrofuran) (PATPϕ−y•PTHFϕ) block copolymers were prepared via reaction of ring-opened poly(chlorothionylphosphazene) with THF and subsequently with excess n-butylamine (to form PBATPϕ−y•PTHFϕ) or methyamine (to form PMATPϕ−y•PTHFϕ). The block copolymers were characterized by NMR, gel permeation chromatography, and differential scanning calorimetry. Films of PBATPϕ−y•PTHFϕ block copolymers containing platinum octaethylporphyrin or [Ru(dpp)3]2Cl2 (dpp = 4,7-diphenyl-1,10-phenanthroline) as the oxygen-sensitive chromophore were prepared, and time-scan experiments were carried out to determine the diffusion coefficients, D0, and solubilities, S0, of oxygen therein. Despite microphase separation, the data fit well to a simple Fick’s law description of oxygen diffusion and gave D0 values smaller than that for the n-butylamino-substituted PBATP635. For films freshly annealed above the melting point of PTHFϕ, the D0 values were 35–50% (dye-dependent) larger than after aging 3 days at room temperature. Films with [Ru(dpp)3]2Cl2 as the dye were evaluated as media for phosphorescent pressure-sensing. The dye-containing polymer films exhibit linear Stern–Volmer-like plots, even at high dye concentrations, as well as good photostability, and significantly higher sensitivity to oxygen quenching than simple mixtures of the analogous homopolymers.

The design of polymeric materials for the construction of sensing devices is an area of intense current interest.1–3 Phosphorescent sensors consisting of transition metal complexes immobilized in polymer matrices have attracted attention as oxygen sensors for both biomedical and barometric applications.4–8 Such systems typically incorporate dyes with oxygen-quenchable excited states, such as platinum octaethylporphyrin (POTEP) or ruthenium(II) polypyridine complexes, which are dissolved or dispersed in a polymer matrix.4–8 The matrix material requires high oxygen permeability and must be chemically robust with respect to singlet oxygen, which is a byproduct of the quenching process. Inorganic polymers with outstanding O2-permeability and thermooxidative stability, such as polysiloxanes, have attracted significant attention. Polysiloxanes, however, generally must be cross-linked (cured) after solution processing in order to obtain dimensional stability.4–8 To obtain a fundamental understanding of the factors that influence the performance of pressure sensing matrices, tunable and structurally well-defined polymers are required to allow structure–function relationships to be established.

In a previous communication we reported that a poly(thionylphosphazene) (PTP) with n-butylamino substituents, PBATPϕ (where ϕ represents the degree of polymerization), provides an excellent polymer matrix for phosphorescent oxygen sensor applications.9 In particular, cross-linking is unnecessary for

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dimensional stability and this gives rise to the additional advantage that the sensing layer can be recycled after use by dissolution in common organic solvents. Unfortunately PBATP₂₈₀ amorphous material with a T_g of −17 °C, forms rather tacky films which, although useful for fundamental studies, are unsuitable for many applications. The visualization of air flow over objects such as aircraft, for example, requires a material that provides a smooth, abrasion-resistant surface so that the sensing process is nonintrusive. In this paper we describe a step toward a resolution of this problem through modification of PBATP₂₈₀ with poly(tetrahydrofuran) (PTHFₓ) resulting in block copolymers of composition PBATPₓ-PTHFₓ (where x is the degree of polymerization of THF).

**Experimental Section**

**Materials.** Polymers were synthesized under nitrogen atmosphere either in an Innovative Technology glovebox or by standard Schlenk line techniques. Solvents were dried according to standard methods. PTHF was prepared according to literature procedures using trimethylsilyl triflate as the initiator at −10 °C (M_w = 8.14 × 10⁴, PDI = 1.6). Cyclic thionylphosphazene (NSCl(NPCl)₂) was the corresponding ring-opened polymer PCTP, the methyl-substituted polymer PMATP (M_w = 5.0 × 10⁴, PDI = 1.5), and the butyl-substituted polymer PBATP (M_w = 3.69 × 10⁴, PDI = 1.8) were all prepared according to literature methods. 1,1,1-Trichloroethane (ACS) was purchased from Aldrich and used as received. [Ru(dpp)Cl]₂ was synthesized according to the procedure described by Lin et al. PTOEP was purchased from Porphyrin Products, Inc. and used as received. Poly(tetrahydrofuran) (PTHFₓ) was prepared by modification of PBATP₂₈₀ through a process involving the following steps:

1. Preparation of Poly(Butyl Amino Thionyl Phosphazene) (PBATP₂₈₀): The synthesis of PBATP₂₈₀ involved the reaction of PMATP with NPCl₂. A solution of 2.0 g of NPCl₂ in 20 mL of THF was heated in a sealed, evacuated Pyrex tube at 65 °C for 4 h. The crude product was obtained by distillation from water and subsequently 3 times by precipitating CH₂Cl₂ solutions into hexanes. The purified product was dried under high vacuum for 24 h at ambient temperature and used for further experiments.

2. Preparation of Poly(methylaminothionylphosphazene)-b-Poly(tetrahydrofuran) (PMATPₓ-PTHFₓ): The synthesis of this copolymer involved the reaction of PBATP with methylene chloride and subsequent precipitation into hexanes. The final product was dried under high vacuum for 24 h at ambient temperature.

3. Preparation of Poly(methylaminothionylphosphazene)-b-Poly(tetrahydrofuran) (PMATPₓ-PTHFₓ): The synthesis of this copolymer involved the reaction of PBATP with methylene chloride and subsequent precipitation into hexanes. The final product was dried under high vacuum for 24 h at ambient temperature.

4. Preparation of Poly(methylaminothionylphosphazene)-b-Poly(tetrahydrofuran) (PMATPₓ-PTHFₓ): The synthesis of this copolymer involved the reaction of PBATP with methylene chloride and subsequent precipitation into hexanes. The final product was dried under high vacuum for 24 h at ambient temperature.

