Luminescence Rigidochromism of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) (4,7-Ph$_2$phen = 4,7-Diphenyl-1,10-phenanthroline) as a Spectroscopic Probe in Monitoring Polymerization of Photosensitive Thin Films

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The complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) (4,7-Ph$_2$phen = 4,7-diphenyl-1,10-phenanthroline) has been found to be strongly luminescent and able to act as a spectroscopic probe in technologically important photosensitive thin films. UV-curable trimethylolpropane triacrylate/poly(methyl methacrylate) (TMPTA/PMMA) and bisphenol-A-novalac/diglycidyl ether of bisphenol-A epoxy resins have been investigated containing the organometallic probe. In each case, the luminescence from these thin films is attributed to a lowest energy triplet-centered metal-to-ligand charge-transfer (MLCT) excited state that arises from the complex. Importantly, the MLCT luminescence characteristics (energy position, band intensity, and lifetime) vary greatly when these acrylate and epoxy resins are exposed to UV light and polymerize. These changes in emission properties are attributed to a luminescence rigidochromic effect and are associated with the varying nature of solvation and dipolar interactions about the metal complex during these cross-linking polymerization reactions.

Introduction

Thin-film polymers which are cured on exposure to UV light form the basis of photoresist technology which in turn comprises an important part of the microelectronics industry.[1] In addition, UV-curable coatings have found applications in the graphic arts, packaging, dental, and medical industries. In all of these applications, it is desirable to have a knowledge of the physical state of the material as the cure of the polymeric material progresses. Previously, various fluorescent probe materials have been employed to monitor the cure kinetics of a variety of *thermally* cured polymer materials with some success.[2] However, to date only a few studies have concentrated on probing *photochemical* cross-linking reactions using fluorescent probes.

Recently, Meijer and Zwiers have used the intrinsic phosphorescence of various cycloaliphatic epoxide networks prepared by photoinitiated cationic polymerization to reveal the molecular mobility of these networks[3] and Scarlata and Ors have utilized a fluorescence polarization technique to determine the cure state of a photocured acrylate system.[4] Apart from these few literature reports, it is notable that luminescent probes have been under-exploited in photosensitive systems. This is largely due to the fact that traditional fluorescent probes have absorption and emission features in the UV and near-UV regions and these spectral properties usually interfere with the photoinitiation process.

Earlier work in our laboratory has focused on the use of visible-light-emitting transition metal complexes to monitor the thermal cure of epoxy resins.[5] The present report extend these studies to encompass the monitoring of cross-linking polymerization in photosensitive thin films. Our initial observations have suggested that phosphorescent organometallic complexes may have application as spectroscopic probes in the study of these technologically important materials.[6]

Metal complexes with the general formula *fac*-XRe(CO)$_3$L (X = Cl, Br, I; L = 1,10-phenanthroline or a substituted phenanthroline) are potentially useful in this regard as they have been previously shown to be strongly emissive in a variety of nonpolar room-temperature solutions as well as in low-temperature organic glassy media at 77 K. These complexes have absorption and emission features in the visible region which are well removed from the chemistry of the photoinitiators. Their emission features are associated with the lowest-lying metal-to-ligand charge-transfer (MLCT) excited state in which electronic transitions take place from a metal-centered molecular orbital to a π^* orbital centered on the ligand.[7] An important feature of these complexes is that the luminescence characteristics are greatly affected by solvent polarity and the rigidity of the surrounding matrix, the latter effect having been referred to as "luminescence rigidochromism".[7,8] In general, this phenomenon is characterized by a more intense, longer lived, and hypsochromically shifted emission as the medium becomes more rigid, although the underlying reasons for this behavior are not fully understood.

Herein, we describe a new approach to monitoring the extent of photoinitiated acrylate and epoxy polymerizations using *fac*-

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$ClRe(CO)_3(4,7\text{-}Ph_2phen)$ (4,7-Ph_2phen = 4,7-diphenyl-1,10-phenanthroline). This complex exhibits readily detectable luminescence upon incorporation into UV-curable coatings, and through an application of the luminescence rigidochromic effect it can act as an effective visible spectroscopic probe, thereby providing a new way of monitoring the progress of photochemical curing reactions. In addition, the results obtained enable us to comment on the nature of the luminescence rigidochromic effect itself.

