

Luminescence of W(CO)₄(4-Me-phen) in Photosensitive Thin Films: A Molecular Probe of Acrylate Polymerization

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The complex W(CO)₄(4-Me-phen) (4-Me-phen = 4-methyl-1,10-phenanthroline) has been determined to be luminescent and act as a spectroscopic probe in UV-curable trimethylolpropane triacrylate/poly(methyl methacrylate) thin films. Electronic absorption and luminescence characteristics have been measured for this complex in room-temperature solutions and low-temperature (80 K) glasses and in 10 mil thin films of the unexposed and exposed acrylate resins. In each environment dual luminescence bands were observed which are attributed to triplet-centered metal-to-ligand charge-transfer (³MLCT) excited states. For the unexposed photoresist these transitions were recorded at 520 and 750 nm and in the exposed material these are moved to 525 and 715 nm, respectively. The lowest energy emission band undergoes a substantial blue-shift and intensifies greatly on polymerization; this phenomenon provides a useful molecular probe of the acrylate cross-linking process. These changes in emission characteristics are associated with a rigidochromic effect imparted on the lowest lying and solvent sensitive b₂ → b₂(π*) ³MLCT electronically excited state in this complex. The complex W(CO)₅(4-CN-py) (4-CN-py = 4-cyanopyridine) was also investigated as a spectroscopic probe in the acrylate system but appears unsuitable for this purpose as it was found to degrade significantly in the resin.

Introduction

Thin-film polymers which are formed on exposure to UV light are used extensively in the microelectronics industry as photoresist materials.¹ Additionally, UV-curable coatings have found widespread applications in dentistry and medicine and in industries such as packaging and graphic arts. It is of fundamental importance in each of these applications, however, to obtain a knowledge of the physical state of the polymer material as the cure proceeds. Previously, a variety of fluorescent molecules have been employed as spectroscopic probes to determine the cure kinetics of several thermosetting polymers.² In only a few cases, though, have photochemical polymerization reactions been monitored because traditional fluorescent probes normally exhibit absorption and emission features in the UV and near-UV regions and these interfere with the spectral properties of the photoinitiators.³

Several approaches have been followed in using fluorescence molecules as probes of photopolymeriza-

tion, and this topic has recently been reviewed.⁴ The formation of excimers (usually involving pyrene or a pyrene derivative) to produce a change in the emission position has been used extensively.⁵ In addition, various studies have focused on multiple fluorescence systems where nonradiative deactivation rates are dependent on the ability of the probe to undergo rotation.⁶ Also, a number of fluorescence probes have been investigated in which the extent of energy transfer to a quencher molecule is affected during the polymerization.⁷

Recently, work in our laboratories has explored the use of a series of rhenium organometallic complexes of the general formula *fac*-XRe(CO)₃L (X = Cl, Br, or I; L

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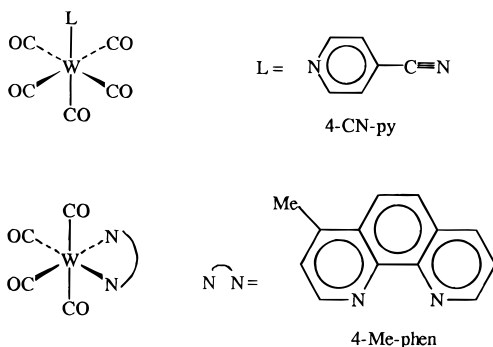
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= 1,10-phenanthroline or a substituted phenanthroline), as spectroscopic probes of polymerization reactions in thermosetting epoxy resin systems⁸ and in UV-curable coatings.⁹ These organometallic complexes exhibit several key features that lend themselves useful to this type of probe application. These include their solubility and thermal stability in nonpolar organic solutions containing the monomer, their intense visible absorptions, and their low-energy excited states which are strongly luminescent in the visible region and sensitive to environmental rigidity over a wide range of solution viscosities.^{8,9} Significantly, the spectral properties of these probe complexes enable low concentrations (<0.5% by weight) to be employed in the photoresist.