**Synthesis of Polymers.** Poly(butylaminothionylphosphazene)-b-Poly(tetrahydrofuran), PMATPₓ-PTHFₓ. NSCl(NPCl)₂ (2.0 g) was heated in a sealed, evacuated Pyrex tube at 165 °C for 4 h. The tube contents were dissolved in ~ 40 mL of CH₂Cl₂, and the solution was then concentrated to ~ 10 mL and added dropwise to 200 mL of stirred hexanes via cannula. The colorless, moisture-sensitive, elastomeric polymer PCTP was dissolved in 100 mL of THF and the solution then stored in the refrigerator at −14 °C for 48 h. A significant increase in solution viscosity was noticed. n-Butylamine was then added dropwise to the polymer solution at 0 °C and allowed to stir for 24 h. The crude product was obtained by dropwise addition of the concentrated solution to water and was purified twice by precipitation of THF solutions into water and subsequently three times by precipitating CH₂Cl₂ solutions into hexanes. The purified product was dried under high vacuum for 24 h at ambient temperature; yield of PMATPₓ-PTHFₓ, a colorless film-forming material, was 0.28 g (84%). ¹³P NMR (CDCl₃) δ (ppm): 2.05, 1.81. ¹H NMR (CDCl₃) δ (ppm): 3.38 (s, br, THF), 3.04 (m, br, NH), 2.84 (m, br, Bu), 1.57 (m, THF), 1.46 (m, Bu), 1.36 (m, br, Bu), 0.91 (m, Bu, CH₃). ¹³C NMR (CDCl₃) δ (ppm): 70.9 (THF), 41.1 (Bu), 34.3 (Bu), 27.0 (THF), 20.7 (Bu), 14.2 (Bu). DSC: T_g = −70 °C and T_m = 40 °C for the PTHFₜ block, T_g = −16 °C for the PBATP block. GPC: PMATP₅₀-PTHFₐ₀, M_w = 3.05 × 10⁴, PDI = 1.9; PMATP₂₅₀-PTHF₇₄₀, M_w = 2.16 × 10⁵, PDI = 1.5; PMATP₁₃₅-PTHF₄₉₂₅, M_w = 2.36 × 10⁵, PDI = 1.9.

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Table 1. Permeation Properties of Oxygen in Polymer Films Containing PtOEP or [Ru(dpp)3]Cl2 as the Oxygen-Sensitive Luminophore, Calculated from Time-Scan Experiments

<table>
<thead>
<tr>
<th>Polymer</th>
<th>D0, ×10^{-6} cm^2 s^{-1} atm^{-1}</th>
<th>S0, ×10^{-4} M atm^{-1}</th>
<th>P0 = D0 S0, ×10^{-12} mol cm^{-2} s^{-1} atm^{-1}</th>
<th>r^2, ×10^{-6} s</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBATP/PtOEP</td>
<td>3.73 ± 0.97</td>
<td>10.3 ± 2.6</td>
<td>3.85 ± 0.20</td>
<td>103 ± 1</td>
<td>59.8 ± 3.1</td>
</tr>
<tr>
<td>PBATP/[Ru(dpp)3]Cl2</td>
<td>3.72 ± 0.74</td>
<td>4.89 ± 0.97</td>
<td>1.82 ± 0.07</td>
<td>5.4 ± 0.1</td>
<td>1.74 ± 0.07</td>
</tr>
<tr>
<td>PBATP /THF 1300 PTOEP (1 h)</td>
<td>10.9 ± 0.69</td>
<td>0.81 ± 0.1</td>
<td>0.86 ± 0.03</td>
<td>92.0 ± 1.0</td>
<td>12.0 ± 0.6</td>
</tr>
<tr>
<td>PBATP /THF 4925 PTOEP (1 h)</td>
<td>1.55 ± 0.07</td>
<td>10.2 ± 0.5</td>
<td>1.58 ± 0.08</td>
<td>96.0 ± 0.5</td>
<td>23.0 ± 1.0</td>
</tr>
<tr>
<td>PBATP /THF 4925 PTOEP (3 d)</td>
<td>1.01 ± 0.03</td>
<td>12.0 ± 0.7</td>
<td>1.19 ± 0.03</td>
<td>94.0 ± 0.5</td>
<td>17.4 ± 0.4</td>
</tr>
<tr>
<td>PBATP /THF 4925 [Ru(dpp)3]Cl2 (1 h)</td>
<td>2.6 ± 0.7</td>
<td>3.7 ± 0.9</td>
<td>1.00 ± 0.06</td>
<td>6.9 ± 0.1</td>
<td>1.05 ± 0.03</td>
</tr>
<tr>
<td>PBATP /THF 4925 [Ru(dpp)3]Cl2 (3 d)</td>
<td>1.4 ± 0.3</td>
<td>6.7 ± 0.4</td>
<td>0.95 ± 0.06</td>
<td>6.9 ± 0.1b</td>
<td>1.00 ± 0.02</td>
</tr>
<tr>
<td>PTHF 1300 PTOEP (1 h)</td>
<td>3.2 ± 0.92</td>
<td>7.4 ± 2.1</td>
<td>2.4 ± 0.2</td>
<td>92.1 ± 0.6</td>
<td>33.5 ± 0.9</td>
</tr>
<tr>
<td>PTHF 4925 PTOEP (10 d)</td>
<td>1.0 ± 0.3</td>
<td>19 ± 5</td>
<td>1.9 ± 0.1</td>
<td>86.1 ± 0.7</td>
<td>24.8 ± 3.5</td>
</tr>
<tr>
<td>PTHF 4925 PTOEP (30 d)</td>
<td>0.68 ± 0.17</td>
<td>25 ± 6</td>
<td>1.7 ± 0.1</td>
<td>75.1 ± 0.5</td>
<td>18.9 ± 1.3</td>
</tr>
</tbody>
</table>

* The time given in parentheses is the aging time after the samples were removed from the annealing oven. ** The unquenched lifetime used here is that of the sample 1 h after annealing.

NMR (CD2Cl2) δ (ppm): 70.6 (THF-a), 30.3 (SNCH3), 27.0 (PNCH3), 26.5 (THF-k). DSC: Tg = −79 °C and Tm = 34 °C for the PTHF block, Tg = 13 °C for PMATP block. GPC: PMATP–

\[ \text{PTHF}_n \] Mw = 1.50 × 10^6, PDI = 1.9.

Precipitation Experiment To Show That PBATP135-

\[ \text{PTHF}_{4925} \] Is Not a Blend. Equivalent precipitation experiments (viscous CH2Cl2 solutions into hexanes, with subsequent cooling) were performed upon both a sample of PBATP135–PTHF4925 and a mechanical blend of PBATP635 and PTHF4925.

