

Oxygen Sensors Based on Quenching of Tris-(4,7-diphenyl-1,10-phenanthroline)ruthenium(II) in Fluorinated Polymers

Amy M. Morin,¹ Wenying Xu,¹ J. N. Demas,^{1,3} and B. A. DeGraff²

Received May 20, 1999; accepted August 24, 1999

Luminescence quenching of Ru(II) complexes by oxygen has proved a powerful method of quantitative oxygen analysis. It has become clear that the polymer support for the sensor molecule plays a pivotal role in the sensor performance. The current work is devoted to understanding how the physical and photophysical properties of a sensor respond to changes in polymer composition. An oxygen quenching study was conducted on [Ru(Ph₂phen)₃]Cl₂ (Ph₂phen=4,7-diphenyl-1,10-phenanthroline), in copolymer supports consisting of GP-163 (a polydimethylsiloxane (PDMS) with varying amounts of pendant acrylate groups) combined with a number of alkyl methacrylates with long chain alkyl or fluorinated alkyl esters. Increasing the chain length or the degree of fluorination on the hydrocarbon chains enhances performance. However, there is an optimal chain length for the fluorinated hydrocarbons for sensitivity, linearity, and physical properties. Too long a chain yields reduced quenching sensitivity and yields cloudy polymers. All systems showed some degree of heterogeneity as indicated by nonlinear Stern-Volmer quenching plots, but their intensity quenching data could be successfully fit with a two-site model.

KEY WORDS: Oxygen sensor; luminescence, ruthenium; fluorinated polymer.

INTRODUCTION

The design and application of molecular sensors based on luminescence quenching is an area of great interest [1–12]. In particular, highly luminescent transition metal complexes (TMCs) are receiving increasing attention as sensors and molecular probes. Analyte specificity and sensitivity can be achieved by altering either the polymer matrix support or the luminescent sensor

molecule. Much work has been done on varying the metal complexes where the sensor behavior is relatively well understood. However, the effect of the polymer support on sensor performance can play a critical role, and yet there is no good foundation for predicting *a priori* the effect of polymer type and composition on behavior. While models have been proposed, there is still no rational basis for even reasonably accurate prediction of trends, although in many cases gross features are explained [13].

In addition to the obvious function of anchoring and protecting the sensor (e.g., coated fiber optic sensor), the polymer can be a significant factor in controlling availability of the analyte to the reporter. The support must allow easy access of the analyte to the sensor, protect the sensor from competitive species, provide a compatible microenvironment for good luminescence properties, and exhibit good mechanical properties.

¹ Department of Chemistry, University of Virginia, Charlottesville, Virginia 22904.

² Department of Chemistry, James Madison University, Harrisonburg, Virginia 22807.

³ To whom correspondence should be addressed. e-mail: demas@virginia.edu

The goals of the current study are to systematically investigate the effect of variations in polymer structure with two types of components in order to delineate their effects on oxygen sensing performance of TMC sensors. We have been interested in oxygen sensors and have found that polydimethylsiloxanes facilitate good sensor response. However, these systems can be improved in terms of sensor compatibility, mechanical properties (e.g., reduced tackiness and greater hardness and rigidity), and more linear responses. To this end we have started with a polydimethylsiloxane polymer support containing polar acrylate regions (GP-163), which we have used previously [2]. This polymer contains both a polydimethylsiloxane (PDMS) region that allows facile oxygen transport and quenching and a polar region that allows solubilization of the polar metal complexes. Starting with this basic polymer we altered the composition by incorporating variable chain length fluorinated and unfluorinated alkyl methacrylate comonomers. The long chain hydrocarbons should decrease the polymer glass transition temperature (T_g) and enhance quenching. Fluorocarbons tend to have high oxygen solubility and good diffusion, and thus long chained fluorinated species should enhance quenching. Polymerized GP-163 is a soft elastomer. We hoped that the other comonomer components could be used to enhance structural integrity and reduce tackiness, a desirable feature in reducing sensor fouling. Figure 1 shows the structures of the macro monomer, Gp-163, and all the comonomers used. In the current work we examine oxygen quenching of $[\text{Ru}(\text{Ph}_2\text{phen})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ ($\text{Ph}_2\text{phen} = 4,7\text{-diphenyl-1,10-phenanthroline}$). This complex demonstrates a high response for oxygen quenching.