Experimental Section

Synthesis. The organometallic probe complex, *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$, was synthesized by refluxing $ClRe(CO)_5$ (Pressure Chemical) with an excess of 4,7-Ph_2phen (Aldrich) in benzene, according to previously outlined literature procedure.[7] The product was purified by column chromatography on neutral alumina, and then repeated sublimations were performed to remove unreacted $ClRe(CO)_5$ and 4,7-Ph_2phen. Recorded infrared spectra are in agreement with the literature report.[7]

Acrylate Films. The model photosensitive acrylate system was formulated by mixing trimethylolpropane triacrylate (TMPTA, Celanese) and medium molecular weight poly(methyl methacrylate) (PMMA, Aldrich) at the stated weight percent ratios and then dissolving this mixture in a 5:2 (wt %) dichloromethane:xylenes solution. To this were added 0.01% by weight of the organometallic probe and 1.0% by weight of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Ciba-Geigy Irgacure 651). The samples were then coated onto a 0.051 mm (2 mil) thick polyester sheet using a coating knife with a 0.254-mm (10-mil) gap and then dried at 358 K for 10 min. The resulting films were exposed to light from a 350-W Oriel mercury lamp, and the samples were maintained under a dry nitrogen environment during photolysis. Excitations were performed with a light intensity of 3.5 mW/cm^2 measured using an International Light Model IL 7000 radiometer.

Epoxy Films. The model photosensitive epoxy system was formulated as follows. The bisphenol-A/novolac resin SU8 (Interz, Inc.) was added as a 50 wt % solution in methyl amyl ketone to 20 g diglycidyl ether of bisphenol-A (DGEBA, Ciba-Geigy Aratronics 5001). Subsequently, 2.5 g of a 50 wt % propylene carbonate/triarylsulfonium hexafluoroantimonate photoinitiator (Union Carbide Cyracure UVI-6974) and 0.002 g of the organometallic probe complex were added. Samples for luminescence studies were prepared by coating the epoxy/probe mixture onto a 0.051 mm (2 mil) thick polyester sheet using a coating knife with a 0.254-mm (10-mil) gap. After coating, the epoxy samples were air-dried for 1 h followed by a pre-exposure bake at 348 K for 10 min. The resulting films were exposed in air using a 350-W Oriel mercury lamp for the specified times. Typical lamp intensities of 3.5 mW/cm^2 were used as determined with an International Light Model IL7000 radiometer. Following exposure, the epoxy films were again heated at 348 K for 10 min.

Spectroscopic Measurements. Emission spectra were recorded on an SLM Instruments Model 8000/8000S dual monochromator spectrometer that incorporates a red-sensitive Hamamatsu R928 photomultiplier tube and photon-counting facilities. Spectra were obtained from the surface of the thin films with the polyester sheets being orientated at an angle of 20° to the incident light. Recorded emission maxima were reproducible to within 1 nm. Emission lifetimes were obtained from samples in an identical configuration on a Photochemical Research Associates (PRA) System 3000 time-correlated pulsed single-photon-counting apparatus. Sample solutions were excited with 400-nm light from a PRA Model 510 nitrogen flash lamp that was transmitted through an Instruments SA Inc. H-10 monochromator; emitted light was detected at 90° via a second H-10 monochromator transmitted onto a thermoelectrically cooled red-sensitive Hamamatsu R955 photomultiplier tube. The resulting photon counts were stored on a Tracor Northern Model 7200 microprocessor-based multichannel analyzer. The instrument response function was subsequently deconvoluted from the emission data to obtain an undisturbed decay that was fitted by means of a PRA least-squares program on an IBM-PC. Excellent single-exponential fits were recorded for each sample; the reported lifetimes represent the average of at least three readings and were found to be reproducible within 10%.

Infrared spectra were recorded on an IBM Instruments IR/98 FTIR spectrometer as attenuated total reflectance (ATR) spectra for the acrylate samples and absorbance spectra for the epoxy samples. Acrylate samples for IR analysis were prepared by cutting 1-cm^2 areas of the photopolymer/polyester film and pressing the film (photopolymer side down) onto a 10 × 5 × 1 mm KRS 45° ATR crystal. Samples were placed in a 4X-beam condenser accessory from Harrick Scientific Corp. In each case, the reaction was monitored by directly observing the disappearance of the 808-cm^{-1} acrylate band; this band was determined[9] at a penetration depth of 7.5 μm. The ATR band was normalized using the band at 843 cm^{-1} as the internal standard. Epoxy samples were prepared for infrared analysis by spin-coating epoxy/probe solutions onto 25 × 5 mm round NaCl plates using a Headway Research Inc. Model 1-EC101D-R485 photoresist spinner. In these measurements, the reaction was monitored by observing the disappearance of the 916-cm^{-1} epoxy band using the phenyl absorbance at 1606 cm^{-1} as an internal standard.[10] The percent epoxy remaining was determined according to eq 1, where A_0 and A_t are the integrated areas under the epoxy band and A_0(std) and A_t(std) are the areas of the internal standard band at times 0 and *t*, respectively.

