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Luminescent Organometallic Complexes as Visible Probes in the Isothermal Curing of Epoxy Resins

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Luminescent transition-metal organometallic complexes are employed as spectroscopic probes in the visible region to monitor the thermal cure of epoxy resin materials. A series of metal carbonyl complexes with the general formula *fac*-$XRe(CO)_3L$ [X = Cl, Br, I and L = 1,10-phenanthroline (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)] have been found to be readily soluble and measurably luminescent in both cycloaliphatic and diglycidyl ether type epoxy resin materials. In each case emission has been recorded between 500 and 750 nm and the obtained excitation spectra indicate that this is associated with the lowest energy metal-to-ligand charge-transfer (MLCT) excited states of these organometallic complexes. Significantly, the MLCT luminescence characteristics vary greatly during the isothermal curing of the epoxy resins; the emission band maximum arises at 575–610 nm in the uncured cycloaliphatic epoxy resin (well removed from any of the epoxide emission features) and when the epoxy resin is cured there is an observed hypsochromic shift of up to 1633 cm^{-1} in the band maximum concurrent with an increase of up to 15-fold in the emission quantum yields and the excited-state lifetimes. The isothermal cure at 393 K of the cycloaliphatic epoxy/anhydride material is monitored by following the blue shift of the organometallic probe's MLCT emission position throughout the cure sequence. These data depict a good correlation with dynamic moduli and complex viscosity measurements obtained during the cure of the resin. Luminescence and complex viscosity measurements have also been obtained from the *fac*-$ClRe(CO)_3(Ph_2\text{-phen})$ complex in the neat cycloaliphatic epoxy resin material as a function of temperature while cooling between 300 and 210 K. It is demonstrated that there is a linear relationship between the observed energy of the probe's MLCT maximum and the complex viscosity (η^*) throughout this temperature range in which η^* changes by approximately 5 orders of magnitude. The room-temperature curing reactions of two diglycidyl ether type epoxy resin curing systems have also been monitored by recording the luminescence of *fac*-$ClRe(CO)_3(Ph_2\text{-phen})$; these experiments demonstrate that the probe luminescence can be effectively used as an in situ technique to follow the isothermal polymerization. Additionally, rheological and dielectric representations of the cure state have been obtained in these room-temperature curing epoxy resin systems and are effectively correlated with the luminescence measurements.

Introduction

Thermosetting polymers such as epoxy resins provide an excellent combination of mechanical and electrical properties and possess a number of useful characteristics such as corrosion resistance, good adhesion, and low cost.[1] These features are desirable in various electronic applications such as electrical moldings, adhesives, matrix resins for dielectrics, encapsulants, and protective coatings.[2] It is of fundamental importance, however, to monitor the chemical and physical changes which accompany the curing of the thermoset. The changes in an epoxy matrix, usually characterized by gelation and vitrification, have been monitored by a number of physical techniques. For example, dynamic mechanical spectrometry, infrared spectroscopy, and gel fraction experiments have been carried out by Enns and Gillham.[3] Furthermore, Brown and Sandreczki have employed nitroxide spin labels and spin probes to investigate the microstructure in the polymer network of an epoxy resin using electron paramagnetic resonance (EPR) spectroscopy.[4]

In addition to these techniques, a number of reports[5] have described the use of various fluorescent or phosphorescent probes to monitor changes in matrix viscosity and morphology during thermal cross-linking or photochemical cross-linking reactions. As early as 1956 Oster and Nishijima characterized a fluorescent probe sensitive to the rigidity of the polymer into which it was incorporated; they concluded that the organic dye, auramine O, undergoes internal quenching when the two phenylene moieties lose their coplanarity in the excited state and that an increase in the rigidity of the medium hinders this quenching mechanism.[6] Indeed, several probe studies make use of the enhanced fluorescence observed in certain organic fluorophores resulting from the elimination of nonradiative decay pathways as the matrix viscosity increases.[7] Sung and Mathisen[8] have characterized the cure of diglycidyl ether of butanediol (DGEB) using *trans*-di-

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(1) Callister, W. D. *Materials Science and Engineering: An Introduction*; John Wiley: New York, 1991.

(2) (a) *Epoxy Resins Chemistry and Technology*; May, C. A., Tanaka, Y., Eds.; Marcel Decker: New York, 1973. (b) *Radiation Curing of Polymers*; Randell, D. R., Ed.; Royal Society of Chemistry: London, 1987. (c) Lee, L. H. *Adhesive Chemistry*; Plenum: New York, 1983.

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

(4) Brown, I. M.; Sandreczki, T. C. *Macromolecules* **1985**, *18*, 2702.

(5) (a) Oster, G.; Nishijima, Y. In *Newer Methods of Polymer Characterization*; Ke, B., Ed.; Wiley-Interscience: New York, 1964; p 207. (b) Winnik, M. A. In *Photophysical and Photochemical Tools in Polymer Science: Conformation, Dynamics, Morphology*; Winnik, M. A., Ed.; D. Reidel: Dordrecht, 1986; p 611. (c) Wang, F. W.; Lowery, R. E.; Pummer, W. J.; Fanconi, B. M.; Wu, E. In *Photophysics of Polymers*; ACS Symposium Series No. 358; Hoyle, C. E.; Torkelson, J. M., Eds.; American Chemical Society: Washington, 1987; p 454.

(6) Oster, G.; Nishijima, Y. *J. Am. Chem. Soc.* **1956**, *78*, 1581.

(7) (a) Loufty, R. O. *Macromolecules* **1980**, *14*, 270. (b) Wang, F. W.; Lowery, R. E.; Grant, W. H. *Polymer* **1984**, *25*, 690. (c) Scarlata, S. F.; Ors, J. A. *Polym. Commun.* **1986**, *27*, 41.

(8) Sung, C. S. P.; Mathisen, R. *Polymer* **1987**, *28*, 941.

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aminostilbene (DAS) as a reactive label. Upon curing, bathochromic shifts were shown to take place in both the ultraviolet absorption and the fluorescence spectra of DAS as the primary amine groups were converted to tertiary amine groups. Concomitant with the bathochromic shift in the fluorescence was an approximate 3-fold increase observed in the emission intensity.

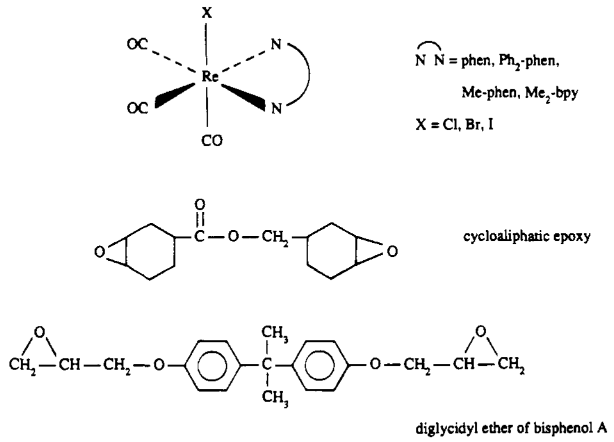
Other studies have addressed the importance of the fluorescence technique to monitor (in situ) the cross-linking reaction of epoxides. The fluorescence techniques reported in these studies relate to measurement of fluorescence depolarization, fluorescence quenching, or excimer fluorescence of the probing molecule due to an increase in the viscosity of the medium.[9]

The current study deals with a new approach to this problem. We present here the results of incorporating a series of transition-metal complexes in an epoxy resin and utilizing their established luminescence properties[10] as probes of polymerization. Luminescent transition-metal complexes, expecially those involving Ru(II) centers have found some use as probes of macromolecular structures;[11] these studies, however, have concentrated on probing biologically important molecules such as DNA. Unfortunately, the ionic character associated with complexes such as $[Ru(bpy)_3]Cl_2$ and $[Ru(phen)_3]Cl_2$ [bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline] usually make them unsuitable for probing relatively nonpolar polymer media due to solubility considerations.