EXPERIMENTAL

Fluorinated Copolymer Preparation. Various polymers were synthesized by varying the weight percentage of comonomer with GP-163 (Genese Polymer, Inc., Flint, MI) (abbreviations used are given in Fig. 1) using either 2,2'-azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO) from PolyScience (Warrington, PA) and Aldrich (Milwaukee, WI), respectively, as the radical chain initiator. The macro monomer GP-163 has the acrylate side chains randomly distributed. 3FEMA, 7FBMA, 15FOMA and OMA were obtained from PolyScience, Inc. MMA and EMA were from Aldrich.

We provide a generic polymer synthesis, which was used for both homo and copolymer syntheses. The initiator (0.3 wt% of the total weight of the components) was dissolved in the appropriate macromonomer or comonomer

and mixed well with any additional components. For more viscous mixtures, 30 minutes was allowed for expulsion of air bubbles before putting the mixture in a Teflon mold. Film thickness was controlled by using different thickness Teflon inserts. All polymerizations were completed in a nitrogen atmosphere. Typical reactions took 16–20 hours at 70°C with AIBN initiator, and 16–20 hours at 85–90°C with BPO initiator. The films were subsequently washed with methylene chloride and then hexane in order to remove excess initiator or impurities. The copolymers were then dried slowly.

The 3FEMA homopolymer was more difficult to synthesize. It was prepared as above except that the reaction vessel was sealed under nitrogen. AIBN initiator was used. The temperature sequence was 55°C for 1 hour and then 65°C for the remaining 6–7 hours. The polymer was then dissolved in a small amount of chloroform, and precipitated in methanol.

For the GP-163 copolymers, the Ru(II) complex was introduced by swelling with a CH_2Cl_2 solution of the complex as described earlier [1,2]. Homopolymer sensor films were prepared by dissolving the complex (50 μM) and polymer in methylene chloride. The solution was then slowly evaporated to give a viscous solution that was cast in Teflon molds.

All sensor films were examined under a microscope to ensure structural homogeneity, absence of microcrystallization, and uniform ruthenium distribution. The films were also examined under a black light for nonuniformities.

Luminescence Measurements. Luminescence intensity measurements were made on a Spex (Edison, NJ) Fluorolog 2 + 2 Spectrofluorometer using 450 nm excitation. Intensities were measured under various oxygen or air pressures in an evacuable cell.

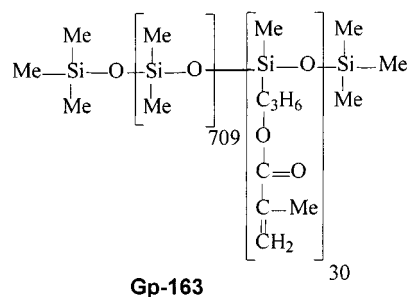
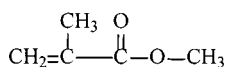
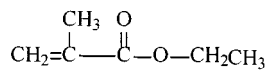
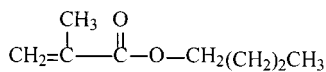
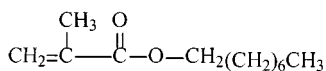
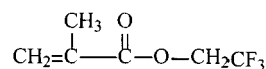
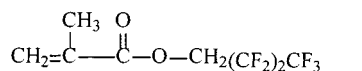
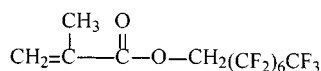
As a simple measure of oxygen quenching, we report S 's given by

$$S = I_0/I_{\text{oxygen}} - 1 \quad (1)$$

where I_0 is the unquenched intensity under nitrogen and I_{oxygen} is the intensity at 1 atm of pure oxygen. An unquenched sample would have $S = 0$. Sensitivities on a sample were typically reproducible to better than 5%. Where multiple polymer films were tested, reproducibility was *ca.* $\pm 10\%$.

Figure 2 shows a typical set of Stern-Volmer curves as a function of percent comonomer. The solid lines are the best fits using the two-site model (*vide infra*).