$$\%\ \text{epoxy remaining} = 100[A_tA_0(\text{std})/A_0A_t(\text{std})] \qquad (1)$$

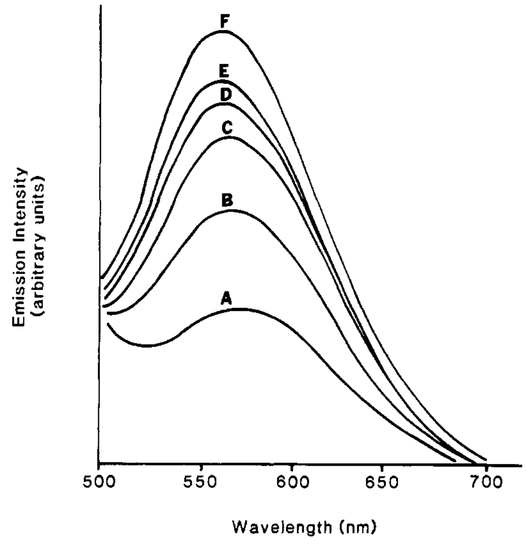

Figure 1. Emission spectra of *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$ in the model PMMA/TMPTA photosensitive system as a function of UV-irradiation time (s): (A) 0; (B) 5; (C) 10; (D) 20; (E) 30; (F) 60. The emission spectra are uncorrected for photomultiplier tube response and the excitation wavelength is 420 nm.

Results and Discussion

General Comments. The *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$ complex was determined to be soluble and thermally stable in the thin-film compositions employed. Emission spectra obtained from the probe complex during the core sequences indicate that it suffers no significant photochemical decomposition during exposure to UV light. Moreover, electronic absorption data obtained earlier for *fac*-$XRe(CO)_3(\alpha,\alpha'$-diimine) compounds in thermosetting epoxy resins have indicated that these organometallics remain stable in these types of materials.[5b]

Acrylate-Based Films. The model photosensitive system used was a formulation utilizing acrylate monomer TMPTA, and medium molecular weight PMMA as a binder. Irradiation of the photosensitive PMMA/TMPTA/probe mixture was carried out using the free-radical-producing photoinitiator 2,2-dimethoxy-2-phenylacetophenone; Figure 1 shows the emission spectra recorded from the organometallic probe *fac*-$ClRe(CO)_3(4,7\text{-}Ph_2phen)$ in the PMMA/TMPTA (50:50 wt %) photoresist system after various photolysis times. It is evident that the intensity of the MLCT emission band of the probe complex increases by a factor of approximately 3 following the UV irradiation. In addition, the center of the MLCT emission band is observed to move from 576 to 562 nm during this photochemical cross-linking reaction (corresponding to a hypsochromic shift of 433 cm^{-1}).

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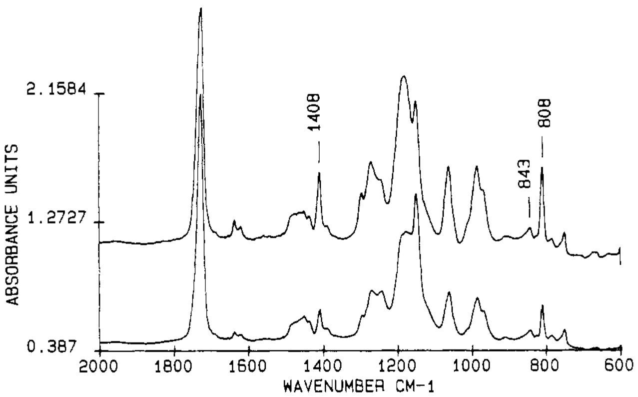

Figure 2. Infrared ATR spectrum from 2000 to 600 cm^{-1} of the model PMMA/TMPTA acrylate photosensitive system using a 45° KRS plate before exposure (top) and after 120 s of UV exposure (bottom).

