Acknowledgment. This work was supported by an operating grant to M.D.H. from NSERC (Canada) and a summer scholarship to C.J.N. from Alberta Heritage Foundation for Medical Research. We thank Prof. J. M. McBride for providing unpublished unit cell parameters for the peroxides and Prof. M. C. Etter for helpful discussions.

Registry No. 1, 131276-33-0; 2, 22584-02-7; 3, 131276-32-9; $NC(CH_2)_6CN$/urea, 131276-34-1; $NC(CH_2)_8CN$/urea, 131276-35-2; $NC(CH_2)_{10}CN$/urea, 25681-95-2.

Supplementary Material Available: Tables of bond distances, bond angles, torsional angles, weighted least-squares planes, hydrogen atom coordinates with *U*'s, and anisotropic and equivalent Gaussian parameters (6 pages); tables of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

Organometallic Compounds as Luminescent Probes in the Curing of Epoxy Resins

Thomas G. Kotch and Alistair J. Lees*

Department of Chemistry
University Center at Binghamton
State University of New York
Binghamton, New York 13902-6000

Stephen J. Fuerniss and Kostas I. Papathomas

Systems Technology Division, IBM Corporation
Endicott, New York 13760

Received October 2, 1990
Revised Manuscript Received December 7, 1990

Epoxy resins possess many attractive features desirable in various electronic applications, such as adhesives, matrix resins for dielectrics, encapsulants, and protective coatings.[1] In all of these applications the polymer undergoes chemical and physical changes throughout the process in forming the final product; these changes have been monitored by a number of physicochemical methods in order to provide a better understanding of the cure process.[2] In contrast to these techniques, a number of reports have described the use of various fluorescent probes to monitor changes in matrix viscosity during thermal cross-linking or photo-cross-linking reactions.[3] Indeed, as early as 1956 Oster and Nishijima characterized a fluorescent probe sensitive to the rigidity of a polymer into which it is incorporated; they concluded that auramine O undergoes internal quenching when the two phenylene residues lose their coplanarity in the excited state and that an increase in the medium rigidity hinders this quenching mechanism.[3d] Furthermore, several studies have specifically addressed the importance of fluorescence techniques to monitor (in situ) the cross-linking reactions of epoxies.[3e,4] The fluorescence measurements reported in these studies relate to either measurements of fluorescence depolarization, excimer fluoresence or fluorescence quenching of the probing molecule due to the increase in the viscosity of the medium.

The present study deals with an entirely new approach to this problem. We demonstrate here that a series of transition-metal complexes with the general formula *fac*-$XRe(CO)_3L$ [X = Cl, Br, I; L = 1,10-phenathroline (phen), 4,7-diphenyl-1,10-phenanthroline (Ph_2-phen), 4-methyl-1,10-phenanthroline (Me-phen), and 4,4′-dimethyl-2,2′-bipyridine (Me_2-bpy)] readily exhibit luminescence in an epoxide/anhydride system and that this luminescence varies greatly as the resin is heated and cured. These organometallic compounds possess a number of properties that facilitate utilizing them as spectroscopic probes to monitor polymerization reactions.

Complexes of the type *fac*-$XRe(CO)_3L$ have been previously found to be strongly emissive both in room-temperature fluid solution and as a low-temperature glassy solution at 77 K. These emissions are associated with a lowest lying metal-to-ligand charge-transfer (MLCT) excited state in which electronic transitions take place from a metal-centered molecular orbital to a ligand-localized π^* orbital.[5] The luminescence characteristics of these *fac*-$XRe(CO)_3L$ complexes are particularly sensitive to solvent changes and environmental rigidity; specifically, a more intense, longer lived, and substantially blue-shifted emission is observed when these solutions become frozen. This effect has been referred to as "luminescence rigidochromism"[5a,6] and is understood to arise from the variations that take place in the interaction of the polar excited molecular species with the local dipoles in the surrounding medium.[7] In this study we make use of this effect, not in the context of solution freezing, but to monitor the changes that take place in the matrix during the curing process of a model cycloaliphatic diepoxide resin.