Data Fitting. All of the Stern-Volmer quenching plots (I_0/I versus oxygen pressure) exhibited varying degrees of nonlinearity (downward curvature). This non-

POLYMER BACKBONE**COMONOMERS****NON-FLUORINATED**Methyl methacrylate
(MMA)Ethyl methacrylate
(EMA)n-Butyl methacrylate
(BMA)n-Octyl methacrylate
(OMA)**FLUORINATED**2,2,2-Trifluoroethyl methacrylate
(3FEMA)1H,1H-Heptafluorobutyl methacrylate
(7FBMA)1H,1H-Pentadecafluorooctyl methacrylate
(15FOMA)**Fig. 1.** Structures of Gp-163 macromonomer and comonomers.

linearity is characteristic of polymer supported sensors, and we have used a two-site model to successfully fit such data [14]. This two site quenching model was used to fit experimental data using a modified Stern-Volmer equation:

$$\frac{I_0}{I} = \frac{I}{\frac{f_1}{1 + K_{sv1}[\text{O}_2]} + \frac{f_2}{1 + K_{sv2}[\text{O}_2]}} \quad (2)$$

where K_{sv1} and K_{sv2} are Stern-Volmer quenching constants, f_1 and f_2 represent the fraction of each of the two sites contributing to the unquenched intensity, and I_0 and I are intensities under vacuum and at various oxygen pressures, respectively. Data fitting was by nonlinear least squares using PSI-Plot (Salt Lake City, UT).

In all cases the two-site model gives excellent fits to the experimental data. However, this should not be construed to mean that there are only two sites in these

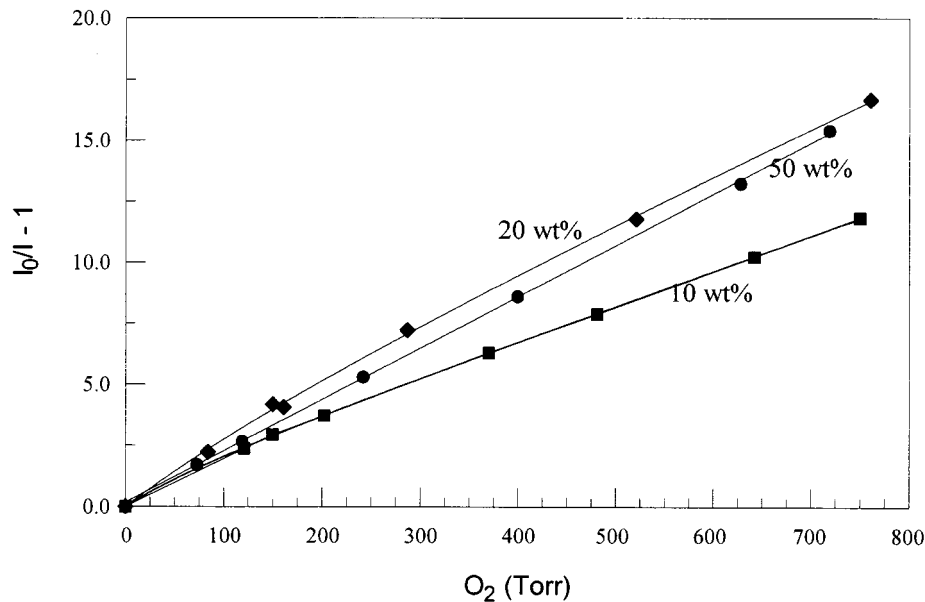


Fig. 2. Stern-Volmer plots for polymers with different percentages of 7FBMA (indicated by each curve). The solid lines are the best fits from the model of eq. 2.

systems. As we have shown earlier the two-site model can accurately approximate a variety of multi-site or continuum models [15]. However, that does not detract from its utility for generating sensor calibration curves.

In addition to the sensitivity parameter, we also report a linearity parameter, L , for the Stern-Volmer plots:

$$L = \left(\frac{I_o}{I_{\text{oxygen}}} - 1 \right) / \left(\frac{1}{0.21} \right) \left(\frac{I_o}{I_{\text{air}}} - 1 \right) \quad (3)$$

where I_{air} is the intensity at one atmosphere of air and the other I_s are defined earlier. The $1/0.21$ is the ratio of the oxygen pressure in pure oxygen to air. L_s were typically good to better than $\pm 5\%$ except for values close to 1.0 where $\pm 10\%$ is more realistic.