To date, however, all of our studies have been confined to the above *fac*-XRe(CO)₃L system, and we have not explored the possibility of other luminescent organometallic complexes¹⁰ as spectroscopic probes in polymers. The present study extends these investigations to the known luminescent W(CO)₅(4-CN-py) (4-CN-py = 4-cyanopyridine)¹¹ and W(CO)₄(4-Me-phen) (4-Me-



phen = 4-methyl-1,10-phenanthroline)¹² complexes in a photosensitive acrylate system. The results on the former complex are disappointing but the chelated tetracarbonyl compound is found to undergo a significant hypsochromic shift in the energy of its lowest lying emission band and is, hence, most effective as a luminescent probe in monitoring the acrylate cross-linking polymerization. Additionally, the emission observed from the W(CO)₄(4-Me-phen) complex is in the red region of the spectrum and well removed from the spectral properties of the acrylate and photoinitiators.

Experimental Section

Materials. Tungsten hexacarbonyl was obtained from Strem Chemicals and purified by sublimation. The 4-cyanopyridine ligand was obtained from Aldrich Chemicals and purified by sublimation. The 4-methyl-1,10-phenanthroline ligand was received from Alfa Chemicals at >99% purity and used without further purification. Solvents used in the spectroscopic studies were high-purity Photrex grade and obtained from Baker Chemicals; other solvents used were obtained as reagent grade from Fisher Scientific. EPA (5:5:2 ether-isopentane-ethanol) was constituted from rigorously

dried solvent components that had been repeatedly distilled to remove emitting impurities. Neutral alumina (80–200 mesh) was obtained from Fisher Scientific and used in chromatographic purifications. Trimethylolpropane triacrylate (TMPTA) was obtained from Celanese Chemicals. Medium weight poly(methyl methacrylate) (PMMA) was obtained from Aldrich Chemicals. The benzophenone and 4,4'-bis(dimethylamine)benzophenone photoinitiators were obtained from Aldrich Chemicals.

Synthesis of W(CO)₅(4-CN-py). The W(CO)₅(4-CN-py) complex was prepared photochemically from W(CO)₆ via the corresponding W(CO)₅(THF) (THF = tetrahydrofuran derivative) according to a procedure described earlier.¹¹ The isolated compound was purified by column chromatography on alumina followed by sublimation to remove any unreacted W(CO)₆. UV-visible and infrared spectra obtained from the complex are in agreement with the literature.^{11,13}

Synthesis of W(CO)₄(4-Me-phen). The organometallic complex, W(CO)₄(4-Me-phen), was prepared by Hg lamp (200 W) irradiation of W(CO)₆ in hexanes solution containing excess 4-Me-phen ligand according to a previously described procedure.¹² Purification was achieved by repeated washings with hexanes followed by passage down a neutral alumina column. The resulting orange-red solid was then vacuum sublimed to remove unreacted W(CO)₆. UV-visible and infrared spectra recorded from the complex are in agreement with the literature.¹²

Preparation of Thin Films. The photosensitive acrylate system was constituted with 4 g of trimethylolpropane triacrylate (TMPTA) and 4 g of medium weight poly(methyl methacrylate) (PMMA) in 10 g of dichloromethane:xylene (3:2 by weight). To this was added 4% (by weight) of benzophenone, 0.5% (by weight) of 4,4'-bis(dimethylamino)benzophenone, and 0.3% (by weight) of the organometallic complex, W(CO)₄(4-Me-phen). The samples were then spun onto 36 mm square quartz plates with a Headway Research Inc. Model 1-EC101D-R485 photoresist spinner and then dried at 353 K for 10–15 min to form thin films of 10 mil thickness. The samples for infrared measurement were coated onto a polyester sheet of 2 mil thickness using a coating knife with a 10 mil gap. These were then dried at 353 K for 10 min.