On the other hand, organometallic complexes of the type *fac*-$XRe(CO)_3L$ have been found to be intensely emissive in both room-temperature nonpolar fluid solutions and low-temperature organic glassy solutions at 77 K. The emission is associated with a lowest lying metal-to-ligand charge-transfer (MLCT) excited state in which the electronic transitions take place between a metal-centered $d\pi$-orbital and a ligand localized π^*-orbital.[12] Moreover, the luminescence characteristics of these *fac*-$XRe(CO)_3L$ complexes are particularly sensitive to environmental rigidity, and it is this property that we thought may make them useful as spectroscopic probes in a polymer matrix. Generally, these compounds give rise to a more intense and longer lived emission and a substantial blue shift in the energy of the emission band as the rigidity of the solution increases. This phenomenon is known as the luminescence rigidochromic effect,[10,12,13] and it is thought to result from the interaction of the polar excited species with local dipoles in the surrounding medium.

Complexes which exhibit intense luminescence features that are subject to rigidochromism are of potential value to the study of materials. McKiernan et al. have used *fac*-$ClRe(CO)_3bpy$ [bpy = 2,2′-bipyridine] as a probe for the structural changes occurring in the sol–gel processing of silicon and mixed aluminum–silicon alkoxides.[14] In our own laboratory we have shown that $W(CO)_4L$ and *fac*-$ClRe(CO)_3L$ [L = 1,10-phenanthroline or a substituted phenanthroline] are well suited to study the UV curing of photosensitive polymer systems.[15]

Scheme I



In this investigation we have made use of the luminescence rigidochromism phenomenon to monitor the changes that take place in the polymer matrix during the curing of a model cycloaliphatic diepoxide resin. This report presents a full study, following on our earlier observation,[16] in which we demonstrate that a series of transition-metal complexes with the general formula *fac*-$XRe(CO)_3L$ [X = Cl, Br, I; L = 1,10-phenanthroline (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)] are soluble and readily exhibit luminescence in epoxide/anhydride and diglycidyl ether systems. Importantly, it is found that the luminescence parameters of these compounds vary greatly as the resins are isothermally cured and that these characteristics can be used as visible spectroscopic probes of the epoxy polymerization. Also, we present for the first time a direct correlation between the rigidochromic shift of the organometallic probe and a physicochemical determination of matrix viscosity. The structures of the metal carbonyl complexes and the epoxide resins employed in this study are shown in Scheme I.

Experimental Section

Materials. The parent metal carbonyls $XRe(CO)_5$ (X = Cl, Br, I) were obtained from Pressure Chemical Co. and used without further purification. Ligands were obtained from Aldrich Chemical Co. at >99% purity and used without further purification. The cycloaliphatic resin 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexylcarboxylate (ERL-4221) was supplied by Union Carbide. The diglycidyl ether of bisphenol-A based epoxy resin (DGEBA) was supplied by the Shell Oil Corporation as EPON 828. *N*-Benzyldimethylamine was purchased from Aldrich Chemical Co. and distilled under vacuum before use. Amine-based and polymercaptan-based room-temperature epoxy-hardening agents are commercially available from Devcon Corp. and Loctite Corp., respectively, with exact compositions of a proprietary nature. All solvents used were high-purity photrex grade (Baker Chemical Co.). Neutral alumina (80–200 mesh) used in the chromatographic purifications was obtained from Fisher Scientific Co.

Syntheses. *fac*-$XRe(CO)_3L$ compounds were prepared by refluxing $XRe(CO)_5$ with the appropriate ligand in benzene under

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[9] (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.; Lowery, R. E.; Fanconi, B. M. *Polym.* Mater. *Sci. Eng.* **1985**, *53*, 180.

[10] Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

[11] (a) Kumar, C. V.; Barton, J. K.; Turro, N. J. *J. Am. Chem. Soc.* **1985**, *107*, 5518. (b) Barton, J. K.; Danishefsky, A. T.; Goldberg, J. M. *J. Am. Chem. Soc.* **1984**, *106*, 2172.

[12] (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. (c) Salman, O. A.; Drickamer, H. G. *J. Chem. Phys.* **1982**, *77*, 3337. (d) Sacksteder, L.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335.

[13] (a) Rawlins, K. A.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 2154. (b) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1989**, *28*, 85. (c) Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 6602. (d) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990**, *29*, 3866.

[14] McKiernan, J.; Pouxviel, J. C.; Dunn, B.; Zink, J. I. *J. Phys. Chem.* **1989**, *93*, 2129.

[15] (a) Rawlins, K. A. Ph.D. Dissertation, SUNY-Binghamton, 1990. (b) Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32*, 124.

[16] Kotch, T. G.; Lees, A. J.; Fuerniss, S. J.; Papathomas, K. I. *Chem. Mater.* **1991**, *3*, 25.

nitrogen according to a procedure described previously.[17] All compounds were carefully purified by column chromatography on neutral alumina or by repeated vacuum sublimation to remove unreacted ligand and $XRe(CO)_5$. Infrared spectra recorded from the compounds are in accordance with the literature values.[12,17] The complexes were observed to decompose in air at the following temperatures: *fac*-$ClRe(CO)_3$(phen), 523 K; *fac*-$ClRe(CO)_3$-(Ph_2-phen), 447 K; *fac*-$ClRe(CO)_3$(Me-phen), 523 K; *fac*-BrRe-$(CO)_3$(Me_2-bpy) 488 K; *fac*-$IRe(CO)_3$(Ph_2-phen), 461 K. The model epoxide/anhydride system was prepared by combining 50 g of ERL-4221 with 50 g of *cis*-cyclohexanedicarboxylic anhydride (HHPA). To this mixture was added 0.5 g of *N*-benzyldimethylamine, 1.0 g of ethylene glycol, and the organometallic probe. Typically, 0.004 g of $XRe(CO)_3L$ was dissolved in 50 g of uncured cycloaliphatic epoxide material. Room-temperature curing systems were formulated by mixing the DGEBA:commercial hardener in a 2:1 weight ratio. The organometallic probe was incorporated into the DGEBA prior to combining the epoxy with hardener.

Spectroscopic Measurements. Emission and excitation spectra were recorded on a SLM Instruments Model 8000/8000S dual monochrometer spectrometer; all data were collected at an angle of 90° from the incident light. This apparatus incorporates photon-counting facilities and a red-sensitive Hamamatsu R928 photomultiplier tube. Recorded emission maxima are considered accurate to within 4 nm. Emission quantum yields (ϕ_{em}) were determined from corrected emission spectra using a solution of *fac*-$ClRe(CO)_3$(phen) in deoxygenated CH_2Cl_2 as a calibrant ($\phi_{em} = 0.036$ at 298 K)[12a] and are considered accurate to ±10%. Emission spectra were collected following excitation of a reaction cell containing the epoxide and organometallic probe; this reaction cell consisted of a silicone rubber gasket pressed between two glass microscope slides to yield internal dimension of 30 mm × 30 mm × 1 mm. Spectra were recorded from the epoxy samples with the reaction cell oriented at an angle of 20° with respect to the incident light beam. The epoxide was heated in an oven at 393 K and the emission was monitored periodically during heating; the temperature was carefully monitored throughout curing with a recording thermocouple.