A blend of PBATP635 homopolymer (60 mg) and PTHF4925 homopolymer (60 mg) was dissolved in CH2Cl2 (5 mL) and added dropwise to hexanes (150 mL). The solution was cooled in an ice bath for 30 min, resulting in the precipitation of a white polymer, which was isolated by decanting off the supernatant liquor and was dried in vacuo. Subsequent analysis confirmed the identity of this solid as being 40 mg of PTHF4925. 1H NMR (prior to precipitation) (CDCl3) δ (ppm): 3.40 (H, br, THF, 3.04 (m, br, NH), 2.56 (m, br, Bu), 1.61 (m, br, THF), 1.41 (m, br, Bu), 0.89 (m, br, Bu-CH3). 1H NMR (after precipitation) (CDCl3) δ (ppm): 3.42 (H, br, THF), 1.61 (m, br, THF).

A sample of PBATP135–PTHF4925 was dissolved in CH2Cl2 and added dropwise to hexanes. After cooling for 30 min, the resultant solid was collected and dried. Analysis by 1H NMR confirmed the identity of the precipitate as PBATP135–PTHF4925. 1H NMR (prior to precipitation) (CDCl3) δ (ppm): 3.40 (s, 36.7H, THF), 2.92 (m, 2.3H, Bu), 1.61 (m, 40.8, THF), 1.36 (m, 32H, Bu), 0.90 (m, 44H, Bu). 1H NMR (after precipitation) (CDCl3) δ (ppm): 3.40 (s, 35.3H, THF), 2.92 (m, 3.5H, Bu), 1.61 (m, 38.6H, THF), 1.36 (m, 37.6H, Bu), 0.90 (m, 39H, Bu).

Oxygen Diffusion Studies. 1,1,1-Trichloroethane solutions containing the dye ([Ru(dpp)3]Cl2) and polymer (PBATP–

\[ \text{PTHF}_{4925} \] were sprayed onto ~2 cm² aluminum plates precoated with the acrylic primer Suprime 1 White manufactured by Pratt & Lambert. The dye concentration in the polymer matrices ranged from 500 to 2500 ppm. Samples were placed in a small pressure chamber controlled using a vacuum pump and compressed air. All measurements were made at ambient temperatures.

The samples were illuminated by a lamp composed of 60 Nichia Single Quantum Well (SQW) 2–3 mW NSBP series blue LEDs with a band maximum at 470 nm and band halfwidth of 20–30 nm. Luminescent light from the sample surface was collected with a camera lens (Nikon Nikkor, 55 mm, 1:1.2) protected by two red filters (Hoya 52 mm R(25A) and Tiffen 52 mm 25 RED 1) and imaged onto a CCD camera (Photometrics CH350) equipped with a cutoff filter (Melles Griot 03FIB004 for [Ru(dpp)3]Cl2). The pressure of the sample chamber was measured by an analog pressure gauge (model FA 233, Wallace & Tiernan) read to an accuracy of ± 0.05 psi. Evidence for the photostability of the [Ru(dpp)3]Cl2 dye in one of the polymer matrices is presented in Table 2.

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DATA AND DATA ANALYSIS

Measuring Oxygen Diffusion via Luminescence Quenching. Diffusion coefficients for oxygen in polymer films were determined by monitoring the time-dependent intensity of dye phosphorescence during both O₂ sorption and desorption experiments (see Experimental Section). Details of such experiments have been published previously and thus only a brief introduction to the underlying theory is provided here.¹⁰,¹⁵,¹⁶

Theoretical Considerations. The rate of quencher (oxygen) diffusion into the film can be anticipated to follow Fick’s second law:

\[
\frac{\partial c(x,t)}{\partial t} = D(\frac{\partial^2 c(x,t)}{\partial x^2})
\]

where \( c(x,t) \) is the concentration of the dissolved gas at time \( t \) and distance \( x \) within the film and \( D \) is its diffusion coefficient. A Henry’s law dependence between the quencher pressure above the film and the gas concentration in the polymer film is assumed when the quencher concentration in the gas phase is constant. With this approximation, the concentration of quencher oxygen absorbed by the film can be related to exposure time by eq 2.1,

\[
Q(x,t) = Q_{eq} \left[ 1 - \frac{4}{\pi} \sum_{n=odd} \exp \left( - \frac{n^2 \pi^2 Dt}{4L^2} \right) \sin \left( \frac{n\pi x}{2L} \right) \right]
\]

oxigen sorption:

\[
Q(x,t) = Q_{eq} \left[ \frac{4}{\pi} \sum_{n=odd} \exp \left( - \frac{n^2 \pi^2 Dt}{4L^2} \right) \sin \left( \frac{n\pi x}{2L} \right) \right]
\]

oxigen desorption:

first derived by Mills and Chang.¹⁷b Here \( Q(x,t) \) is the concentration of oxygen in a film of thickness \( L \) at a depth \( x \) and time \( t \). The subscript \( eq \) refers to the film in equilibrium with oxygen. That is, \( Q_{eq} \) is the equilibrium concentration of oxygen in the film.

During either the O₂ sorption or desorption experiments, the concentration of oxygen in the film changes as a function of time, resulting in a time-dependent emission intensity, \( I(t) \). The measured intensity is the sum of the integral intensities of the dye molecules located at various depths in the film, which in turn are related to \( Q(x,t) \). From the Stern–Volmer equation for oxygen quenching, we obtain the expression¹⁰,¹⁵

where the superscript 0 is used here to indicate that no quencher is present in the film. \( I^0 \) is, thus, the emission intensity when \( Q(x,t) = 0 \). \( B \) is defined in eq 4. Here \( \alpha \) is the radius of the encounter complex (~10 Å), \( \alpha \) is the probability an encounter complex results in quenching (typically assumed to be one), \( N_A \) is 6.023 \times 10²³ (Avogadro’s number divided by 1000), and \( r_0^2 \) is the lifetime of the dye in the absence of quencher. \( D_0 \) and \( S_0 \) are the diffusion coefficient and solubility of oxygen in the polymer film, respectively, and \( p_0 \) is the pressure of oxygen above the polymer film. In the time-scan experiments described below, \( p_0 \) is equal to 0.2 atm. From values of \( B \), one can calculate the permeability \( (P_{D,O}_2 = D_0 S_0) \) of oxygen if \( r_0^2 \) and \( \alpha \) are known. Clearly, the solubility of oxygen in the polymer films can be calculated from \( p_0 \), and \( B \) once \( D_0 \) is determined.