The observed energy shift is attributed to be related to the "luminescence rigidochromic effect" that has been recognized for a number of substituted metal carbonyl complexes exhibiting MLCT emission. Generally, this phenomenon occurs when solutions of these complexes are cooled through their glass transition point, resulting in a blue shift of the emission band as the matrix viscosity increases.[7,8,11,12] It is thought to arise from variations in the dipolar interactions between the polar excited molecular species and the local solvent dipoles of the surrounding medium.[5b,11-14] Recently, in a series of experiments dealing with thermosetting diepoxide resins, this luminescence shift was correlated directly to the viscosity changes that take place about the metal complex.[5b] This point is relevant to the changes occurring in these photochemical cross-linking processes and will be further discussed below.

The photoinitiated reaction has also been monitored by infrared spectroscopy. Figure 2 shows the infrared ATR spectra obtained from the PMMA/TMPTA (50:50 wt %) mixture containing the organometallic probe and the 2,2-dimethoxy-2-phenylacetophenone initiator throughout a UV-irradiation sequence. The decrease in the intensity of the absorption band at 808 cm^{-1} during this photochemical reaction is due to the disappearance of the acrylate monomer. This IR band corresponds to the CH_2 wagging vibration of the residual fraction of the acrylate molecule, and its intensity, therefore, reflects the extent of cross-linking that takes place.

The observed increase in the MLCT emission intensity of the probe complex as a function of photolysis time has been monitored throughout the polymerization reaction, and the results are plotted in Figure 3a. No further enhancement of the probe luminescence was observed after 60 s of irradiation had elapsed. Additionally, in the absorbance of added photoinitiator, the luminescence intensity of the probe in the PMMA/TMPTA mixture was observed to remain constant (see Figure 3a), confirming that the metal complex does not undergo significant photodegradation or itself initiate polymerization in the film. Figure 3b represents the change in the integrated area of the infrared band at 808 cm^{-1} as a function of irradiation time. Taken together, the emission and infrared ATR data represented in Figure 3 clearly demonstrate that there is a concomitant increase in the phosphorescence of the probe as the acrylate monomer is consumed and the photochemical cross-linking reaction proceeds in the thin film.

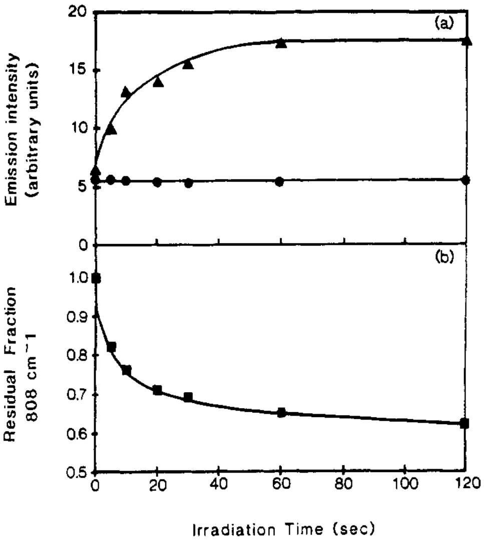

Figure 3. (a) Plots of the emission intensity (recorded at the MLCT band maximum) of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the model photosensitive PMMA/TMPTA system as a function of UV-irradiation time: (▲) with and (●) without added photoinitiator. The emission spectra are uncorrected for variations in photomultiplier response, and the excitation wavelength is 420 nm. (b) Plot of normalized area of acrylate monomer FTIR band (recorded at 808 cm^{-1}) as a function of time in the model PMMA/TMPTA system.

Excited-state lifetimes have been measured for the complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the PMMA/TMPTA thin film during the polymerization reaction. The emission lifetime is observed to increase by approximately a factor of 3 during the cure, from 0.85 μs in the unirradiated sample to 2.5 μs in a sample that has been exposed for 120 s. The radiative (k_r) and nonradiative (k_{nr}) rate constants can be interrelated with the experimental emission quantum yield (ϕ_{em}) and lifetime data (τ_{em}) according to eqs 2 and 3. As noted above, both the emission