Emission lifetimes (τ_{em}) were recorded on a Photochemical Research Associates (PRA) system 3000 time-correlated pulsed single-photon counting apparatus.[18] Samples were excited at 400 nm with light from a PRA Model 510 nitrogen flash lamp transmitted through an Instruments SA Inc. H-10 monochrometer. Emitted light was detected via a second H-10 monochrometer transmitted onto a thermoelectrically cooled red-sensitive photomultiplier tube. The resulting photon counts were stored on a Tracor Northern Model 7200 microprocessor based multichannel analyzer and the instrument response function was subsequently deconvoluted from the emission data to yield an undisturbed decay that was fitted using PRA software. In each case excellent single-exponential fits were obtained; the reported emission lifetimes represent the average of at least three runs and were found to be reproducible to within 10 ns.

Temperature dependence studies of the luminescence were performed by using an Oxford Instruments Model DN1704K variable-temperature liquid nitrogen cryostat fitted with synthetic sapphire inner windows and quartz outer windows. Sample temperatures were maintained within ±0.2 K by means of an Oxford Instruments Model 3120 controller.

Viscosity data were collected on a Rheometrics System 4 rheometer using dynamic oscillatory parallel plates with a strain of 0.2% and at a frequency of 6.3 radians (1 Hz). The temperature was raised at 3 K/min in the temperature-dependence studies. Dielectric analyses were conducted using a Micromet Eumetric System II microdielectrometer which consists of an interdigitated comb electrode dielectric sensor and the results were obtained over the 10–10 000-Hz range.

Infrared data were collected using an IBM Instruments IR/85 FTIR spectrometer. The consumption of epoxy was monitored by observing the disappearnce of the epoxy ring vibration at 916 cm^{-1}, using the phenyl absorbance at 1609 cm^{-1} as an internal calibrant.[19] The percent epoxy remaining was calculated according to eq 1, where A_t and A_0 are the integrated areas under

$$\%\ \text{epoxy remaining} = 100\left[\frac{A_t A_0(\text{std})}{A_0 A_t(\text{std})}\right] \qquad (1)$$

the epoxy band and A_t(std) and A_0(std) are the areas under the internal standard band at times 0 and *t*, respectively.

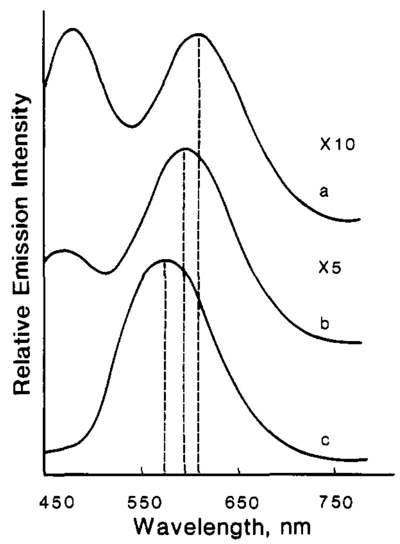

Figure 1. Emission spectra of 2 × 10^{-4} M *fac*-$ClRe(CO)_3$(Ph_2-phen) in a model cycloaliphatic epoxy/anhydride (ERL-4221/HHPA) system at 293 K: (a) before curing; (b) partially cured by heating at 393 K for 30 min; (c) cured by heating at 393 K for 60 min. Excitation wavelength is 400 nm. The emission spectra are uncorrected for wavelength variations in photmultiplier tube response; spectral intensities of a and b have been scaled ×10 and ×5, respectively.

Results

The *fac*-$XRe(CO)_3L$ complexes were found to be readily soluble and both thermally and photochemically stable in a wide range of solvents; these compounds are moderately air stable and no special care was needed in their handling. Once incorporated in the cycloaliphatic epoxide/anhydride or room-temperature curing diglycidyl ether epoxy materials it was determined spectroscopically that they retained their stability and showed no sign of thermal degradation during the cure sequences which were performed as high as 413 K. The complexes were observed to decompose in air at temperatures between 447 and 523 K (see Experimental Section). The electronic absorption and emission spectral features of these organometallic *fac*-$XRe(CO)_3L$ complexes in solution have been studied in detail previously.[12a–c] The complexes all exhibit an intense low-energy metal-to-ligand charge-transfer (MLCT) absorption feature which extends into the visible region and a strong emission feature appearing at much longer visible wavelengths.

Figure 1 illustrates the emission spectra recorded upon 400-nm excitation from *fac*-$ClRe(CO)_3$(Ph_2-phen) during three stages of the isothermal curing process of the model cycloaliphatic epoxide/anhydride system at 393 K. These spectra are representative of the series of *fac*-$XRe(CO)_3L$ complexes studied; data obtained from the other compounds are summarized in Table I. In each case it is evident that the epoxy/organometallic probe mixture gives rise to dual emission features centered at approximately 480 and 600 nm. The relative emission intensity of the

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(17) Abel, E. W.; Wilkinson, G. *J. Chem. Soc.* **1959**, 1501.

(18) O'Connor, D. V.; Phillips, D. *Time Correlated Single-Photon Counting*; Academic: London, 1984.

(19) Jahn, H.; Goetzky, P. In *Epoxy Resins Chemistry and Technology*; May, C. A., Tanaka, Y., Eds.; Marcel Dekker: New York, 1973; p 675.

Table I. Absorption (λ_{abs}) and Emission (λ_{em}) Maxima of the MLCT Bands Observed from 2 × 10^{-4} M *fac*-XRe$(CO)_3$L Compounds in Deoxygenated Methylene Chloride and the Cycloaliphatic Epoxy/Anhydride (ERL-4221/HHPA) System at 293 K[a]

		λ_{em}, nm			
compound	λ_{abs}, nm CH_2Cl_2	CH_2Cl_2	epoxy uncured	epoxy cured[b]	ΔE,[c] cm^{-1}
fac-ClRe$(CO)_3$(phen)	378	591	592	543	1524
fac-ClRe$(CO)_3$-(Me-phen)	372	587	575	543	1025
fac-ClRe$(CO)_3$-(Ph_2-phen)	381	598	610	556	1592
fac-IRe$(CO)_3$-(Ph_2-phen)	410	602	608	581	764
fac-BrRe$(CO)_3$-(Me_2-bpy)	382	587	585	534	1633

[a] Emission spectra are uncorrected for wavelength variations in photomultiplier response; excitation wavelength is 400 nm. [b] Cured by heating at 393 K for 180 min; observed emission intensity is approximately 10-fold greater than uncured sample. [c] Energy difference between observed emission bands of the organometallic probes in uncured and cured epoxy samples.

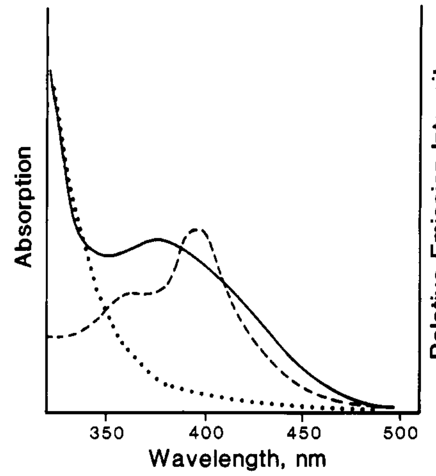

Figure 2. Absorption (—) and excitation (---) spectra of 2× 10^{-4} M *fac*-ClRe$(CO)_3$(Ph_2-phen) in a model uncured cycloaliphatic epoxy/anhydride (ERL-4221/HHPA) system at 293 K. The excitation spectrum was recorded while light was monitored at 610 nm. The absorption spectrum (···) of the uncured epoxy/anhydride (ERL-4221/HHPA) mixture without added organometallic probe is also depicted.