fac-$XRe(CO)_3L$ compounds were synthesized by refluxing $XRe(CO)_5$ with the appropriate ligand in benzene according to a procedure described previously.[7b] The model epoxide/anhydride system was prepared by combining 50 g of (3,4-epoxycyclohexyl)methyl 3,4-epoxycyclohexanecarboxylate (Union Carbide ERL-4221) with 50 g of *cis*-cyclohexanedicarboxylic anhydride. To this mixture was added 0.5 g of benzyldimethylamine, 1.0 g of ethylene glycol, and 0.004 g of the *fac*-$XRe(CO)_3L$ probe material. This formulation was placed in a 30 mm × 30 mm × 1 mm reaction cell constructed of a silicone rubber gasket sandwiched between two glass microscope slides. The epoxide was heated in an oven maintained at 120 °C; the curing temperature was carefully monitored by utilizing a recording thermocouple. Emission spectra were collected on a SLM Instruments Model 8000/8000S spectrometer that incorporates a red-sensitive Hamamatsu R928 photomultiplier and photon counting detection capabilities. Spectra were obtained by orienting the reaction cell at an angle of 20° to the incident light. Emission lifetimes were recorded on a PRA System 3000 time-correlated pulsed single-photon counting apparatus in an identical configuration.

---

(1) *Epoxy Resins Chemistry and Technology*; May, C. A., Tanaka, Y., Eds.; Marcel Decker: New York, 1973.

(2) Enns, J. B.; Gillham, J. K. *J. Appl. Polym. Sci.* **1983,** *28,* 2567 and references therein.

(3) (a) Loufty, R. O. *Macromolecules* **1980,** *14,* 270. (b) Wang, F. W.; Lowry, R. E.; Grant, W. H. *Polymer* **1984,** *25,* 690. (c) Scarlata, S. F.; Ors, J. A. *Polym. Commun.* **1986,** *27,* 41. (d) Oster, G.; Nishijima, Y. *J. Am. Chem. Soc.* **1956,** *78,* 1581. (e) Oster, G.; Nishijima, Y. In *Newer Methods of Polymer Characterization*; Ke, B., Ed.; Wiley-Interscience: New York, 1964; p 207.

(4) (a) Levy, R. L. *Polym. Mater. Sci. Eng.* **1984,** *50,* 124. (b) Sung, C. S. P.; Chin, I. J.; Yu, W. C. *Macromolecules* **1985,** *18,* 1510. (c) Wang, F. W.; Lowry, R. E.; Fanconi, B. M. *Polym. Mater. Sci. Eng.* **1985,** *53,* 180.

(5) (a) Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1974,** *96,* 998. (b) Giordano, P. J.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979,** *101,* 2888.

(6) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978,** *100,* 2257.

(7) (a) Lees, A. J. *Chem. Rev.* **1987,** *87,* 711. (b) Salman, O. A.; Drickamer, N. G. *J. Chem. Phys.* **1982,** *77,* 3337. (c) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1989,** *28,* 85. (d) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* **1989,** *28,* 2154. (d) Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* **1989,** *111,* 6602. (f) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990,** *29,* 3866.

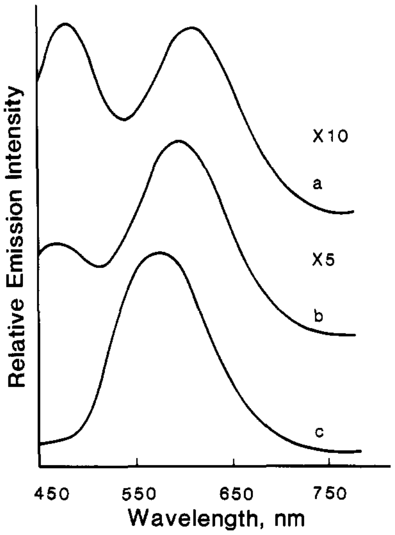

Figure 1. Emission spectra of 2×10^{-4} M *fac*-ClRe(CO)$_3$(Ph$_2$-phen) in a model epoxy/anhydride (ERL-4221) system at 20 °C: (a) before curing; (b) partially cured by heating at 120 °C for 30 min; (c) cured by heating at 120 °C for 60 min. The excitation wavelength is 400 nm. The emission spectra are uncorrected for wavelength variations in photomultiplier tube response; spectral intensities of a and b have been scaled ×10 and ×5, respectively.