To determine values for \( D_{O_2} \), eq 3 must be related to our experimental observable, \( I(t) \), which is accomplished using eq 5.

\[
I(t) = \frac{I^0}{\int_0^L B Q(x,t)^{-1} \, dx}
\]

\( I(t) \) values calculated using eq 5 are compared with experimental data, using \( D_{O_2} \) as the variable for the evaluation of \( Q(x,t) \) (see eqs 2). The correct value of \( D_{O_2} \) is then taken to be that which results in the best correlation between the experimental and calculated data.

Variable Reference Point Stern–Volmer Plots. If we use \( p_1 \) and \( p_2 \) to represent two different oxygen pressures, the ratio of the emission intensities of the dye-containing films under these two different pressures, \( I_1/I_2 \), is given by eq 6 if the Stern–Volmer equation applies to the system over this pressure range. When \( p_1 \) refers to a reference pressure, eq 6 can be rewritten as eq 7 by

\[
I_{ref} = I_{2}^{\frac{1}{1 + B}} + B \left( \frac{p_2}{p_{ref}} \right)
\]

considering \( B = K_{p_{ref}} \) and \( K_{p_{ref}} = B_{p_2}/p_{ref} \). In the study of air pressure profiles by luminescence barometry, the air pressure \( P \) replaces the oxygen pressure \( p \) in the above equation. Taking \( p_{ref} \) as 1 atm (\( P_{1,0} \), the emission intensity (I) at P is related to that (\( I_{1,0} \)) at 1 atm air pressure, by the expression

\[
I_{1,0} = \frac{1}{1 + B} + B \left( \frac{P}{P_{1,0}} \right)
\]
When we fit intensity data as a function of air pressure, we commonly rewrite this expression as

\[ I_{1.0} = A + Q_S(P/P_{1.0}) \]  

where \( Q_S = B/(1 + B) \) is a measure of the sensitivity of the dye–matrix combination to quenching due to a change in air pressure. In this type of experiment, we refer to \( Q_S \) as the “quenching sensitivity”. We note that while \( B \) can take a wide range of values, depending upon the magnitude of \( D_0 \), values of \( Q_S \) range from 0 to 1. When \( B = 1 \), \( Q_S = 0.5 \), whereas when \( B \) is very large, \( Q_S \approx 1.0 \). It should be clear that \( Q_S \) is not equivalent to \( K_{SV} \), the Stern–Volmer constant, which requires the reference point to be the intensity and pressure when the concentration of oxygen is zero.

RESULTS

Synthesis and Characterization of Poly(n-butylaminothiophosphazene)-b-Poly(tetrahydrofuran) Block Copolymers. Poly(thionylphosphazenes) are an interesting new class of inorganic polymers with a backbone of sulfur(VI), nitrogen, and phosphorus atoms. These materials can be regarded as hybrids of poly(oxothiazenes) \([S(O)R=N]_n\) and polyphosphazenes \([PR_2=N]_n\)\(^{16,19}\) and can be prepared via the ring-opening polymerization (ROP) of the cyclic monomer, NSOC\((NPCl_2)_2\), either thermally at 165 °C or at ambient temperature in solution with a Lewis acid initiator such as GaCl\(_3\).\(^{20,21}\) In a manner analogous to the preparation of hydrolytically stable poly(organophosphazenes) from \([NPCl_2]_n\),\(^{19,22}\) the hydrolytically sensitive halogenated polymer PCTPy can be reacted with nucleophilic reagents to afford hydrolytically stable polymers such as PBATPy.\(^{20}\) We believe the ROP mechanism involves initiation by a cationic intermediate generated via loss of chloride from the sulfur(VI) center followed by propagation steps in which ring opening of monomer molecules generates a linear polymer with an electrophilic sulfur(VI) center at the chain end.\(^{23}\)

Dissolution of PCTPy in PTHF led to an increase in solution viscosity with time. The product of this reaction, PCTPy–PTHFx, is hydrolytically sensitive due to the reactive halogen–element bonds. Hydrolytically stable products were produced by subsequent reactions with primary amines (see Scheme 1) to form the block copolymers PBATPy–PTHFx (from the reaction with butylamine) and PMATPy–PTHFx (from the reaction with methylamine). The identity of the products was confirmed by NMR. THF
polymerization is believed to be initiated by cationic chain ends of PCTP.

Characterization of the block copolymers was achieved by $^1$H, $^{13}$C, and $^{31}$P NMR, and by GPC. Significantly, the $^{31}$P NMR spectra of the block copolymers were identical to those of the corresponding homopolymers, indicating that noRAFT copolymers (in which PMATP would join the PTP backbone at various phosphorus or sulfur sites) had been formed. Switching groups (alkyl groups on the sulfur(VI)) in the copolymer could not be identified, presumably as a consequence of the high molecular weights of the materials (by GPC broad, essentially monomodal peaks were detected with $M_w > 10^5$ and PDI values of 1.5–1.9). Control of PMATP block length was attempted by varying factors such as reaction time and temperature. No conclusive relationships were determined, but three polymers with different compositions, PBATP$_{280}$–PTHF$_{1300}$, PBATP$_{280}$–PTHF$_{2900}$, and PBATP$_{135}$–PTHF$_{4925}$, were prepared and identified by $^1$H NMR and GPC.

Assignment of a block copolymer structure was further supported by the following experiment: first, addition of a CH$_2$Cl$_2$ solution of a mechanical blend of PBATP$_{135}$ and PTHF$_{1810}$ to cold hexanes resulted exclusively in the precipitation of PTHF$_{1810}$. I n Figure 1 it can be clearly seen that peaks associated with PBATP are no longer present in the $^1$H NMR spectrum of the precipitated solution of a mechanical blend of PBATP$_{135}$ and PTHF$_{1810}$ to cold hexanes, PTHF$_{1810}$.

As shown by the first experiment).

In addition, a dramatic increase in molecular weight was observed when samples of PMATP$_x$ and PMATP$_y$–PTHF$_x$, synthesized from the same batch of PCTP, are analyzed by GPC. TheGPC (run in THF relative to polystyrene standards) data showed $M_w = 7.0 \times 10^5$ (PDI = 1.5) for PMATP$_x$ and $M_w = 1.5 \times 10^6$ (PDI = 1.9) for PMATP$_y$–PTHF$_x$. The PTHF block of the latter species has much more favorable interactions with solvent than the PMATP$_x$ block, resulting in a large increase in hydrodynamic radius between PMATP$_x$ and PMATP$_y$–PTHF$_x$. In GPC, molecular weight is related to retention time on the column, which is itself related to hydrodynamic radius. When the hydrodynamic radius of an analyte in a given solvent is different from that of the polystyrene standards, the molecular weights so determined are only approximate.