$$k_r = \phi_{em}/\tau_{em} \qquad (2)$$

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

intensity and the lifetime values were observed to increase by approximately a factor of 3 during this light-induced cross-linking reaction, and hence, it can be concluded from eq 2 that k_r changes very little throughout the process. Consequently, the increase in the emission parameters is mainly due to a decrease in k_{nr}. Qualitatively, these changes in the vibrational and rotational nonradiative decay pathways can be related to the increasing rigidity of the matrix and the corresponding reduction in the matrix free volume. Previously, the importance of free volume and polymer viscosity has been pointed out in the case of paraffins, 1,3-bis(*N*-carbazoyl)propane excimers, the rhodamine dyes.[15] Also, this relationship has been previously examined in the context of decreasing free volume during the polymerization of ethyl methacrylate by Loufty.[16] In general, it has been found that the nonradiative relaxation rate processes demonstrate an exponential dependence on polymer free volume (v_f), the observed nonradiative rate constant (k_{nr}) decreasing as free volume is reduced according to eq 4. Here $k_{nr}{}^0$ is the intrinsic rate of molecular nonradiative relaxation, v_0 is the van der Waals volume of the probe species,

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Table I. Emission Data for fac-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the Model Photosensitive Acrylate PMMA/TMPTA System as a Function of Resin Composition

PMMA: TMPTA ratio (wt %)	λ_{em}, nm[a] uncured resin	cured[b] resin	ΔE_{em} cm^{-1} [c]	I_f/I_0[d]
30:70	583	561	672	6.9
40:60	580	561	584	4.6
50:50	576	562	432	2.5
60:40	567	562	160	2.1

[a] Emission maxima are uncorrected for photomultiplier response; excitation wavelength is 420 nm. [b] Following UV-light exposure for 120 s. [c] Energy difference at the MLCT band maxima between the uncured and cured materials. [d] Ratio of the initial (I_0) and final (I_f) emission intensities recorded at the MLCT band maxima.

$$k_{nr} = k_{nr}^{\ 0} \exp(-v_0/bv_f) \tag{4}$$

and b is a constant particular to the probe molecule. The changes we have observed in the emission parameters (intensity and lifetime) of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the model photosensitive PMMA/TMPTA thin-film system are entirely consistent with such an interpretation.

Results have also been obtained on varying the composition of the polymer, and these are shown in Table I. The magnitude of the rigidochromic shift (ΔE_{em}) and the intensity ratio (I_f/I_0) of the probe emission (where I_f is the intensity of the probe's MLCT emission band following 120 s of UV-light exposure and I_0 is the emission intensity prior to exposure) both decrease as the starting mixture increases in PMMA binder content. As the ratio of PMMA:TMPTA increases, the overall viscosity of the starting material is greater, and so upon irradiation the net change in viscosity is somewhat less. In accordance with our previous findings for thermosetting resins,[5b] these matrix viscosity changes are seen to influence both the magnitude of the rigidochromic shift and the increase in the emission intensity of the complex within the polymer.

Epoxy-Based Films. The model photosensitive epoxy formulation was based on a mixed epoxy resin system. This formulation included the bisphenol-A/novolac solid resin and the diglycidyl ether of bisphenol-A (see Experimental Section). Irradiation of the photosensitive epoxy resin/probe mixture was carried out using a cation-generating photoinitiator consisting of triarylsulfonium hexafluoroantimonate salts. Figure 4 illustrates emission spectra obtained for *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the model photosensitive epoxy system following various irradiation times. In each case, it is evident that the epoxy/probe mixture gives rise to dual emission features. The high-energy band centered at 460 nm is observed even upon exclusion of the organometallic probe and is, therefore, attributed to Raman scattered light arising from the epoxy material itself. Indeed, this emission band was found to concomitantly shift in energy on varying the exciting wavelength. In contrast, the low-energy band is observed only upon the incorporation of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) and is clearly due to the MLCT phosphorescence of the metal complex.