Table I. Emission Maxima of the MLCT Bands from 2×10^{-4} M *fac*-XRe(CO)$_3$L Compounds in Deoxygenated Methylene Chloride and a Model Epoxy/Anhydride (ERL-4221) System at 20 °C[a]

	λ, nm			
compound	CH$_2$Cl$_2$	epoxy uncured	epoxy cured[b]	ΔE,[c] cm^{-1}
fac-ClRe(CO)$_3$(phen)	591	592	543	1524
fac-ClRe(CO)$_3$(Me-phen)	587	575	543	1025
fac-ClRe(CO)$_3$(Ph$_2$-phen)	598	610	556	1592
fac-IRe(CO)$_3$(Ph$_2$-phen)	602	608	581	764
fac-BrRe(CO)$_3$(Me$_2$-bpy)	587	585	534	1633

[a] Emission spectra are uncorrected for wavelength variations in photomultiplier response; the excitation wavelength is 400 nm. [b] Cured by heating at 120 °C for 180 min; the observed emission intensity is approximately 10-fold greater than for the uncured sample. [c] Energy difference between observed emission bands of organometallic probes in uncured and cured epoxy samples.

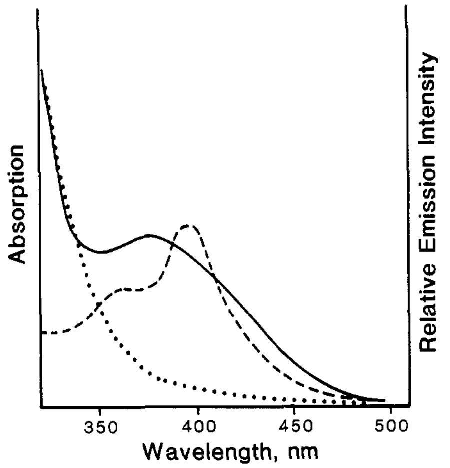

Figure 2. Absorption (—) and excitation (- - -) spectra of 2×10^{-4} M *fac*-ClRe(CO)$_3$(Ph$_2$-phen) in a model uncured epoxy/anhydride (ERL-4221) system at 20 °C. The excitation spectrum was recorded while light was monitored at 610 nm. The absorption spectrum (···) of the uncured epoxy/anhydride mixture without the organometallic probe is also depicted.

Figure 1 illustrates emission spectra recorded from *fac*-ClRe(CO)$_3$(Ph$_2$-phen) during three stages of the curing process. These spectra are representative of the *fac*-XRe(CO)$_3$L series; results obtained from the other compounds are summarized in Table I. In each case it is evident that the epoxy/probe mixture gives rise to dual emission features. The relative intensity of the higher energy band diminishes substantially upon curing. Furthermore, this emission band is still observable from samples that exclude the *fac*-XRe(CO)$_3$L material, and its energy position varies concomitantly with changes in the excitation wavelength; it is, therefore, attributed to the epoxide material itself.[8] In contrast, the lower energy emission band is observable only when the organometallic probe is incorporated in the resin and is clearly associated with the MLCT phosphorescence of *fac*-XRe(CO)$_3$L.[5,7a] Its energy maximum was not found to be excitation-wavelength dependent, consistent with this assignment. Excitation spectra recorded while detecting light at the lowest energy emission maximum of the probe/resin material further confirm that the emission originates from the organometallic compound's lowest lying MLCT absorption features (see Figure 2).[9] Our results indicate that the organometallic *fac*-XRe(CO)$_3$L probe emissions are, in the uncured epoxy mixture, only slightly shifted from those observed in deoxygenated CH$_2$Cl$_2$ solution but shift up to 1633 cm^{-1} when the epoxide material undergoes curing (see Table I). Moreover, it is striking that the MLCT emission intensity increases approximately 10-fold when the epoxy system is cured (see Figure 1), whereas the intensities of the *fac*-XRe(CO)$_3$L emission in uncured resin and CH$_2$Cl$_2$ solution are approximately equal. These changes are attributed to the substantial reduction in the competing nonradiative deactivation mechanisms of the MLCT emitting state as the resin polymerizes and hardens. Emission lifetimes obtained from *fac*-ClRe(CO)$_3$(Ph$_2$-phen) of the uncured and fully cured epoxy systems are 280 ns and 4.1 μs, respectively, further reflecting these matrix changes.

In this paper we have illustrated that the luminescence characteristics of these transition-metal organometallic species are useful for monitoring the curing of epoxy resins. However, these compounds have a number of key properties that may enable them to be used as probes in a wider range of polymer applications. These features include their solubility and thermal stability in nonpolar organic media, their intense absorptions that extend into the visible region, and their low-energy excited-state levels that are measurably luminescent in the red region of the spectrum. Another important aspect is that via the appropriate choice of the ligand system the MLCT emission band of these materials can be tuned in energy throughout a wide range of visible wavelengths. This last possibility allows one to design highly sensitive in situ probes of polymer mobility with absorption and emission features that do not interfere with the spectroscopic properties of a prepolymer/polymer mixture.