DSC analysis of PBATP$_y$–PTHF$_x$ and PMATP$_y$–PTHF$_x$ showed distinct thermal transitions for the PATP and PTHF blocks, indicating that the blocks are immiscible and phase separate in the solid state. PBATP$_{105}$–PTHF$_{1300}$, for example, exhibited a $T_g$ of $-70$ °C and a $T_m$ of $40$ °C due to the PTHF$_{1300}$ block and a $T_g$ of $-16$ °C due to the PBATP$_{105}$ block. PMATP$_y$–PTHF$_x$ similarly, exhibited independent thermal transitions for the PTHF block. PBATP$_{135}$–PTHF$_{4925}$, the emission decay can be fitted to a sum of two exponential terms. The mean decay lifetime we calculate, $\langle \tau \rangle = 6.9 \mu$s is, however, the same as the unquenched decay lifetime in PBATP$_y$. The platinum porphyrin dyes in the absence of oxygen, in contrast, do show exponential decays of their phosphorescence intensity in various PATP$_y$ matrices. For PTOEP, we find simple exponential decays in both PBATP$_y$ and PMATP$_y$–PTHF$_x$ with lifetimes of 103 and 96 μs, respectively, while the lifetime in freshly

Figure 1. 200 MHz $^1$H NMR spectra (in CDCl$_3$) of (A) a mechanical blend of PBATP$_y$ and PTHF$_{1810}$ and (B) the product isolated from precipitation into hexanes, PTHF$_{1810}$.

Figure 2. 200 MHz $^1$H NMR spectra (in CDCl$_3$) of (A) PBATP$_{135}$–PTHF$_{4925}$ and (B) the product isolated from precipitation into hexanes.

annealed PTHF is slightly shorter at 92 μs. These lifetimes were found to be dependent on film age for both PBATPy−PTHFy and PTHFx. The emission lifetime in a PTHFx film aged 10 days drops to 86 μs, and to 75 μs in a film aged 30 days. In a PBATPy−PTHFy film aged 3 days, the observed PtOEP emission lifetime was 94 μs. Another example of this sensitivity of τ to a dye’s environment concerns the value τ0 = 79 μs reported for PtOEP−PBATPy in our initial publication on the system. Upon revisiting this system, it was shown that the shorter lifetime was due to small amounts of residual solvent left in the samples (which were dried in air at room temperature). In the experiments reported herein, all samples were initially air-dried and subsequently heated under vacuum to drive off all solvent. This accounts for the discrepancy between the data reported herein and those reported in ref 15.

Evaluation of the Block Copolymers PBATPy−PTHFy

The parameters B, D0x, S0x, and P0x were determined for the PBATPy−PTHFy block copolymers by measuring the phosphorescence as a function of time, as outlined in the Experimental Section. The time-scan luminescence intensity profiles for PtOEP in PBATPy−PTHFy are given in Figure 3. Curve a shows the rapid quenching which occurs when the nitrogen-equilibrated film is suddenly exposed to 1 atm of air, and curve b shows the much slower growth in intensity when the air-equilibrated film is exposed to nitrogen. The data from these experiments is fitted to eq 5, using the magnitude of D0x as the fitting parameter. The parameter B is determined independently from the ratio of the luminescence intensities in the presence of nitrogen and air at equilibrium.

In this way we find D0x = 9.80 × 10−6 cm2s−1 for the oxygen sorption measurement and D0x = 9.85 × 10−6 cm2s−1 for the desorption measurement. This experiment was carried out 1 h after removing the sample from the annealing oven. Films of PBATPy−PTHFy however, become noticeably hazy on standing, and sample age affects the results. The average D0x value obtained from 12 measurements on three film samples (all aged ~1 h) was D0x = (10.9 ± 0.6) × 10−6 cm2s−1. Substituting D0x and B into eq 4, a value of S0x = 0.8 ± 0.1 × 10−4 M·atm−1 is calculated.

When films of PBATPy−PTHFy containing PtOEP are examined within 1 h or so of annealing, they give plots strongly resembling those in Figure 3. The simulated and experimental data overlap, and the D0x values from the sorption and desorption experiments agree to better than 5%. For three films, values of B = 23.0 ± 1.0 and D0x = (1.55 ± 0.07) × 10−6 cm2s−1 were obtained, from which a value of S0x = (10.2 ± 0.5) × 10−4 M·atm−1 is calculated. We draw the initial conclusion that the oxygen diffusion coefficient for PBATPy−PTHFy is a factor of 7 lower than that for PBATPy−PTHFy.

This difference in D0x values is very important. Examining the desorption curves in Figures 3 and 4, we see that O2 desorption in PBATPy−PTHFy requires ~10 s to increase the PtOEP emission intensity to half its final value in a film 0.092 mm thick. In PBATPy−PTHFy, this requires nearly 20 s in a film only 0.058 mm thick. Note that film thicknesses in these experiments were chosen arbitrarily to provide sorption times sufficiently long for data collection. The larger D0x value for PBATPy−PTHFy is offset by a lower value for B compared to PBATPy−PTHFy (12.0 vs 23.0, see Table 1). Since the unquenched lifetimes of

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**Figure 3.** Plot of the luminescent intensity of PtOEP (100 ppm) in a film of copolymer PBATPy−PTHFy (L = 0.092 mm) on glass as a function of time. Curve a (D0x = 9.80 × 10−6 cm2s−1) is obtained from an oxygen sorption experiment, curve b (D0x = 9.85 × 10−6 cm2s−1) from an oxygen desorption experiment. The insets are plots of residuals (Iexp − Ith) vs time for data collection. The larger D0x values in PBATPy−PTHFy are due to short film age, and sample age affects the results. The average D0x value obtained from 12 measurements on three film samples (all aged ~1 h) was D0x = (10.9 ± 0.6) × 10−6 cm2s−1. Substituting D0x and B into eq 4, a value of S0x = 0.8 ± 0.1 × 10−4 M·atm−1 is calculated.