The MLCT emission band intensity can be seen to be even more greatly enhanced by the polymerization of this resin material, as it increases by a factor of approximately 5.5 during the cure sequence. Moreover, the MLCT band initially appears as a shoulder at 581 nm, and it subsequently shifts to 522 nm after 60 s of exposure (this corresponds to a hypsochromic shift of 1945 cm^{-1}, significantly greater than that for the PMMA/TMPTA system). After 60 s of irradiation, no further enhancement of the emission intensity occurs. Additionally, the determined emission lifetime of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in this UV-cured epoxy resin material is 6.4 μs, which is appreciably longer than that recorded in the above acrylate system. Indeed, this value is consistent with the ^{3}MLCT emission lifetimes observed from these types of complexes in rigid glassy environments at low temperature.[7,12,13]

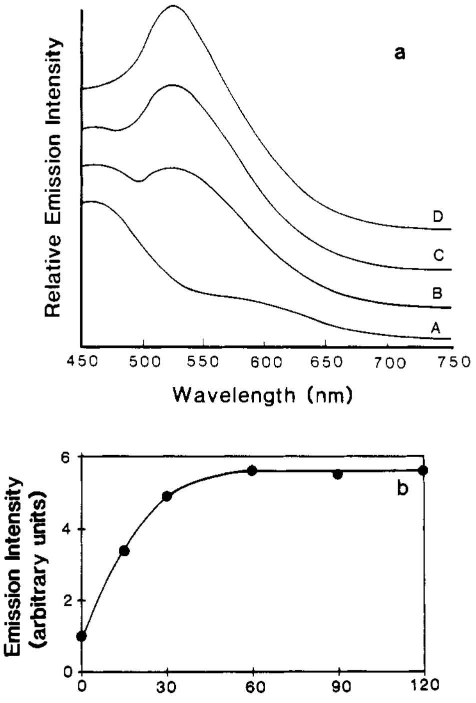

Figure 4. (a) Emission spectra of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the model photosensitive epoxy system at 293 K as a function of UV-irradiation time (s): (A) 0; (B) 15; (C) 30; (D) 60. The emission spectra are uncorrected for photomultiplier tube response, and the excitation wavelength is 420 nm. The spectra are vertically displaced for clarity. (b) Plot of emission intensity (recorded at the MLCT band maximum) of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) as a function of UV-irradiation time.

As noted above, the substantial increase in the MLCT emission intensity can be related to a reduction in the nonradiative relaxation mechanism of the organmetallic complex during the photochemical cross-linking reaction of the epoxy material. Once again, the changes in the vibrational and rotational nonradiative decay pathways can be associated with the increasing rigidity of the matrix and the corresponding reduction in polymer-free volume. We attribute the especially large rigidochromic shift (1945 cm^{-1}) observed for the MLCT maximum of the probe complex in this matrix environment to the highly polar nature of the cured epoxy network [δ = 9.7–10.9 (cal/cm^3)$^{1/2}$][17] and the local dipolar interactions around the excited-state molecular probe species. By way of comparison, acrylates such as the PMMA/TMPTA system studied above are known to form considerably less polar networks [$\delta \sim 9.4$ (cal/cm^3)$^{1/2}$].[17] As the cross-linking reaction proceeds and the microviscosity increases, there will be a reduction in the random solvent orientation in the polymer matrix. Moreover, the rearrangement of the solvent molecules about the probe complex will become increasingly hindered as the matrix environment becomes more rigid. These aspects relate to the luminescence rigidochromic effect and will be further discussed below.

Figure 5a depicts FTIR spectral data recorded for the mixed epoxy resin material before and after UV irradiation. The decrease in the area of the absorption band at 916 cm^{-1} reflects the consumption of the epoxy groups during the cationic polymerization reaction. Figure 5b illustrates a plot of the normalized area of the epoxy 916-cm^{-1} band as a function of UV-irradiation time for the mixed epoxy film. It is interesting to note that toward the end of the photolysis (after 30 s) the IR spectra show little change, whereas the emission peak continues to grow and then finally levels off after irradiation for 60 s (see Figure 4). It should be recognized that while the IR spectra

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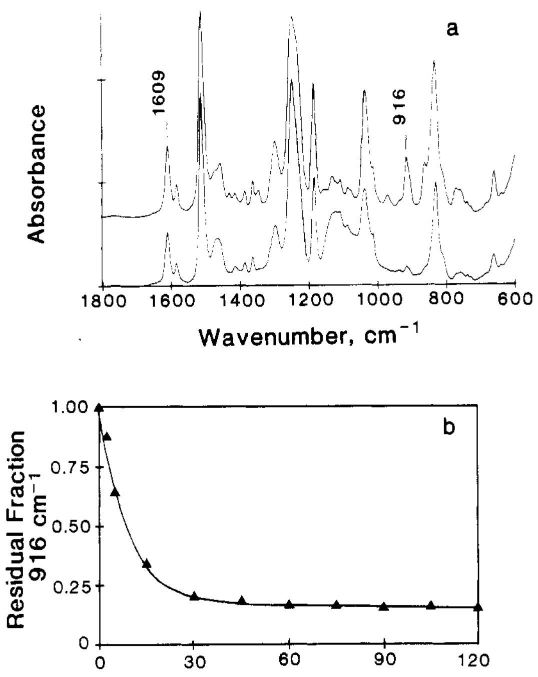