Rather than base our L_s on two points, we fit the complete data set to the two-site model, and then calculate L from the predicted response at 0.21 and 1 atm of oxygen. This gives a more reliable L based on the shape of the entire curve rather than just two points. An L of 1 is perfectly linear while an L of 0.21 shows no change in quenching between 0.21 and 1.0 atm of oxygen. From an analytical standpoint, $L = 1$ is ideal, but this is not generally realizable with polymer supported samples.

RESULTS AND DISCUSSION

Our goals of being able to alter physical and quenching properties while maintaining solubility of the complex

were successfully realized. The inclusion of a polar acrylate in the comonomer components provides enough polarity to solubilize the Ru(II) complex while altering the physical/photophysical properties of the polymers.

In terms of physical properties, poly-GP-163 is a transparent elastomer. Poly-OMA was a gooey liquid, presumably because of the low T_g . Even up to 50% comonomer, the copolymers were still elastomers although with decreasing elasticity at the higher percentages. Where we could obtain them, the remaining pure polymers were rigid. Addition of short chain acrylates (e.g., MMA and EMA) stiffens the polymer and at 100% produces brittle polymers with little quenching.

At higher loading the longer chain fluorinated copolymers become cloudy. The cloudiness is probably attributable to the appearance of domains with different refractive indices. The highest percentages shown are for samples that were clear or only slightly cloudy, but still transparent enough to make reliable measurements.

Polymer flexibility seems to be determined mainly by chain length rather than level of fluorination. For example, 10 wt% of 15FOMA and OMA had similar flexibilities and were much more flexible than comparable 3FEMA and EMA mixtures. This is probably just the consequence of intramolecular plasticization.

We had expected several trends in the luminescence quenching. First, since longer hydrocarbon chains decrease T_g and increase segmental motion, we expected better transport and quenching as the chain length

increased for an homologous series. Second, since fluorinated hydrocarbons have high oxygen permeability and solubility [16], we anticipated that the fluorinated systems would show better quenching properties than similar hydrocarbon systems. Finally, in accordance with our earlier work, we expected that there would be monotonic changes in quenching properties with increasing fraction of the comonomer.

In Fig. 3 we show S as a function of the amount and chemical composition of the comonomer components. There are large changes in sensitivity with the amount and nature of the additive.

Our expectations were largely realized. Figure 3 shows roughly monotonic changes with increasing percentage of the comonomer. While in no case did the hydrocarbon comonomer systems yield performance even equal to that of pure GP-163, increasing the chain length of the hydrocarbon enhanced sensitivity relative to shorter chain hydrocarbons. Also, except for MMA, 10–20% of the comonomer additive yielded limiting behavior. As expected, the fluorocarbon systems were all superior in response to their analogous hydrocarbon counterparts. Finally, the fluorinated systems appeared to respond more rapidly due to greater oxygen solubility and diffusion.

However, in contrast to expectations, there was not a monotonic increase in sensitivity for increasing chain length in the fluorocarbon systems. The 7FBMA and 15FOMA were clearly superior to the 3FEMA, but at higher percentages the 15FOMA was distinctly inferior in sensitivity to the 7FBMA. A plausible interpretation is that the longer hydrophobic chains on the 15FOMA produce larger hydrophobic regions, which are less com-

patible with the metal complex, and this forces the complex into the acrylate regions, which are less conducive to quenching. This interpretation is consistent with the sample optical properties. The 15FOMA shows domain separation at lower percentages than the 7FBMA.

We turn now to the linearity. An L of 0.8 is reasonably linear. An L of 0.7 shows serious nonlinearity, and $L = 0.64$ (5% MMA) is so nonlinear as to be of doubtful utility as a sensor.

For pure GP-163, L is a distinctly nonlinear 0.74. With hydrocarbon comonomers, L tends to degrade further with increasing percentage of comonomer. With the fluorinated comonomers, linearity improves with increasing comonomer percentage. With 7FBMA, linearity improves to a value of 1.0 at 50% 7FBMA (see Fig. 2).