Table II. Photophysical Parameters for Several *fac*-XRe$(CO)_3$L Complexes in the Uncured and Cured Cycloaliphatic Epoxy/Anhydride (ERL-4221/HHPA) System at 293 K[a]

complex		ϕ_{em}[c]	τ_{em}, ns	k_r, s^{-1}	k_{nr}, s^{-1}
fac-ClRe$(CO)_3$-	uncured	0.042	280	1.5×10^5	3.4×10^6
(Ph_2-phen)	cured[b]	0.44	4100	1.1×10^5	1.3×10^5
fac-ClRe$(CO)_3$-	uncured	0.039	306	1.3×10^5	3.1×10^6
(Me-phen)	cured[b]	0.56	2360	2.4×10^5	1.8×10^5
fac-IRe$(CO)_3$-	uncured	0.048	1049	4.6×10^4	9.1×10^5
(Ph_2-phen)	cured[b]	0.56	8100	6.9×10^4	5.4×10^4
fac-BrRe$(CO)_3$-	uncured	0.035	77	4.5×10^5	1.3×10^7
(Me_2-bpy)	cured[b]	0.37	600	6.2×10^5	1.0×10^6

[a] Excitation wavelength is 400 nm. [b] Cured by heating at 393 K for 180 min. [c] Obtained from corrected emission spectra using emission quantum yield of *fac*-ClRe$(CO)_3$(phen) in deoxygenated CH_2Cl_2 as a calibrant (see ref 12a).

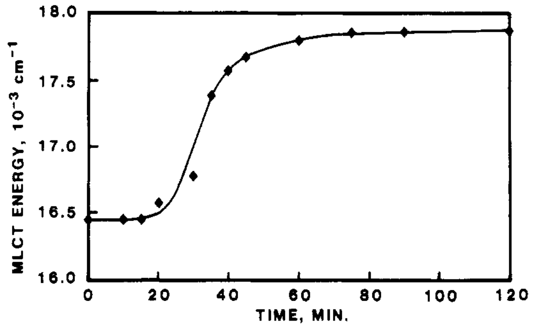

Figure 3. Energy position of the uncorrected MLCT emission band maximum of 2 × 10^{-4} M *fac*-ClRe$(CO)_3$(Ph_2-phen) in the cycloaliphatic epoxy/anhydride (ERL-4221/HHPA) material as a function of time at the isothermal cure temperature of 393 K. Spectra were acquired at 293 K following excitation at 400 nm.

higher energy band was found to diminish substantially upon curing at 393 K for 120 min (see Figure 1). Furthermore, this emission band was still observable from samples which excluded the added luminescent organometallic probe material and the position of it varied with changes in the excitation energy; for the cycloaliphatic epoxy/anhydride mixture alone it was observed to be centered at 427 nm (excitation at 360 nm), 447 nm (excitation at 380 nm), 462 nm (excitation at 400 nm), and 480 nm (excitation at 420 nm). Therefore, it is attributed to the epoxide/anhydride mixture itself and apparently this radiation mainly consists of light scattering from the epoxy resin sample, although a component of it may also be due to fluorescence or to an impurity emission arising from the resin. In contrast, the lower energy band was only observed upon inclusion of the *fac*-XRe$(CO)_3$L probe material and it is attributed to the well recognized MLCT phosphorescence of these and closely related molecules.[10,12,13] Prior to any cure at 393 K the probe emission maximum for *fac*-ClRe$(CO)_3$(Ph_2-phen) is at 610 nm (16 394 cm^{-1}) and when the cure is considered complete (following heating at 393 K for 180 min) the band maximum is substantially blue shifted and is centered at 556 nm (17 986 cm^{-1}). It is also notable that there is an approximately 10-fold increase in the emission intensity of this band throughout the isothermal cure sequence concomitant with the observed blue-shifting of the MLCT emission position.

Figure 2 shows the absorption and excitation spectra obtained from *fac*-ClRe$(CO)_3$(Ph_2-phen) in the uncured cycloaliphatic epoxide/anhydride system. The excitation spectrum was collected while detecting light at the MLCT emission maximum (610 nm) of the organometallic probe; a similar spectrum was, however, obtained from this complex in deoxygenated CH_2Cl_2 solution. A complete listing of the electronic absorption and luminescence bands obtained from all the complexes studied in CH_2Cl_2 solution and the uncured and cured epoxy resin materials is incorporated in Table I. Photophysical parameters were calculated from the emission quantum yield (ϕ_{em}) and lifetime (τ_{em}) values according to eqs 2 and 3. Here, k_r

$$k_r = \phi_{em}/\tau_{em} \tag{2}$$

$$k_{nr} = (1/\tau_{em}) - k_r \tag{3}$$

and k_{nr} are the determined radiative and nonradiative decay constants, respectively; in calculating these rate constants it is explicitly assumed that the emitting state is formed with unit efficiency.[20] Derived rate constants for the series of *fac*-XRe$(CO)_3$L complexes in both the uncured and cured epoxy resins are given in Table II.

As noted above, the position of the MLCT emission maximum of these probe complexes in the cycloaliphatic

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[20] This assumption is made on the basis that the intersystem crossing rates are extremely fast in these heavy atom organometallic systems. See ref 10 for a detailed discussion of this point.

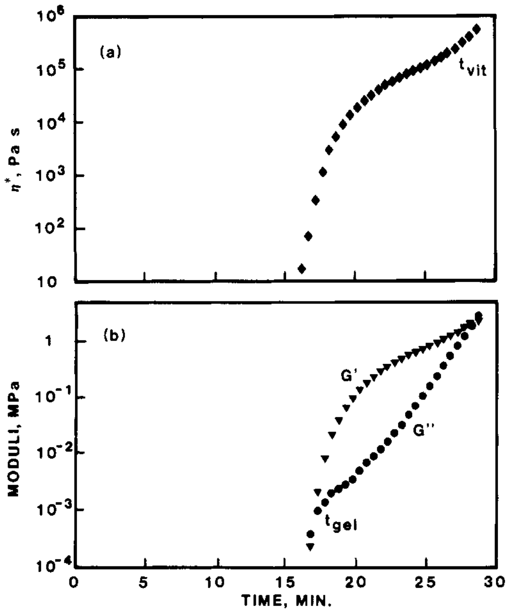

Figure 4. (a) Complex viscosity (η^*) and (b) dynamic moduli (G' and G'') results as a function of time in the cycloaliphatic epoxy/anhydride (ERL-4221/HHPA) material at the isothermal cure temperature of 393 K. Here t_{gel} and t_{vit} denote the times to gelation and vitrification, respectively.

epoxide/anhydride system exhibits a large hypsochromic shift during the cure process. Figure 3 illustrates the behavior of the emission maximum of *fac*-ClRe(CO)$_3$(Ph$_2$-phen) as a function of cure time in the cycloaliphatic epoxy/anhydride system. These results were obtained with an isothermal cure temperature of 393 K and the spectra were obtained by removing the sample from the oven and cooling to room temperature for each reading. It is seen that during the cure the energy of the MLCT maximum sharply increases eventually producing an S-shaped curve with a plateau being reached following about 40–60 min of cure time. Dynamic mechanical analyses have also been performed on these materials in a parallel plate geometry, and the resulting stress amplitude and phase angle were determined and the dynamic moduli (G' and G'') were obtained. From these measurements the complex modulus and hence the complex viscosity were then obtained according to the following relationships (eqs 4 and 5).[21] Here G' is the storage or elastic modulus, G''

$$G^* = [(G')^2 + (G'')^2]^{1/2} \qquad (4)$$

$$\eta^* = G^*/\omega \qquad (5)$$

is the loss modulus, G^* represents the complex modulus, η^* is the complex viscosity, and ω is the angular frequency in rad/s. The dynamic moduli and complex viscosity data are shown in Figure 4 for the isothermal cure of the cycloaliphatic epoxide/anhydride system at 393 K. Here t_{gel} represents the time to gelation based on the dynamic moduli crossover ($G' = G''$).[22]