---

(8) This emission band apparently consists of both fluorescence and a scattering function from the epoxide/anhydride mixture or to impurity emissions; in uncured and cured epoxy samples without the organometallic compound present, the emission was observed to be centered at 427 (λ_{ex} = 360 nm), 447 (λ_{ex} = 380 nm), 462 (λ_{ex} = 400 nm), and 480 nm (λ_{ex} = 420 nm).

(9) The disparity between the MLCT absorption envelope and the recorded excitation spectrum may be associated with the photophysical deactivation mechanisms that are taking place. This is currently being further investigated.

Chem. Mater. **1991**, *3*, 27–29

Acknowledgment. We gratefully acknowledge the IBM Corp. for support of this research. We also thank Union Carbide for providing the ERL-4221 epoxy resin samples.

Structures and Properties of New Zeolite X-Type Zincophosphate and Beryllophosphate Molecular Sieves

William T. A. Harrison,[†] Thurman E. Gier,[†]
Kelly L. Moran,[†] Jacqueline M. Nicol,[‡]
Hellmut Eckert,[†] and Galen D. Stucky*,[†]

Department of Chemistry, University of California
Santa Barbara, California 93106-0001
Reactor Radiation Division
National Institute of Standards and Technology
Gaithersburg, Maryland 20899 and
University of Maryland
College Park, Maryland 20742

Received October 10, 1990
Revised Manuscript Received December 17, 1990

The solid-state chemistry of non-aluminosilicate molecular sieves has recently undergone a renaissance, following the discovery of a number of aluminophosphate (AlPO)[1] and new gallosilicate (GaSiO)[2] phases a few years ago. Recently, several beryllophosphate (BePO)[3,4] materials have been reported. Some of these AlPOs, GaSiOs, and BePOs are isostructures of known aluminosilicates, while others are new framework topologies. We have recently prepared a number of zeolitic zincophosphates (ZnPOs), zincoarsenates (ZnAsOs), and berylloarsenates (BeAsOs) for the first time, extending the variety of framework compositions still further. In particular, the hypothetical beryllium/zinc phosphate/arsenate "framework" formula $((Be/Zn)O_2(P/As)O_2)^-$ is electronically equivalent with the aluminosilicate framework $(AlO_2SiO_2)^-$, as found in zeolites with a Si:Al ratio of 1:1. In this paper, we report the structures of new beryllophosphate (BePO–X) and zincophosphate (ZnPO–X) phases that are analogues of the industrially important zeolite-X framework. Their formulas are $Na_{96}(BePO_4)_{96}\cdot 192H_2O$ and $Na_{67}TMA_{12}Zn_8(ZnPO_4)_{96}\cdot 192H_2O$ (TMA = tetramethylammonium cation), respectively. Zeolite-X and zeolite-Y are synthetic isostructures of the mineral faujasite and have been widely studied by diffraction and other techniques, especially with respect to cation-exchange and molecular absorption properties.[5,6] Faujasite-type phases contain one of the largest pore openings of any known zeolite (ca. 8 Å) and are of industrial importance for petroleum cracking and other reactions.[7]

Table I. Final Atomic Coordinates for BePO–X (Cubic, Space Group $Fd\bar{3}$, a = 23.368 (2) Å)

atom	x	y	z	occ[a]	$100U_{iso}$
Be(1)	−0.0525 (6)	0.1247 (7)	0.0357 (6)		1.1 (2)
P(1)	−0.0547 (8)	0.0370 (8)	0.1226 (10)		1.1 (2)
O(1)	−0.1071 (6)	0.0071 (6)	0.1043 (6)		1.1 (2)
O(2)	−0.0066 (6)	−0.0013 (6)	0.1477 (4)		1.1 (2)
O(3)	−0.0279 (4)	0.0687 (7)	0.0694 (7)		1.1 (2)
O(4)	−0.0730 (5)	0.0768 (8)	0.1740 (7)		1.1 (2)
Na(1)	0	0	0	1.08 (7)	2.8 (6)
Na(2)	0.067 (2)	0.067 (2)	0.067 (2)	0.47 (4)	2.8 (6)
Na(3)	0.2442 (6)	0.2442 (6)	0.2442 (6)	1.04 (7)	2.8 (6)

[a] Fractional site occupancy.