Physical Measurements. The acrylate thin films were photoexcited under an oxygen-free environment with 366-nm light from a 500-W Oriel Model 82310 mercury lamp. The excitation wavelength was isolated using an interference filter (Ealing) with a 10-nm bandpass. Electronic absorption spectra and emission spectra were subsequently obtained at various stages during the light exposure. Electronic absorption spectra were recorded on a Hewlett-Packard Model 8450A UV-visible spectrometer, and luminescence emission spectra were obtained on a SLM Instruments Model 8000/8000S dual-monochromator emission spectrometer which incorporates photon-counting facilities. A red-sensitive Hamamatsu R928 photomultiplier tube was employed in the emission measurements. The luminescence spectra were acquired from the surface of these thin films with the sample oriented at an angle of 25–30° to the incident beam to reduce light scattering. Emission spectra were subsequently corrected for wavelength variations in the photomultiplier tube response and on recording in triplicate were determined to be reproducible to within ±2 nm. Low-temperature measurements were performed with an Oxford Instruments Model DN1704K variable-temperature liquid nitrogen cryostat fitted with synthetic sapphire inner windows and quartz outer windows. These solution samples were deaerated by successive freeze-pump-thaw cycles and maintained at ±0.2 K in a fused-quartz 1 cm cell. Attenuated total reflectance (ATR) infrared spectra were recorded on an IBM Instruments IR/98 FTIR spectrometer. The acrylate samples were prepared by cutting 1 cm² 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 inserted in a 4X-beam condensor accessory from Harrick Scientific Corp. The reaction was monitored by direct observation of the decline in intensity of the 808 cm⁻¹ acrylate

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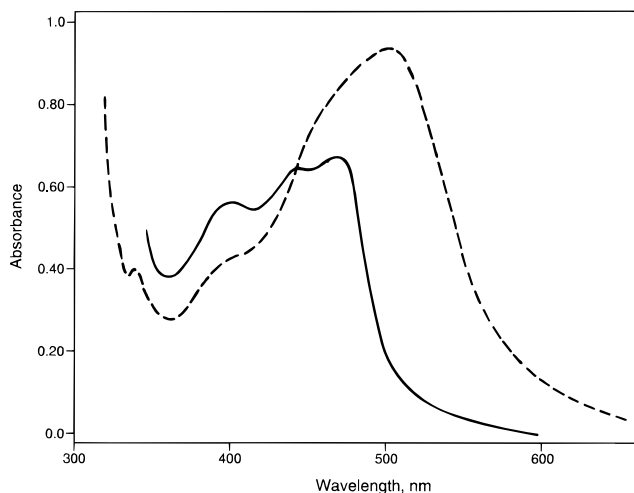


Figure 1. Electronic absorption spectra of $W(CO)_4(4\text{-Me-phen})$ (---) in deoxygenated benzene at 293 K and (—) in an EPA glass at 80 K.

band, determined at a penetration depth of $7.5\ \mu\text{m}$. The area of this ATR band was normalized using the $843\ \text{cm}^{-1}$ band as an internal standard.

Results and Discussion

General Observations. The $W(CO)_5(4\text{-CN-py})$ complex was found to be soluble but not thermally stable in the TMPTA/PMMA system. Electronic absorption spectra recorded from the constituted probe/acrylate mixture revealed substantial thermal degradation of the organometallic compound over a period of just a few hours; this material was not further investigated as a spectroscopic probe. In contrast, the $W(CO)_4(4\text{-Me-phen})$ complex was determined to be both soluble and thermally stable in the acrylate thin films studied, and, in fact, decomposition was found to be negligible over a period of a week when the sample was stored in the dark at $5\ ^\circ\text{C}$. UV-visible and emission spectra recorded during the acrylate photopolymerization illustrate that the molecular probe suffers no significant photochemical decomposition on exposure to light over the period of these experiments (vide infra). In constituting the thin films the concentrations of monomer and polymer were varied; the mixture containing a 1:1 ratio of monomer to polymer produced a film which coated evenly and was most suitable for the photophysical study of the metal complex.