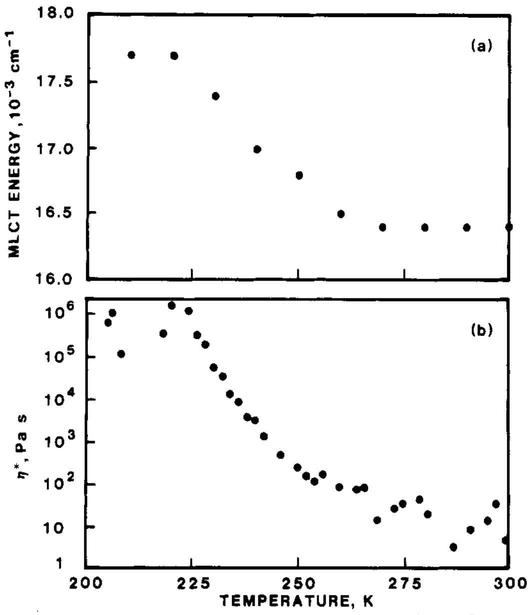

Figure 5. (a) Energy position of the uncorrected MLCT emission band maximum of 2×10^{-4} M *fac*-ClRe(CO)$_3$(Ph$_2$-phen) and (b) complex viscosity (η^*) behavior as a function of temperature in the neat cycloaliphatic epoxy (ERL-4221) material. In (a) the excitation wavelength is 400 nm.

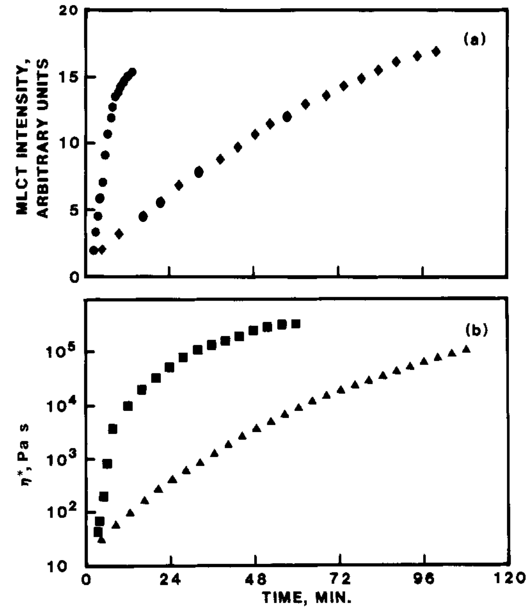

Figure 6. (a) Intensity of the MLCT emission at 600 nm of 2×10^{-4} M *fac*-ClRe(CO)$_3$(Ph$_2$-phen) in the (●) DGEBA/polymercaptan and (◆) DGEBA/amine epoxy materials and (b) complex viscosity (η^*) results from (■) DGEBA/polymercaptan and (▲) DGEBA/amine systems as a function of time at the isothermal cure temperature of 293 K. In (a) the excitation wavelength is 400 nm.

Temperature-dependence studies were carried out on the cycloaliphatic resin with added probe material. The complex *fac*-ClRe(CO)$_3$(Ph$_2$-phen) was incorporated into neat cycloaliphatic epoxy resin material (ERL-4221) and cooled. As the epoxy freezes the emission maximum of the probe blue shifts eventually producing a reversed S-shaped curve (see Figure 5a). Complex viscosity measurements (η^*) made on the resin material as a function of temperature depict a similar relationship (see Figure 5b) and indicate that the viscosity increases approximately 5 orders of magnitude as the solution is cooled from 300 to 210 K.

Figures 6 and 7 depict a series of measurements made on two room-temperature curing epoxy/hardener materials; unlike the earlier results this material facilitated in situ acquisition of the emission spectra, and thus the probe behavior can be readily monitored by recording the emission intensity at a fixed wavelength throughout the cure sequence. Figure 6a shows the changes in luminescence intensity of *fac*-ClRe(CO)$_3$(Ph$_2$-phen) complex in-

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[21] Sherman, P. *Industrial Rheology*; Academic Press: London, 1970; p 24.

[22] (a) Tung, C.-Y. M.; Dynes, P. J. *J. Appl. Polym. Sci.* **1982**, *27*, 569. (b) Winter, H. H.; Chambon, F. J. *Rheology* **1986**, *30*, 367. (c) Heise, M. S.; Martin, G. C.; Gotro, J. T. *Polym. Eng. Sci.* **1990**, *30*, 83.

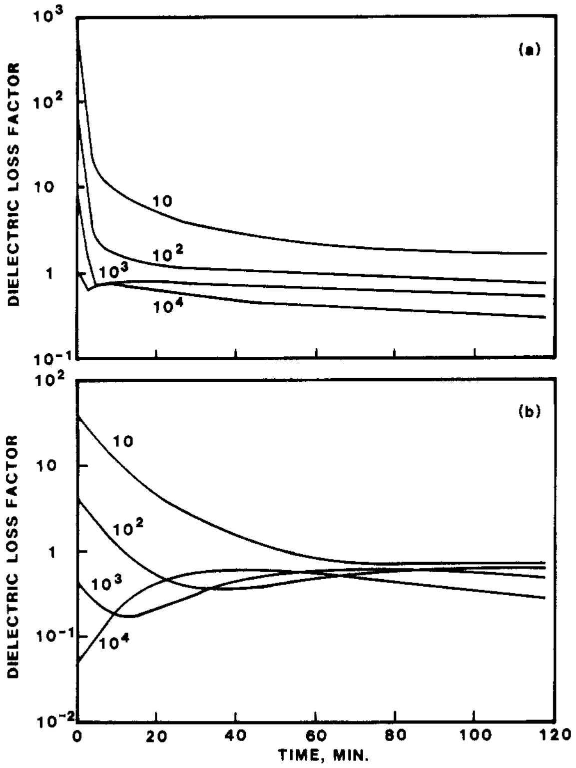

Figure 7. Dielectric loss factor (ϵ'') as a function of cure temperature for (a) DGEBA/polymercaptan and (b) DGEBA/amine epoxy materials. In each case the frequency of measurement (in hertz) is indicated.