Figure 5. (a) FTIR spectra obtained for the model photosensitive epoxy resin before exposure (top) and after UV exposure for 120 s (bottom). (b) Plot of normalized area of epoxy vibration at 916 cm^{-1} as a function of irradiation time in the photosensitive model thin-film system.

reflect the concentration of the epoxy functional groups, the luminescence results from the phosphorescent organometallic probe molecule may be providing a more sensitive probe of the microviscosity changes and hence the degree of cross-linking in these thin polymer films at the latter stages of polymerization.

Luminescence Rigidochromism. The observed hypsochromic shift in the emission maxima of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) and related complexes with changes in the rigidity of the solvent medium has been referred to as "luminescence rigidochromism".[7,12] It is important to realize that the emission from this complex originates from a rhenium-to-ligand charge-transfer excited state with considerable triplet character.[7,18] Also noteworthy is the fact that luminescence rigidochromism is not observed in complexes such as *cis*-XRe(CO)$_4$L (X = Cl, I; L = pip, PPh$_3$),[19] *fac*-XRe(CO)$_3$(phosphine)$_2$,[20] CpRe(CO)$_2$(py),[13c,d] and W(CO)$_4$(en),[13b] which exhibit emission from ligand field (LF) excited states.

In order to rationalize the rigidochromic effect, we compare here electronic absorption and emission results obtained during the curing of these photosensitive acrylate- and epoxy-based polymers with our earlier reported results for the thermosetting cycloaliphatic epoxy resin system (see Table II).[5b,21] It is immediately apparent that, compared to the emission energies, the absorption maxima show relatively little dependence upon variation in the matrix rigidity, although there is a slight blue shifting of the absorption band maximum, consistent with the solvatochromic shifts that have been previously observed for organometallic species.[12,13] On the other hand, it is evident that the greatest changes taking place between a nonrigid and a rigid solvent environment occur with respect to the MLCT emission which originates from the relatively long-lived (i.e., relaxed) ^{3}MLCT excited state. This apparent decoupling between the absorption and emission phenomena can be understood by recognizing that the ^{1}MLCT excited state is likely to be extremely short-lived, as efficient nonradiative relaxation to the ground state and very rapid intersystem crossings to ^{3}MLCT excited states are expected in such systems.[12,22] The spectroscopic results obtained here lead us to suggest that it is the relatively long-lived triplet-centered excited state which is most affected by the environmental changes because it is this one that is most susceptible to alterations in dipolar interactions with the solvent molecules.

Table II. Energy Changes Observed at the MLCT Absorption (ΔE_{abs}) and Emission (ΔE_{em}) Maxima for fac-XRe(CO)$_3$L Complexes upon Curing the Thermosetting and Photosensitive Resin Materials

complex	resin material	ΔE_{abs}, cm^{-1}	ΔE_{em}, cm^{-1}
fac-ClRe(CO)$_3$(4,7-Ph$_2$phen)	thermosetting epoxy[a]	211	1592
fac-ClRe(CO)$_3$(4-Mephen)	thermosetting epoxy[a]	73	1025
fac-BrRe(CO)$_3$(4,4′-Me$_2$bpy)	thermosetting epoxy[a]	292	1633
fac-IrRe(CO)$_3$(4,7-Ph$_2$phen)	thermosetting epoxy[a]	369	764
fac-ClRe(CO)$_3$(4,7-Ph$_2$phen)	photosensitive epoxy[b]		1945
fac-ClRe(CO)$_3$(4,7-Ph$_2$phen)	photosensitive acrylate[b]		433[c]

[a] Cycloaliphatic epoxy/anhydride materials; absorption data taken from ref 21 and emission data taken from ref 5b. [b] This work; absorption data were not obtained from these thin films. [c] From a 50:50 (wt %) PMMA:TMPTA composition.