Solution Spectra. Electronic absorption spectra obtained from $W(CO)_4(4\text{-Me-phen})$ in deoxygenated benzene at 293 K and in an EPA glass at 80 K are depicted in Figure 1. The room-temperature spectrum of this substituted phen complex is dominated by an intense metal-to-ligand charge-transfer (MLCT) absorption manifold centered at 500 nm ($\epsilon_{\text{max}} = 9250\ \text{M}^{-1}\ \text{cm}^{-1}$), although weaker ligand field (LF) transitions were also observed at 340 nm ($\epsilon_{\text{max}} = 3550\ \text{M}^{-1}\ \text{cm}^{-1}$) and 391 nm (sh).^{12a} At low temperature there is significant band sharpening and two MLCT features are resolved. In considering the electronic characteristics, it should be noted that the $W(CO)_4(4\text{-Me-phen})$ compound is part of a wider series of $M(CO)_4(\alpha, \alpha'\text{-diimine})$ complexes where the electronic structures have been studied in considerable detail.^{12,14} Recently, a series of resonance Raman (RR) and magnetic circular dichroism (MCD) techniques have shown that the low-energy MLCT absorption band envelope of $M(CO)_4(\alpha, \alpha'\text{-di-}$

imine) complexes comprises three MLCT transitions, the most intensely observed one having been assigned to a z -polarized ($d_{yz}b_2 \rightarrow b_2(\pi^*)$) transition that is directed along the dipole vector of the complex.^{14d,f} The solvent dependence of these complexes has also been related to the degree of mixing between the metal and ligand orbitals. In $W(CO)_4(4\text{-Me-phen})$ the amount of mixing between the metal d_{yz} and ligand π^* orbitals is relatively small and the complex is extremely solvent sensitive.^{12,14c,f,15} Additional y -polarized ($d_{x^2-y^2}a_1 \rightarrow b_2(\pi^*)$) and x -polarized ($d_{xy}a_2 \rightarrow b_2(\pi^*)$) MLCT components have been identified in RR excitation profiles of the $M(CO)_4(\alpha, \alpha'\text{-diimine})$ complexes, although the latter transition is fairly weak for a substituted phen derivative.^{14f} Consequently, the hypsochromic shift observed on cooling the complex to an 80 K EPA glass (see Figure 1) is entirely consistent with these MLCT assignments. The strongest two MLCT features at 80 K, which now appear resolved in the spectrum at 444 and 468 nm, are attributed to the $a_1 \rightarrow b_2^*$ and $b_2 \rightarrow b_2^*$ transitions, respectively, in accordance with the above interpretation.

Luminescence spectra have been recorded for 400-nm excitation of $W(CO)_4(4\text{-Me-phen})$ in deoxygenated room-temperature solution and a low-temperature frozen glass. In each case dual emission bands are observed; these are centered at 585 and 782 nm (benzene, 293 K) and at 527 and 677 nm (EPA, 80 K). Only a weak emission band at 584 nm and a long tail in the emission with a maximum longer than 780 nm have been observed in EPA solution at 293 K.^{12b} These emission bands have been previously shown to be very solvent dependent, consistent with their $^3\text{MLCT}$ assignment.^{12,16} At low temperature the higher energy emission band also comprises an overlapping ^3LF transition which is believed to be the dominant feature.^{12b} It should be noted that the lowest energy $b_2 \rightarrow b_2^*$ $^3\text{MLCT}$ band significantly blue shifts when the solution is cooled to 80 K and forms a rigid glass. This effect, known as "luminescence rigidochromism", is recognized for a number of substituted metal carbonyl complexes^{10,11b,12,17,18} and is discussed further below.

Polymer Films. The electronic absorption spectrum recorded from the TMPTA/PMMA thin film with incorporation of the benzophenone photoinitiators and the $W(CO)_4(4\text{-Me-phen})$ probe complex is shown in Figure 2. The main feature, centered at 353 nm, is due to the photoinitiator absorption. It should be noted that the organometallic complex is present in only low concentration (0.3% by weight), and so its MLCT features absorb very weakly ($A < 0.1$) between 400 and 550 nm.