CONCLUSION

Fluorinated comonomers are shown to be useful components in the polymer matrix for altering physical and quenching properties. These effects depend on both the type and amount of comonomer added. Structural characteristics, such as crosslinker chain length and rigidity, play a large part in the increased sensor response obtained for fluorinated copolymers. Longer chains on the ester generally help quenching, but for hydrocarbons the film quality can become unacceptable, and for fluorinated hydrocarbons performance actually degrades with longer chains. GP-163 copolymers with 7FBMA appear to be the optimum in terms of sensitivity, linearity and clarity. An additional advantage of the copolymers is that they are less tacky than GP-163 or high percentage PDMS polymers. This feature would be an advantage in pressure sensitive paints used in wind tunnels where sticky surfaces lead to model fouling.

These systems never achieve the sensitivity of some nearly pure PDMS polymers. This is not always a fault. For use at high oxygen pressures, one does not want too high a sensitivity or there will be little emission intensity at the higher pressures.

ACKNOWLEDGMENTS

The authors wish to thank the National Science Foundation (CHE 97-26999, 94-19074, and REU CHE-93-22225).

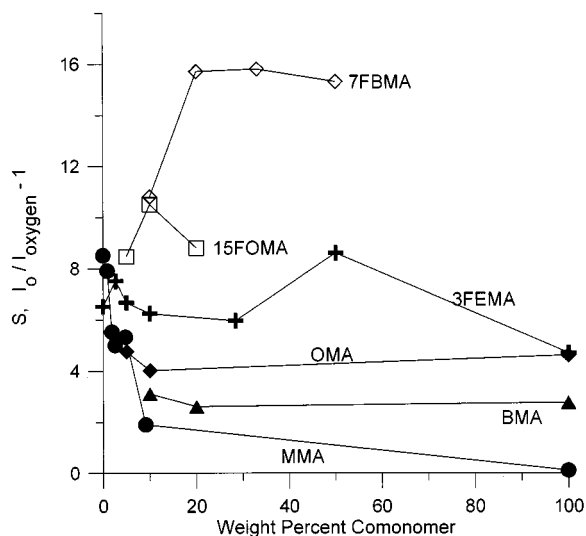


Fig. 3. Comparison of the quenching effects with fluorinated and unfluorinated copolymers.

REFERENCES

1. W.-Y. Xu, R. C. MacDonough, III, B. Langsdorf, J. N. Demas, and B. A. DeGraff (1994) *Anal. Chem.* **66**, 4133–4141.
2. W.-Y. Xu, J. N. Demas, and B. A. DeGraff (1994) *SPIE* **2131**, 417–425.
3. C. Preininger, I. Klimant, and O. S. Wolfbeis (1994) *Anal. Chem.* **66**, 1841–1846.
4. J. N. Demas and B. A. DeGraff (1993) *Sensors Actuators B* **11**, 35–41.
5. J. R. Bacon and J. N. Demas (1987) *Anal. Chem.* **59**, 2780–2785.
6. M. E. Cox and B. Dunn (1986) *J. Polym. Sci. A Polym. Chem.* **24**, 621–636.
7. M. E. Cox and B. Dunn (1986) *J. Polym. Sci. A Polym. Chem.* **24**, 2395–2400.
8. E. R. Carraway, J. N. Demas, and B. A. DeGraff (1991) *Anal. Chem.* **63**, 332–336.
9. J. N. Demas, B. A. DeGraff, and W.-Y. Xu (1995) *Anal. Chem.* **67**, 1377–1380.
10. E. R. Carraway, J. N. Demas, B. A. DeGraff, and J. R. Bacon (1991) *Anal. Chem.* **63**, 337–342.
11. J. N. Demas and B. A. DeGraff (1991) *Anal. Chem.* **63**, 829A–837A.
12. O. S. Wolfbeis, I. Klimant, T. Werner, C. Huber, U. Kosch, C. Krause, G. Neuraüter, and A. Durkop (1998) *Sens. Actuat. B* **51**, 17–24.
13. A. Mills (1998) *Sens. Actuat. B* **51**, 66–76.
14. E. R. Carraway, J. N. Demas, B. A. DeGraff, and J. R. Bacon (1991) *Anal. Chem.* **63**, 337–342.
15. J. N. Demas and B. A. DeGraff (1992) *SPIE* **1681**, 2–11.
16. A. H. M'Hamed, G. Serratrice, S. Marie-Jose, and J.-J. Dulpuech (1981) *J. Am. Chem. Soc.* **103**, 3733–3738.