corporated in both the DGEBA/polymercaptan and DGEBA/amine epoxy systems. It is evident that the luminescence intensity of the probe increases dramatically in both cases as the thermal cure proceeds. In the case of the "quick setting" polymercaptan-based hardener a sharp rise in the emission intensity is immediately evident at the onset of the reaction. Complex viscosity measurements (η^*) have been obtained throughout this reaction (see Figure 6b) and these results exhibit a parallel trend to that observed in the emission experiment. Similar behaviors in the emission intensity and η^* data have also been observed from the room-temperature DGEBA/amine epoxy system (compare parts a and b of Figure 6). Additionally, the dielectric loss factor has been obtained; this is essentially a measurement of ionic conductivity (σ)[23] in the epoxy material throughout the cure sequence. A relationship can be written between the two quantities:

$$\epsilon'' = \sigma/\omega\epsilon_0 + \epsilon''_{\mathrm{d}} \tag{6}$$

where ϵ'' is the dielectric loss factor, σ is the ionic conductivity, ϵ_0 is the permittivity of a vacuum, ω is the frequency, and ϵ''_{d} is the sum of all dipolar contributions. Chloride ions are present in the DGEBA resin as a result of the synthetic preparation[24] and it is these ions that enable σ to be measured. The conductivity can be expressed according to

$$\sigma = \sum_i N_i q_i \mu_i \tag{7}$$

where N_i is the number of ions present of species i per unit volume, q_i is the charge on each ion, and μ_i is the ionic mobility. In the case of the epoxy material N_i and q_i are constant making σ directly proportional to μ_i. Figure 7 shows ϵ'' plotted as a function of cure time for the two room-temperature resin/hardener systems; it can be observed that the viscosity increases as the ionic mobility decreases, which is consistent with the dynamic rheological results. The energy position of the MLCT maximum for *fac*-ClRe(CO)$_3$(Ph$_2$-phen) was also observed to blue shift from 594 nm in the uncured DGEBA/amine mixture to 568 nm following curing at 293 K for 100 min, corresponding to a hypsochromic energy shift of 711 cm^{-1} during the isothermal cure. This energy shift is somewhat less than that recorded from *fac*-ClRe(CO)$_3$(Ph$_2$-phen) in the high-temperature cycloaliphatic epoxy/anhydride curing system due to the fact that the viscosity changes that take place during the curing of these room-temperature resins are less pronounced (see Figure 6b).

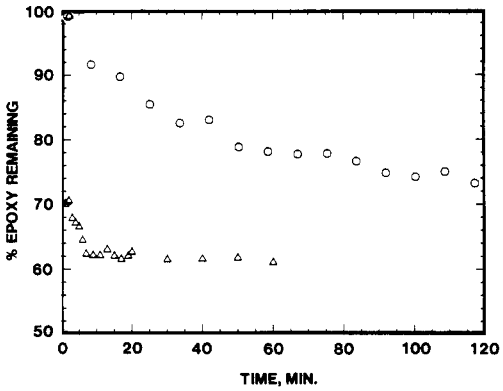

Figure 8. Plot of percent epoxy remaining as a function of cure time from FTIR data for (△) "quick-setting" polymercaptan/DGEBA and (○) amine/DGEBA based epoxy systems as a function of cure time at 293 K.

Figure 8 depicts FTIR spectral data obtained from the two room-temperature curing epoxy systems during the cure sequences. The decrease in the area of the 916-cm^{-1} absorption band reflects the consumption of the epoxy groups during the polymerization reaction. At 293 K it is observed that the consumption of the epoxy groups reaches a plateau after approximately 10 min in the "quick setting" polymercaptan/DGEBA system while the reaction appears much more gradual in the case of the amine-cured epoxy.

Discussion

Assignment of the Organometallic Luminescence. The electronic absorption and emission characteristics of the *fac*-XRe(CO)$_3$L complexes have been the subject of several prior investigations, and the lowest energy absorption maxima in these molecules have been assigned as Re(dπ) to ligand (π^*) charge transfer in nature (MLCT).[12] Likewise, the emission features observed from these complexes in the epoxy resin materials are associated with a lowest lying triplet MLCT excited state. Confirmation of this assignment from the epoxy resin/probe mixture is derived from the excitation spectra recorded from *fac*-ClRe(CO)$_3$(Ph$_2$-phen) in the cycloaliphatic epoxy resin (see Figure 2). Although there is a general agreement in the MLCT solution energies as represented by the recorded absorption and excitation spectra, there is a noticeable disparity between their spectral line shapes. This can be explained by considering the complicated photophysical deactivation pathways that are taking place within the complex itself. Indeed, resonance Raman and magnetic circular dichroism experiments on similar organometallic compounds involving charge-transfer transitions to α,α'-diimine ligands have demonstrated that the MLCT band

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[23] Gotro, J.; Yandrasits, M. *Polym. Eng. Sci.* **1989**, *29*, 287.

[24] (a) Potter, W. G. *Epoxide Resins*; Butterworths: London, 1970; p 9. (b) Lee, H.; Neville, K. *Epoxy Resins*; McGraw-Hill: New York, 1957; p 8.

is comprised of several electronic transitions, including in this particular system the presence of an underlying ligand field (LF) absorption.[25] Thus, varying inefficiencies of the radiative deactivation from one or more of these excited-state levels will result in absorption and excitation spectral line shapes that are noncongruent.

Moreover, the results of recent experiments have suggested that a ligand-to-ligand charge-transfer (LLCT) transition[26] occurs in complexes of this type whereby the LLCT excitation takes place between the halide donor ligand and the π-acceptor phen ligand. Therefore, it seems reasonable to attribute the observed absorption and excitation spectral disparity to the presence of a LLCT band in this region. In the particular *fac*-XRe(CO)$_3$L system studied here the LLCT transition is thought to be nonradiative and able to effectively deactivate to the ground state by radiationless processes. Although the LLCT transition may substantially participate in the molecular photophysics it is not observed in absorption, probably because this feature is obscured by the presence of the intense overlapping MLCT absorption band.

High-Temperature Curing. The emission data of Figures 1 and 3 clearly illustrate the effectiveness of using the luminescence rigidochromic effect to monitor the cure reaction of the cycloaliphatic epoxy/anhydride system. During curing the epoxy resin forms a cross-linked three-dimensional network of increasing molecular weight, and because of this the viscosity is observed to increase by about 5 orders of magnitude, from approximately 10 to almost 10^6 Pa s (see Figure 4a). Likewise, the energy position of the emission bands from each of the probe molecules blue shifts substantially (up to 1633 cm^{-1}; see Table I) when the resin is cured. It is interesting to note that the evolution of the S-shaped curve illustrated by Figure 3 occurs in basically three stages; on heating there is initially no change observed in the MLCT band maximum, this is subsequently followed by a sharp increase in the energy position upon the onset of gelation in the epoxy/anhydride material, and then finally the curve levels out again after vitrification has taken place. The organometallic probe emission as represented by the S-shaped curve of in Figure 3 yields a t_{gel} value of about 18–25 min as indicated by the sharp change in slope of the curve of emission energy versus cure time. This slope subsequently levels off gradually indicating that vitrification occurs around 40–45 min.

Examination of the dynamic moduli curves (see Figure 4b) shows that, at a cure temperature of 393 K, gelation (t_{gel}) occurs at 18 min; this estimate is based on the dynamic moduli crossover ($G' = G''$).[22] Furthermore, vitrification appears to occur at approximately 28 min, basing this estimate on the inflection point of Figure 4a.[27] Thus, there is an apparent discrepancy with respect to the determined cure kinetics between the measurements made using the luminescent probe and those of the dynamic rheological test. This, however, is not unexpected and is attributed to the fact that the viscosity measurements were carried out in situ whereas the samples prepared for emission work were heated for a given amount of time in an oven at 393 K, then removed and quenched to room temperature, and subsequently placed in the spectrometer for measurement. Moreover, it takes a few minutes for the epoxy/probe/anhydride mixture to attain the nominal core temperature of 393 K when initially placed in the oven. Therefore, *in these experiments it is important to recognize* that there is effectively a lag time between obtaining the viscosity and emission data.