**Figure 4.** Plot of the luminescent intensity of PtOEP (100 ppm) in a film of copolymer PBATPy−PTHFy (L = 0.058 mm) on glass as a function of time. Curve a (D0x = 1.6 × 10−6 cm2s−1) is obtained from a freshly annealed film, curve b (D0x = 1.0 × 10−6 cm2s−1) from a film aged 3 days. The inset plots show the difference in D0x values is very important. Examining the desorption curves in Figures 3 and 4, we see that O2 desorption in PBATPy−PTHFy requires ~10 s to increase the PtOEP emission intensity to half its final value in a film 0.092 mm thick. In PBATPy−PTHFy, this requires nearly 20 s in a film only 0.058 mm thick. Note that film thicknesses in these experiments were chosen arbitrarily to provide sorption times sufficiently long for data collection. The larger D0x value for PBATPy−PTHFy is offset by a lower value for B compared to PBATPy−PTHFy (12.0 vs 23.0, see Table 1). Since the unquenched lifetimes of
PtOEP are very similar in the two films, the higher B value for PBATP_{135}–PTHF_{4925} means that its lower O_2 diffusion is accompanied by a much higher oxygen solubility! Thus, we see S_{O_2} = 0.8 \times 10^{-4} \text{ M} \cdot \text{atm}^{-1} for PBATP_{705}–PTHF_{1300} and S_{O_2} = 10.2 \times 10^{-4} \text{ M} \cdot \text{atm}^{-1} for PBATP_{135}–PTHF_{4925}. The overall permeability of oxygen (P_{O_2}) in the two polymers, however, differs by only a factor of 2 (Table 1).

The aging effects of PBATP_{135}–PTHF_{4925} were examined in greater detail, since the large proportion of PTHF makes them much more significant than those observed for PBATP_{705}–PTHF_{1300}. Films of PBATP_{135}–PTHF_{4925} are initially clear upon removal from the annealing oven but become hazy and eventually turbid as the PTHF_{4925} phase crystallizes. Time-scan experiments were performed after allowing the samples to age in the dark for 3 days at room temperature. The dye lifetime was found to be essentially unchanged, but the value of B had decreased from 23.0 to 17.4. The time-scan experiments (see Figure 4b) showed evidence for a distribution of diffusion coefficients in the system.

For example, if a film is allowed to age for 3 days in the dark, the best fit to the midpoints of the sorption and desorption curves, we find D_{O_2} = (1.01 \pm 0.03) \times 10^{-4} \text{ cm}^2 \text{s}^{-1}. The values of S_{O_2} and P_{O_2} obtained from this experiment are given in Table 1. In an attempt to appreciate the breadth of the distribution of D values, the early and late parts of the desorption experiment were fitted separately. Intensity profiles that fit the early and late time data were generated, and although they appear very different, the D_{O_2} values differ by only ~20%.

The time-scan experiments on PBATP_{135}–PTHF_{4925} were repeated using [Ru(dpp)_3]Cl_2 as the dye. For the samples measured ~1 h after annealing, B = 1.05 \pm 0.03 and similar values of D_{O_2} are obtained from the sorption and desorption experiments. For three films, an average value of D_{O_2} = (2.6 \pm 0.7) \times 10^{-6} \text{ cm}^2 \text{s}^{-1} was obtained. This is ~70% larger than the value determined with PtOEP. From the B value, using \rho^2 = (\rho^2) = 6.9 \mu s, S_{O_2} = (3.7 \pm 0.9) \times 10^{-4} \text{ M} \cdot \text{atm}^{-1}. The nonexponential decay of the ruthenium dye, however, introduces uncertainty into the calculation of the oxygen solubility. Nevertheless, it appears that [Ru(dpp)_3]Cl_2 senses an environment in this copolymer with a lower oxygen solubility and somewhat higher oxygen diffusivity than does PtOEP.

After the films were allowed to age for 3 days in the dark, the time-scan experiments were repeated. These are now very turbid films, but while deviations from a perfect fit of the data to eq 5 were found, they were less pronounced than those with PtOEP. The B value (B = 1.00 \pm 0.02) remained identical to that for the fresh film, and the best fit D_{O_2} values for the sorption and desorption experiments were very similar, yielding D_{O_2} = (1.4 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}. With the ruthenium dye, the effect of aging was a decrease of ~50% in D_{O_2}, compared to ~35% for PtOEP.

**Evaluation of PTHF, Homopolymer.** To understand the aging effects seen for the block copolymers, the aging of PTHF was investigated. Time-scan luminescence intensity profiles for PtOEP in PTHF are presented in Figure 5. Figure 5a shows the data for a polymer film 1 h after removal from the annealing oven. At this point in time, the film is relatively clear, since little crystallization of the polymer has occurred. The D_{O_2} values obtained from the time-scan experiments were very similar and resulted (for a series of experiments) in a value of D_{O_2} = (3.2 \pm 0.9) \times 10^{-6} \text{ cm}^2 \text{s}^{-1}. From the B value (33.5 \pm 0.9), using \rho^2 = 92.
of the percentage of PTHF, the blends exhibit a quenching sensibilities similar to that of PTHF itself.

Unlike the blends, the block copolymer matrixes show quenching sensibilities closer to that of PBATPy than to PTHF (see Table 4). For example, PBATP_{705}–PTHF_{2740} has a QS (0.56) within experimental error of that of PBATPy. Polymers PBATP_{280}–PTHF_{2740} and PBATP_{135}–PTHF_{4925} have QS values (0.50 and 0.47, respectively) somewhat smaller than (but again within experimental error of) that of PBATPy. Overall, the PTHF block length appears to have a slight effect on QS. The data currently available, however, are insufficient to quantify this effect.

The polymer PBATP_{135}–PTHF_{4925} was chosen for the dye concentration and photostability experiments due to its desirable physical attributes (see Discussion). If QS were found to be sensitive to the concentration of dye dispersed in the matrix, this would indicate the formation of dye aggregates, which are fluorescent but have luminescent lifetimes different from that of isolated dye molecules. Such behavior is observed in silicone-based resins, and results in curvature of the SV plots (and thus variation in the values of QS). Experiments using [Ru(dpp)_3]Cl_2 concentrations varying from 500 to 2500 ppm all resulted in linear plots with QS values independent of dye concentration (see Table 5).

There is, thus, no evidence for association of the ruthenium dye in the block copolymer matrixes for this range of dye concentrations. While this experiment is not definitive, it does point to miscibility at the molecular level of the dye in the block copolymer matrix.