Both the sodium BePO-X and sodium/tetramethylammonium ZnPO–X were prepared at ambient conditions, as described elsewhere;[8] for example, ZnPO–X can be synthesized in 30 min at 4 °C. Preliminary X-ray powder diffraction data revealed highly crystalline phases, which could be indexed as face-centered cubic cells with dimensions a = 23.383 (5) Å for BePO–X and a = 25.226 (5) Å for ZnPO–X, suggesting that these phases were related to aluminosilicate zeolite-X (a = ca. 25.03 Å). For ZnPO–X, high-resolution powder X-ray data were collected on a Scintag PAD X diffractometer operating in θ–θ geometry (λ = 1.541 78 Å), between 2θ = 20 and 80° by using 0.02° steps to give 3000 data points. For BePO–X, a 5-g sample was dehydrated under vacuum at 150 °C overnight, and low-temperature powder neutron diffraction data were measured by using the high-resolution, five-detector, powder diffractometer on beam line BT-1, at the National Institute of Standards and Technology (NIST), Gaithersburg, MD. The sample was enclosed in a cylindrical vanadium can, and the data were collected at 10 (1) K, using a neutron wavelength of 1.553 Å between 2θ = 5 and 120°, with a step size of 0.05°. Prior to analysis, the data were corrected for detector effects and collated.

Rietveld profile refinement was carried out with the program GSAS,[9] using the starting framework model of aluminosilicate zeolite-X as determined by Olson from single-crystal X-ray data,[10] in space group $Fd\bar{3}$ (No. 203). Our BePO–X and ZnPO–X models assumed a fully ordered 1:1 distribution of Be/Zn and P over the framework tetrahedra, and strict alternation of Be/Zn and P between adjacent tetrahedra, as would be the case for an X-type zeolite with a 1:1 Si:Al ratio, showing perfect cation alternation. For each phase, the usual profile parameters, including scale factor, detector zero-point correction, background coefficients, the unit-cell parameter and peak shape-width variation terms, and the framework-atom positional and isotropic thermal parameters, were refined. Before any guest species were included in the model, the profile R factor was over 30%. For BePO–X, sodium cations were positioned at the sites found in previous studies of dehydrated faujasite-type materials. For ZnPO–X, extraframework species were progressively located by difference Fourier syntheses and added to the refinement. The largest difference peaks were assigned to the guest sodium cation, and those remaining were assigned to extraframework water molecules. No reasonable geometry corresponding to the tetramethylammonium

---

[†] University of California.

[‡] National Institute of Standards and Techology and University of Maryland.

* Author for correspondence.

(1) Flanigen, E. M.; Lok, B. M.; Patton, R. L.; Wilson, S. T. *New Developments in Zeolite Science and Technology*; Elsevier: Amsterdam, 1986; p 103.

(2) (a) Newsam, J. M.; Vaughan, D. E. W. *New Developments in Zeolite Science and Technology*; Elsevier: Amsterdam, 1986; p 457. (b) Newsam, J. M.; Jacobsen, A. J.; Vaughan, D. E. W. *J. Phys. Chem.* **1986**, *90*, 6858.

(3) Rouse, R. C.; Peakor, D. R.; Merlino, S. *Am. Mineral.* **1989**, *74*, 1195.

(4) Harvey, G.; Meier, W. M. In *Zeolites: Facts, Figure, Future: Studies in Surface Science and Catalysis*; Elsevier: Amsterdam, 1989; Vol 49.

(5) Breck, D. W. *Zeolite Molecular Sieves*; Wiley-Interscience: New York, 1974.

(6) Szostak, R. *Molecular Sieves. Principles of Synthesis and Identification*; Van Nostrand: New York, 1989.

(7) Magee, J. S.; Blazek, J. J. *Zeolite Chemistry and Catalysis*; American Chemical Society: Washington, DC, 1976; p 615.

(8) Gier, T. E.; Stucky, G. D. *Nature (London)*, in press.

(9) Larson, A. C.; Von Dreele, R. B. GSAS *User Guide*; Los Alamos National Laboratory: Los Alamos, NM, 1985–1988.

(10) Olson, D. *J. Phys. Chem.* **1970**, *74*, 2758.

0897-4756/91/2803-0027$02.50/0