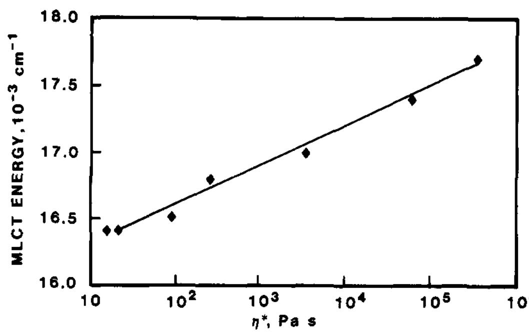

Figure 9. Plot of energy position of the uncorrected MLCT emission band maximum of 2×10^{-4} M *fac*-ClRe(CO)$_3$(Ph$_2$-phen) versus the determined complex viscosity (η^*) values in the neat cycloaliphatic epoxy (ERL-4221) material. Data taken from Figure 5 between 220 and 273 K.

Temperature-Dependence Studies. To elucidate the effect that viscosity has on the energy position of the emission band, the probe molecule, *fac*-ClRe(CO)$_3$(Ph$_2$-phen), was incorporated into a neat ERL-4221 epoxy resin without the addition of anhydride and the emission was monitored as a function of temperature. These results are depicted in Figure 5a. It is evident that when the solution is cooled, the MLCT emission band shows a similar shift toward higher energy as observed in the case of high-temperature curing (compare Figures 3 and 5a). Furthermore, the obtained rheological data demonstrate that the viscosity of the resin material gradually increases until the entire solution forms a frozen glass (see Figure 5b). From these results we have determined that there is a direct correlation that exists between the energy position of the MLCT emission band maximum and the recorded viscosity; a semilog plot of the MLCT band energy position versus the complex viscosity is shown in Figure 9, confirming this relationship. Clearly, as the solvent molecules become more ordered and packed with respect to the probe molecules (i.e., when the solution freezes) the luminescence band of the *fac*-ClRe(CO)$_3$(α,α'-diimine) system is subjected to the rigidochromic effect. This aspect is further discussed below.

Luminescence Data. Emission quantum yields (ϕ_{em}) and lifetimes (τ_{em}) have been obtained for several *fac*-XRe(CO)$_3$L complexes in both the uncured and cured cycloaliphatic epoxy/anhydride samples (see Table II). Typically, both the lifetimes and quantum yields increase approximately by an order of magnitude in going from an uncured state to a cured material. This type of behavior is similar to previous observations made for luminescent organometallic molecules in organic fluid solutions on cooling to their glassy state.[10,12,13] Calculated radiative (k_r) and nonradiative (k_{nr}) rate decay constants are contained within Table II, and it is notable that in each case k_{nr} decreases by at least 10-fold upon curing, whereas k_r is relatively unchanged. This is in good agreement with the observation made by Loufty,[7a] who examined the effect of polymerization of methyl methacrylate on the fluorescence properties of a series of [*p*-(dialkylamino)-benzylidene]malononitriles. In that particular study it was observed that the quantum yields of fluorescence of these fluorophores increased by 2–4 orders of magnitude when embedded in a PMMA matrix. In general, it was found

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(25) (a) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1978**, *28*, 133. (b) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015. (c) Servaas, P. C.; van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.

(26) (a) Volger, A.; Kunkely, H. *Comm. Inorg. Chem.* **1990**, *9*, 201. (b) Stor, G.; Stufkens, D. J.; Oskam, A.; Ninth International Symposium on the Photochemistry and Photophysics of Coordination Compounds; Fribourg, Switzerland, 1991; presentation P-61.

(27) Gotro, J. T., personal communication.

that the nonradative decay rate constant demonstrates an exponential dependence on polymer-free volume; this parameter decreasing as free volume is reduced (and hence ϕ_{em} increases). Thus, although the present study deals with phosphorescence, it does appear to be analogous in that the observed decrease in k_{nr} is a consequence of the microscopic changes in the free volume of the polymer matrix and the subsequent effects on the rotational and vibrational nonradiative deactivation pathways of the probe moiety.

Room-Temperature Curing. The utility of the organometallic probe was again examined in two room-temperature curing formulations. In these experiments there was somewhat less of a hypsochromic shift in the energy of the emission maximum observed from *fac*-$ClRe(CO)_3$-(Ph_2-phen) (711 cm^{-1} in the DGEBA/amine system) because the viscosity changes upon curing in these resins are less pronounced, and while the emission band intensity still increases appreciably (approximately by a factor of 6), this is also less than in the high-temperature cycloaliphatic epoxy system. Monitoring the emission intensity at a constant wavelength as a function of cure time, however, was found to provide a most valuable in situ technique; it can be seen that in both the room-temperature curing systems examined that the change in intensity of the emission band of *fac*-$ClRe(CO)_3(Ph_2$-phen) is most sensitive to the cure reaction (see Figure 6a). In both the quick setting polymercaptan/DGEBA and the amine/DGEBA systems, the intensity of the MLCT emission band is paralleled by the behavior of the complex viscosity, dielectric loss factor, and FTIR results (see Figures 6b, 7, and 8).

It can be seen that the dielectric loss factor curves (see Figure 7) measured at higher frequencies (i.e., 10^3 and 10^4 Hz) exhibit a decay followed by a rise or, indeed, just increase to form a maximum. The initial decay is a result of decreasing ionic mobility caused by the increasing polymer viscosity (see eq 6). At a point where the ionic contribution falls below that of the dipolar contribution the loss factor starts to rise again eventually resulting in a peak.[28] For the purpose of this discussion it is sufficient to compare the relative rates of the decrease in ionic mobility. It is immediately obvious that in the case of the rapidly curing polymercaptan/DGEBA based material the initial rapid decrease in ionic mobility takes place within the first 8–10 min of cure, whereas in the slower curing amine/DGEBA material this decrease is more gradual, taking place over the entire cure sequence. The emission and infrared data also confirm the kinetic behavior of these two epoxy/hardener systems.

Rigidochromism. It has been known for some time that luminescence organometallic complexes exhibiting emission from MLCT excited states exhibit the phenomenon of luminescence rigidochromism in organic solutions.[10,12,13] In general this involves a hypsochromic shifting of the MLCT band energy position coupled with an increase in the emission intensity (because of a higher quantum yield) as the rigidity of the matrix becomes greater with the freezing of the solution, although the underlying reasons for this effect are not fully understood at this time. The emission data recorded from the epoxy resin/probe materials (represented by Figures 1 and 3) taken together with the temperature-dependence data of the solutions (see Figure 5) and the in situ measurements from the room-temperature epoxy systems (depicted in Figure 6) clearly illustrate that increasing viscosity leads to these observed blue shifts of the probe's emission band. This conclusion is considerably reinforced by the direct correlation of the emission energy with the log of the measured viscosity for the neat cycloaliphatic epoxide system (as illustrated in Figure 9).

Consequently, we believe that the "luminescence rigidochromic effect" can be explained in terms of the changing solvent environment (and hence the dipolar interactions) surrounding the organometallic probe species. In the MLCT transition an electron is transferred from a metal-centered Re(dπ) orbital to a ligand-centered π^* orbital, thus producing an excited-state dipole with a finite lifetime. As the solvent becomes more viscous, either as a result of a polymerization reaction (such as an epoxy cure) or through cooling and eventual freezing of the solution, the solvent molecules have an opportunity to interact with the excited state species more closely and hence cause a higher degree of dipole–dipole interaction. Such an effect is analogous to those observed in the emission spectra on moving from a less polar to a more polar solvent environment; in room-temperature fluid solution a number of metal complexes exhibiting MLCT emission have been observed to undergo a substantial blue shifting of their emission energy position as solvent polarity increases.[10,29] Indeed, the environment in a cured epoxy resin is known to be one of the most polar for any polymer system and the solubility parameters are typically quite high (δ = 9.7–10.9 cal/cm^3),[30] reflecting this polarity. Furthermore, it is important to recognize that the dipolar solvent interactions will be enhanced around the metal complex as the epoxy resin matrix forms, because of the decreasing random solvent orientation in the cross-linked matrix. This will effectively reduce the ability of the solvent molecules in rearranging themselves to accommodate the excited-state dipole moment of the probe molecule.