Photostability of this dye–matrix combination was evaluated by continuously illuminating the sample and collecting data at a number of times. These data show that emission intensities measured over a 2 h interval do not decrease significantly (see Table 2), indicating that the dye molecules are not significantly photobleached on this time scale. To verify that the sensor matrix does not degrade, QS was determined three times during 4 h of

### Table 3. Quenching Sensitivity (QS) of PBATPy/PTHFx Blends as a Function of Blend Composition

<table>
<thead>
<tr>
<th>wt %PBATP_{635}</th>
<th>wt %PTHFx</th>
<th>QS</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>0.520 ± 0.039</td>
</tr>
<tr>
<td>75</td>
<td>25</td>
<td>0.353 ± 0.038</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>0.365 ± 0.031</td>
</tr>
<tr>
<td>25</td>
<td>75</td>
<td>0.365 ± 0.032</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0.370 ± 0.029</td>
</tr>
</tbody>
</table>

* PBATP_{635}, M_w = 3.69 × 10^5, PDI = 1.8. † PTHF, M_w = 8.14 × 10^6, PDI = 1.6.

### Table 4. Quenching Sensitivity (QS) of [Ru(dpp)_3]Cl_2 in the Copolymers PBATPy–PTHFx as a Function of the Degree of Polymerization of PTHF

<table>
<thead>
<tr>
<th>polymer</th>
<th>M_w (PDI)</th>
<th>QS</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBATP_{635}</td>
<td>3.69 × 10^5 (1.8)</td>
<td>0.519 ± 0.031</td>
</tr>
<tr>
<td>PBATP_{130}–PTHF_{1300}</td>
<td>3.05 × 10^5 (1.9)</td>
<td>0.556 ± 0.029</td>
</tr>
<tr>
<td>PBATP_{280}–PTHF_{2740}</td>
<td>2.61 × 10^5 (1.5)</td>
<td>0.470 ± 0.031</td>
</tr>
<tr>
<td>PBATP_{135}–PTHF_{4925}</td>
<td>2.36 × 10^5 (1.9)</td>
<td>0.495 ± 0.033 *</td>
</tr>
</tbody>
</table>

* The standard deviation in six separate experiments of this sample was found to be 0.495 ± 0.007.
Table 5. Quenching Sensitivity ($Q_S$) of [Ru(dpp)$_3$]Cl$_2$ in PBAT$_{135}$–PTHF$_{4925}$ as a Function of Dye Concentration

<table>
<thead>
<tr>
<th>dye concn (ppm)</th>
<th>$Q_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>0.486 ± 0.033</td>
</tr>
<tr>
<td>1000</td>
<td>0.495 ± 0.029</td>
</tr>
<tr>
<td>1500</td>
<td>0.494 ± 0.026</td>
</tr>
<tr>
<td>2000</td>
<td>0.488 ± 0.031</td>
</tr>
<tr>
<td>2500</td>
<td>0.482 ± 0.034</td>
</tr>
</tbody>
</table>

Table 6. Quenching Sensitivity ($Q_S$) of [Ru(dpp)$_3$]Cl$_2$ in PBAT$_{135}$–PTHF$_{4925}$ as a Function of Time

<table>
<thead>
<tr>
<th>time (h)</th>
<th>$Q_S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.491 ± 0.033</td>
</tr>
<tr>
<td>3</td>
<td>0.486 ± 0.027</td>
</tr>
<tr>
<td>4</td>
<td>0.486 ± 0.024</td>
</tr>
</tbody>
</table>

constant illumination. The SV plots remained linear, and the $Q_S$ values were unaffected within experimental error (see Table 6).

DISCUSSION

Films of PBAT$_x$ have high oxygen permeability, and this polymer is effective at dissolving a number of dyes with long luminescence lifetimes. These are very desirable properties for a PSP matrix material. Unfortunately PBAT$_x$ films are soft and tacky. PTHF$_x$ also has high oxygen permeability, but it is a crystalline polymer that forms brittle films. As the polymer crystallizes, its permeability to oxygen decreases, as does the rate of diffusion of oxygen in the polymer. When these polymers are joined into a block copolymer, one can obtain films with synergistic properties. The block copolymer forms free-standing films that are not tacky and have reasonable mechanical properties. In addition, we find that the block copolymer films have oxygen permeabilities close to those of PBAT$_x$, even in polymers in which the PTHF$_x$ block is much longer than the PBAT$_x$ block.

DSC analysis of the block copolymers in the bulk state revealed thermal transitions corresponding to those of the individual components. This type of behavior is common to block copolymers in which the two blocks are immiscible and form separate microphases in the solid state. If the two polymers were miscible, one would observe a glass transition at a temperature intermediate between those of the two components. One of the transitions found in the block copolymer films is a melting transition of the PTHF$_x$ block. The crystalline domains are the likely source of the mechanical rigidity of the block copolymer films and their surface hardness. Nevertheless, the slow crystallization of these blocks leads to time-dependent gas permeability for the block copolymers. Freshly prepared films are clear. As these films age, they become turbid or hazy, whereas films of PBAT$_x$ remain transparent. As the weight fraction of PTHF$_x$ in the block copolymers is increased, the mechanical characteristics (film rigidity and surface hardness) of the films improve. These are the films with the highest fraction of crystalline polymer, and for films with thicknesses on the order of 0.1–0.3 mm, the most turbid. Fortunately, the oxygen-quenching sensitivity of the matrix, as measured in steady-state Stern–Volmer quenching experiments, is not significantly affected by the block copolymer composition. For this reason, PBAT$_{135}$–PTHF$_{4925}$ (the block copolymer with the highest weight fraction of PTHF$_x$) was chosen as the matrix of choice for the dye concentration and photostability experiments.

Gas permeability (time-scan) experiments were carried out to determine the diffusion coefficients ($D_{O_2}$), solubilities ($S_{O_2}$), and permeabilities ($P_{O_2}$) of oxygen in films of the various polymers. In these experiments, we find that the time scale for the major changes in dye emission intensity for oxygen desorption from the film is much longer than the corresponding time scale for oxygen sorption into the films. Determination of the diffusion coefficients of the films results in sorption and desorption curves in which the time scale of desorption is much longer than that for sorption. This type of difference in response and recovery times has been mentioned many times in the literature about oxygen sensors, and we emphasize here that this behavior is a natural consequence of the oxygen concentration profile generated by diffusion that follows Fick’s laws.