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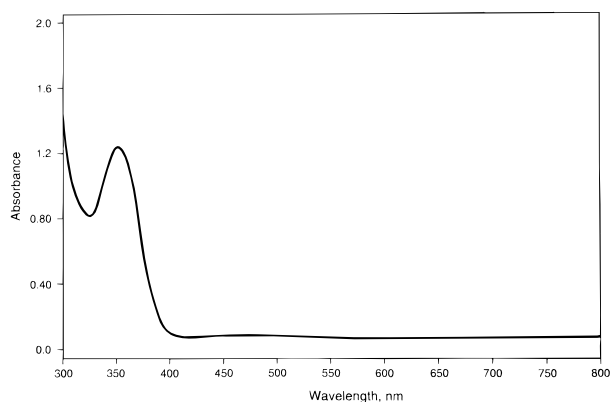


Figure 2. Electronic absorption spectrum of a TMPTA/PMMA thin film containing the benzophenone photoinitiators and $W(CO)_4(4\text{-Me-phen})$ at 293 K.

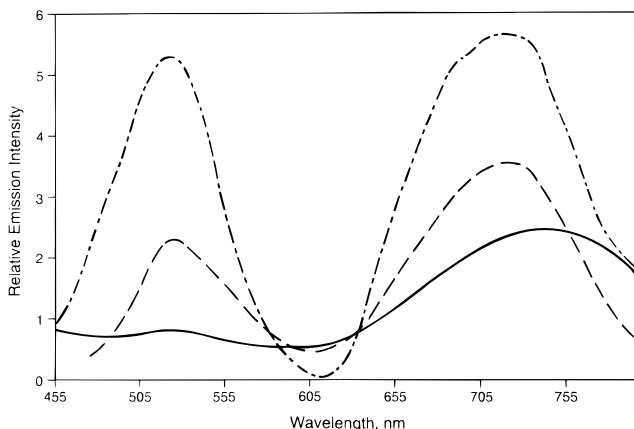


Figure 3. Emission spectra of a TMPTA/PMMA thin film containing $W(CO)_4(4\text{-Me-phen})$ and the benzophenone photoinitiators after (—) 0 s, (---) 10 s, and (- - -) 60 s UV exposure at 293 K. Excitation wavelength is 400 nm in each case.

Indeed, the complex does not undergo photodecomposition when it is present in the acrylate film and excited with UV light; this is because the photoactive LF states are masked by the strong photoinitiator absorption. Significantly, no changes were observed in this absorption spectrum upon exposing the thin film to UV light at 366 nm from the mercury lamp.

Luminescence spectra have been acquired from the TMPTA/PMMA film incorporating the benzophenone photoinitiators and organometallic probe complex at various irradiation times; these results are shown in Figure 3. Prior to UV light exposure the characteristic dual $^3\text{MLCT}$ emission bands of $W(CO)_4(4\text{-Me-phen})$ were recorded at 520 and 750 nm. It is notable that the higher energy band is of considerably lower intensity, and, indeed, this spectrum is very similar to that observed for the complex in solution.^{12b} Following UV light excitation for 60 s, however, the emission maxima shift to 525 and 715 nm, respectively, and it is noticeable that these two emission bands become almost equal in intensity. Luminescence spectra have also been obtained from the acrylate films without the incorporation of the metal complex. In the absence of added organometallic probe there was no detectable emission from an unexposed thin film sample but, importantly, on UV excitation substantial emitted and scattered light was detected in the region between 420 and 620 nm. Consequently, the intensity increase of the higher energy emission band is attributed to this increased

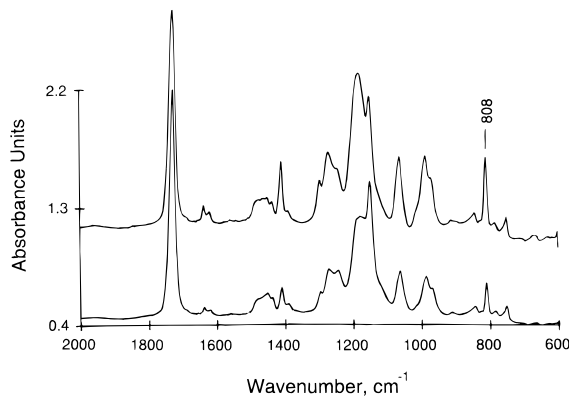


Figure 4. ATR infrared spectra of the photosensitive TMPTA/PMMA thin film before (top) and after (bottom) 120 s of UV exposure.