Conclusions

The MLCT luminescence characteristics of a series of *fac*-$Re(CO)_3(\alpha,\alpha'$-diimine) organometallic complexes have enabled us to use these molecules as visible spectroscopic probes in the isothermal cure of cycloaliphatic and diglycidyl ether-type epoxy resin materials. These luminescence parameters have been effectively correlated with rheological, dielectric, and FTIR measurements obtained throughout the curing process. It is demonstrated that the luminescence rigidochromic features of these organometallic compounds provide an in situ measurement of the cure state and relative cure kinetics of several epoxy-based resin materials.

These complexes have a number of key features that lend themselves useful to these types of probe applications. These include their solubility and thermal stability in nonpolar organic media, their intense visible absorptions, and their low-energy excited-state levels that give rise to measurable luminescence in the yellow-red region of the spectrum. Through the appropriate choice of the coordinated ligand it is demonstrated that it is possible to tune the energy position of the MLCT emission band of the compounds to design in situ probes that are useful at different visible wavelengths and which are not affected by the spectroscopic (absorption and emission) properties of the resin. Moreover, the emission features of these

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(28) Day, D. R. In *New Characterization Techniques for Thin Polymer Films*; Tong, H., Nguyen, L. T., Eds.; Wiley-Interscience: New York, 1990; p 14.

(29) (a) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1983**, *22*, 3825. (b) Manuta, D. M.; Lees, A. J. *Inorg. Chem.* **1986**, *25*, 3212. (c) Zulu, M. M.; Lees, A. J. *Inorg. Chem.* **1988**, *27*, 3325.

(30) Salomon, G. In *Adhesion and Adhesives*; Salomon, G.; Houwink, R., Eds.; Elsevier: Amsterdam, 1962; p 17.

organometallic complexes are shown to be sensitive to environmental rigidity over a wide range of viscosity changes.

Acknowledgment. We gratefully acknowledge the IBM Corp. for support of this research. We also thank Union Carbide and Shell Oil Corp. for providing the ERL-4221 and EPON-828 epoxy resin samples, respectively, Dr. J. T. Gotro for helpful discussions and Mr. G. Kohut for technical assistance. T.G.K. thanks the IBM Corp. for receipt of an IBM Graduate Fellowship.

Registry No. *fac*-ClRe(CO)$_3$(phen), 56846-58-3; *fac*-ClRe(CO)$_3$(Me-phen), 131544-70-2; *fac*-ClRe(CO)$_3$(Ph$_2$-phen), 140849-51-0; *fac*-IRe(CO)$_3$(Ph$_2$-phen), 131544-71-3; *fac*-BrRe(CO)$_3$(Me$_2$-bpy), 122279-31-6; ERL-4221, 25085-98-7; Epon 828, 25068-38-6; Me$_2$NCH$_2$Ph, 103-83-3.

Nonlinear Optical Properties of Poly(*p*-phenylenebenzobisoxazole)

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The third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of the conjugated rigid-rod polymer poly(*p*-phenylenebenzo[1,2-*d*:5,4-*d*′]bisoxazole) (PBO) has been investigated by third-harmonic generation spectroscopy and theoretical modeling in the wavelength range 0.9–2.4 μm (1.4–0.5 eV). The $\chi^{(3)}$ spectrum of PBO exhibits a strong three-photon resonance with a three-photon resonance enhanced $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ value of 7.0×10^{-11} esu at 1.2 μm. The nonresonant $\chi^{(3)}$ value at 2.4 μm was 8.1×10^{-12} esu, which is large and comparable to some of the best conjugated polymers. The $\chi^{(3)}$ dispersion data were found to be well described by a theoretical two-level essential states model. These results for the oxygen-containing heterocyclic rigid-rod polymer (PBO) were compared and contrasted with those previously reported for the structurally analogous sulfur-containing poly(*p*-phenylenebenzobisthiazole) (PBZT). The results indicate that the magnitude of $\chi^{(3)}$ is essentially identical in PBO and PBZT, suggesting the absence of an effect of the heteroatom on the nonlinear optical response of this class of heterocyclic rigid-rod polymers in contrast to prior oligomer model compound studies which had shown a factor of 3 enhancement by the sulfur heteroatom.

Introduction

Organic nonlinear optical materials with large third-order electronic susceptibility $\chi^{(3)}$ are currently receiving much attention from many research groups and laboratories because of the potential these materials hold for diverse applications in photonic devices.[1–15] The advantages of conjugated polymers as third-order nonlinear optical (NLO) materials have been well cited in many recent publications.[1–7] In an effort to understand the molecular design criteria for conjugated polymers with large $\chi^{(3)}$, several classes of conjugated polymers[1–6] and model compounds[7] have been investigated. Although some molecular design concepts are emerging, polymers that meet the material figure of merit (e.g., the ratio of the real part of $\chi^{(3)}(-\omega;\omega,-\omega,\omega)$ to the absorption coefficient α) required for practical photonic device applications are yet to be found. Thus, the challenge of elucidating all the relevant structure-$\chi^{(3)}$ relationships and molecular design criteria is still an open one. While several new classes of conjugated polymers have recently been synthesized as potential NLO materials,[8] investigation of the NLO properties of existing polymers can serve as a guide to the

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(1) (a) Khanarian, G., Ed. *Nonlinear Optical Properties of Organic Materials II*, SPIE Proceedings Vol. 1147; The International Society for Optical Engineering: Bellingham, WA, 1990. (b) Prasad, P. N.; Williams, D. J. *An Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991. (c) Bre'das, J. L., Chance, R. R., Eds. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer Academic Publishers: Dordrecht, Holland, 1990. (d) Khanarian, G., Ed. *Nonlinear Optical Properties of Organic Materials III*, SPIE Proceedings vol. 1337; The International Society for Optical Engineering: Bellingham, WA, 1990. (e) Marder, S. R., Sohn, J. E., Stuky, G. D.; Eds. *Materials for Nonlinear Optics: Chemical Perspectives*; ACS symposium Series No. 455; American Chemical Society: Washington, DC, 1991. (f) Meissier, J., Kajzar, F., Prasad, P., Ulrich, D. R., Eds. *Nonlinear Optical Effects in Organic Polymers*; Kluwer Academic Publishers: Dordrecht, Holland, 1989. (g) Heeger, A. J., Orenstein, J., Ulrich, D. R., Eds. *Nonlinear optical properties of* polymers; Material Research Society Proceeding, 1988; vol. 109. (h) Prasad, P. N., Ulrich, D. R., Eds. *Nonlinear Optical Properties of Polymers*, Plenum: New York, 1988. (i) Chemla, D. S., Zyss, J., Eds. *Nonlinear optical properties of organic molecules and crystals*; Academic Press: New York, 1987; Vols. 1 and 2.

(2) (a) Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* 1991, *3*, 218–221. (b) Jenekhe, S. A.; Roberts, M.; Agrawal, A. K.; Meth, J. S.; Vanherzeele, H. *Mater. Res. Soc. Proc.* 1991, *214*, 55–59. (c) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* 1991, *3*, 765–768. (d) Vanherzeele, H.; Meth, J. S.; Jenekhe, S. A.; Roberts, M. F. *Appl. Phys. Lett.* 1991, *58*, 663.

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