In freshly prepared block copolymer films, the intensity vs time plots fit very well to the shape predicted for Fickian diffusion of oxygen into or out of the films, and the $D_{O_2}$ values obtained from both experiments were very close (within 5–10%). One should not interpret the clarity of these films as an indication of polymer miscibility. Based on our DSC measurements, there is no evidence for polymer miscibility, and strong evidence in favor of microphase separation. Film clarity is simply an indication that the sizes of the microdomains are too small to scatter light. Under these circumstances, we think that it is remarkable that we find such good agreement between the results of the time-scan experiments and the predictions of simple Fick’s law diffusion in the film. The dyes are not covalently bound to the polymer. They are free to partition between the two different microdomains. Oxygen will also partition between the two domains, and its solubility and diffusivity in the two domains should be different. As a consequence, we anticipated a more complex behavior. Both components of the block copolymer are characterized by high oxygen solubilities and oxygen diffusivities (Table 1), but as the Stern–Volmer experiments show, the block copolymers do not behave like a simple blend of the two homopolymers. Despite the high content of PTHF$_x$ in the block copolymers, the quenching sensitivity is more like that of PBAT$_x$, itself than PTHF$_x$.

As the block copolymer films were allowed to age, they became more turbid. When the time-scan experiments on the aged films were repeated, the signal was noticeably noisier than the signal from experiments carried out on the freshly annealed and transparent films. This effect became more marked with film aging. In addition, the individual time-scan plots for the aged films did not fit as well to the model of Fickian diffusion based upon a single diffusion constant. There were two types of differences from the behavior predicted by the model. First, individual intensity vs time plots exhibited deviations from the model curve (faster diffusion at early times; slower diffusion at later times). Second, there were somewhat larger differences in the $D_{O_2}$ values obtained...
from the oxygen sorption experiments compared to the desorption experiments. While these deviations were not very large, they indicate that changes in the properties of the film toward oxygen diffusion and oxygen permeation have taken place.

Despite these problems, it was still possible to estimate $D_{O_2}$ values by choosing the best fit to the model at the midpoint of the time-scan trace. $P_{O_2}$ values could be calculated from the measured values of $B$ and the unquenched lifetime $r^0$. As the data in Table 1 show, aging leads to a decrease in $D_{O_2}$ values, but much smaller changes in $P_{O_2}$ values. For example, with PtOEP in PBATP$_{135}$–PTHF$_{4925}$, $D_{O_2}$ values decreased by $\sim 65\%$ after 3 days aging at room temperature, whereas $P_{O_2}$ decreased by $25\%$. With the ruthenium dye, there was also a decrease in $D_{O_2}$, but hardly any change in $P_{O_2}$. In addition, the $D_{O_2}$ and $P_{O_2}$ values determined with the two dyes were significantly different. Ordinarily, one might expect the gas permeability properties measured to be independent of the probe, but in the block copolymer samples, one has to take account of the possibility that the dyes are distributed differently between the different domains in the system.

While these turbidity effects proved problematic for the determination of $D_{O_2}$ values, they seemed not to be a problem in the much thinner films employed for sensor applications. In sensor applications, thin films are desired to provide response times as short as possible. Much thicker films were used in the time-scan experiments to allow sufficiently long data acquisition times.

In closing, we would like to note two unusual features of our data that remain difficult to explain. First, the $D_{O_2}$ value of PBATP$_{705}$–PTHF$_{1300}$ determined with PtOEP was found to be almost 1 order of magnitude larger than that of PBATP$_{135}$–PTHF$_{4925}$. The latter polymer had a correspondingly higher oxygen solubility ($S_{O_2}$) such that the permeability of oxygen in the two polymers differed by only a factor of 2. Recall that $P_{O_2}$ is calculated via eq 4 from measured values of $B$ and $r^0$, whereas $P_{O_2}$ is calculated directly from the shape of the intensity vs time plot in the time-scan experiments. There was excellent reproducibility in both sets of experiments.

The second curious result is found in the comparison of the time-scan and Stern–Volmer plots. Although the $B$ value of PtOEP in PBATP$_{705}$–PTHF$_{1300}$ is only half that of PBATP$_{135}$–PTHF$_{4925}$ (for freshly prepared samples), the $Q_S$ value of [Ru(dppe)$_2$]Cl$_2$ in the former polymer (0.56) is larger than that of the latter polymer (0.47). Since $Q_S = B/(1 + B)$, this would not appear to be reasonable. These experiments involve different dyes, and unfortunately, there was not enough of the PBATP$_{705}$–PTHF$_{1300}$ material to carry out time-scan experiments with both dyes. As a consequence, we are not able to compare $B$ values and $Q_S$ values for the same dye. Nevertheless, this change in behavior is unexpected. We ascribe this occurrence both to aging effects in PBATP$_{135}$–PTHF$_{4925}$, which are much more dramatic than in PBATP$_{705}$–PTHF$_{1300}$, and to the possibility that the dyes occupy different sites in the copolymers. While we cannot definitively address this issue, it is worth noting that the blend experiments may tend to suggest that [Ru(dppe)$_2$]Cl$_2$ is preferentially solvated in the PTHF$_x$ domains. This would account for the quenching sensitivity values being similar to those in PTHF$_x$ even when PATP is the dominant component of the blend. The effect of the PTHF$_x$ block length on the magnitude of $Q_S$ is not, however, fully understood.

**SUMMARY**

We have prepared PATP$_y$–PTHF$_x$ block copolymers and examined their properties as matrices for dyes whose excited states serve as oxygen sensors. PtOEP exhibits an exponential decay in PBATP$_x$, PBATP$_{705}$–PTHF$_{1300}$, and PBATP$_{135}$–PTHF$_{4925}$ and was used to determine the coefficients of oxygen diffusion and oxygen solubility in the matrices. These experiments established that $D_{O_2}$ values determined for the block copolymers decreased as a function of time following removal of the films from the oven, where they had been annealed above the melting temperature of the PTHF$_x$ block. For films of PBATP$_{135}$–PTHF$_{4925}$ with similar thermal histories, but containing different phosphorescent dyes, we calculate somewhat higher $D_{O_2}$ values and lower $Q_S$ values for [Ru(dppe)$_2$]Cl$_2$ than for PtOEP.

The block copolymers PBATP$_y$–PTHF$_x$ with [Ru(dppe)$_2$]Cl$_2$ as the dye have excellent properties for air pressure sensor applications. They exhibit good quenching sensitivity and linear Stern–Volmer-like plots when the emission intensity is determined at different air pressures. Further, the block copolymers form freestanding films with much better mechanical properties (i.e., nontacky films) than PATP$_x$ and have $Q_S$ values for [Ru(dppe)$_2$]Cl$_2$ much higher than those in PATP$_y$–PTHF$_x$ blends. Work aimed at using these and related polymers for specific sensor applications is currently underway.

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