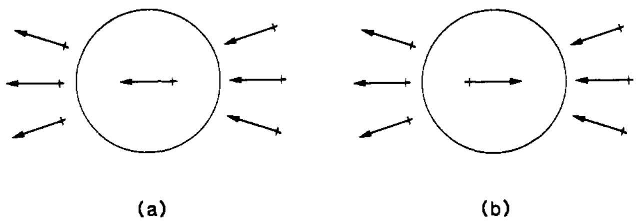

Figure 6. Diagram showing solvation of (a) a ground-state molecule and (b) a molecule existing in a ^{3}MLCT exited state. The dipole moment of the molecule is depicted to change direction upon excitation.

One can consider a complex such as *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) existing in the ground state with surrounding solvent molecules orientated to accommodate the ground-state dipole moment of the complex (see Figure 6a).[24] Upon excitation, this complex exhibits a different dipole moment than its ground-state counterpart,[24] and hence it will be destabilized (see Figure 6b) unless the solvent molecules can rearrange themselves to allow for a more favorable electrostatic interaction. As solvent viscosity increases (either as a result of the solution freezing or because of a cross-linking process in the case of our thermally and photochemically cured polymers), the rearrangement of the solvent molecules around the excited-state species will become increasingly sluggish, and consequently, this will affect the dipolar interaction. Additionally, as a result of decreased free volume in a frozen glass or cured polymer, the solvent molecules may be actually closer to the excited-state molecules, further enhancing the dipole–dipole forces. The effect of changing the environment, the hence the nature of the dipolar interaction, will be manifested predominantly in the relatively long-lived ^{3}MLCT emitting state, which is normally able to achieve a relaxed form. The extreme case of the rigidochromic shift is observed when one reaches a completely frozen solvent glass or a tightly cross-linked polymer matrix because the solvent motion will be almost entirely restrained and there is, thus, an inability of the solvent molecules and their dipoles to rearrange about the ^{3}MLCT excited state.

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(18) The heavy metal center in this organometallic complex precludes a pure triplet assignment (see ref 12 for further discussion).
(19) Glezen, M. M.; Lees, A. J. *J. Am. Chem. Soc.* **1988**, *110*, 3892.
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(23) Dodsworth, E. S.; Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 499.
(24) The excited-state dipole moment is deliberately shown to be reversed in accordance with potential-energy representations involving Re–N compressions in ^{3}MLCT states of closely related complexes (see refs 8b and 13d).

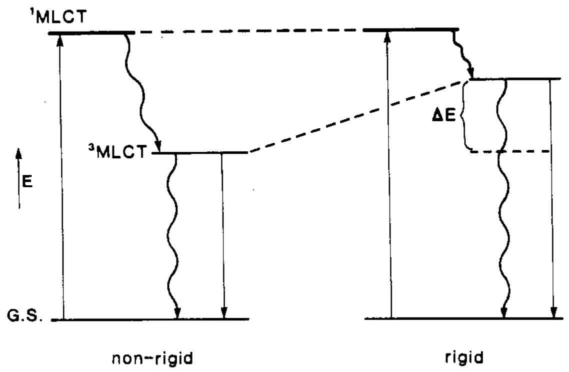

Figure 7. Simplified-state energy diagram showing the effect of nonrigid and rigid environments upon the ¹MLCT and ³MLCT excited states in a *fac*-XRe(CO)$_3$L complex.

Finally, a simplified-state energy diagram summarizing the relative differences in energies of the ¹MLCT and ³MLCT states in both nonrigid and rigid environments is depicted in Figure 7. The energy destabilization and consequent blue shifting of the emission band maxima of the *fac*-XRe(CO)$_3$L complexes on polymerization can be visualized by considering a vertical (upward) displacement of the ³MLCT potential energy curve, although it is recognized that horizontal displacement of the ³MLCT potential curve or a change in the shape of the ground-state potential well[11a] would also influence the emission energies.

Conclusions

The luminescent complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) has been incorporated in technologically important UV-curable acrylate and epoxy thin film materials and shown to act as a spectroscopic probe in monitoring environmental changes throughout polymerization. Organometallic complexes of this type possess several key properties that enable them to be of use in probe applications of photosensitive resins. These include their solubility and thermal stability in nonpolar thin film materials, their intense visible absorptions that are removed from exciting wavelengths normally used for the photoinitiators, and their low-lying ³MLCT excited states that yield readily detectable emission in the yellow–red region of the spectrum. Furthermore, the ³MLCT emission parameters of these complexes are highly sensitive to the local environmental changes that take place during these cross-linking polymerization reactions.

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