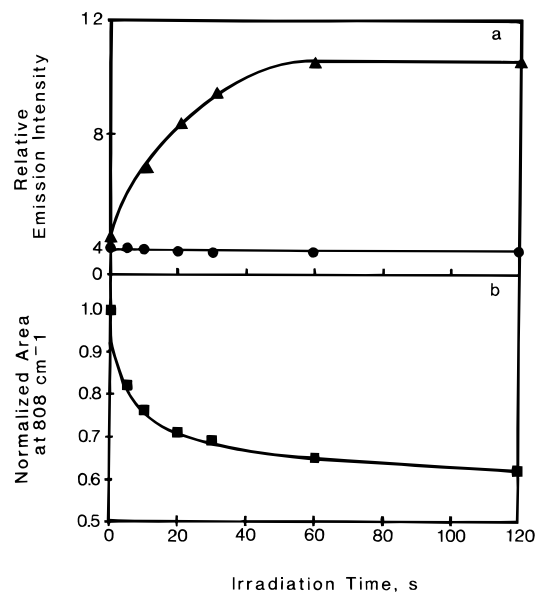


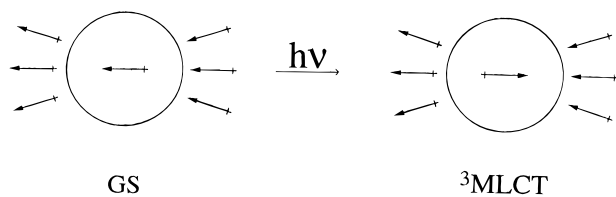
Figure 5. (a) Plots of emission intensity at 715 nm of $W(CO)_4(4\text{-Me-phen})$ in a TMPTA/PMMA thin film as a function of UV irradiation time (▲) with and (●) without photoinitiator. Excitation wavelength is 400 nm in each case. (b) Plot of normalized area of acrylate monomer band at 808 cm^{-1} in the photosensitive thin film as a function of UV irradiation time.

scattered light from the polymer surface. On the other hand, the lower energy emission feature cannot be associated with the thin-film emission or scattered light and is exclusively assigned to the $^3\text{MLCT}$ emission from the organometallic probe complex.

The photopolymerization reaction has also been monitored by ATR infrared spectroscopy. Figure 4 depicts the FTIR spectra recorded from the TMPTA/PMMA thin film before and after UV light exposure. The absorption band at 808 cm^{-1} corresponds to the CH_2 wagging vibration of the acrylate monomer and, therefore, the change in its intensity represents the extent of the cross-linking reaction taking place.¹⁹ Figure 5 illustrates a plot of the normalized area of this band at 808 cm^{-1} as a function of irradiation time. These results clearly show that the acrylate monomer is substantially consumed over the first 60 s of UV excitation. As a comparison, Figure 5 also illustrates the observed changes in the $^3\text{MLCT}$ emission intensity at 715 nm as a function of UV irradiation time, revealing a concomi-

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Scheme 1



tant increase in the probe's phosphorescence as the acrylate monomer is consumed. This emission intensity increase can be attributed to a reduction in the nonradiative relaxation processes of the organometallic complex as the polymer matrix becomes more rigid.^{8,10} No further increase in emission intensity at 715 nm was observed after 60 s of UV excitation. Moreover, in the absence of added photoinitiator the emission intensity of the organometallic probe in the TMPTA/PMMA resin was determined to remain constant, indicating that the probe complex does not undergo photochemical decomposition or itself initiate polymerization in these thin films.

Rigidochromism. As noted above, the substantial blue-shift in the lowest energy emission maximum of $W(CO)_4(4\text{-Me-phen})$ as the solvent medium is cooled and becomes more rigid is an example of "luminescence rigidochromism".^{17,18} This phenomenon is rationalized by considering the variations in dipolar interactions between the 3MLCT excited state of the complex and the local solvent dipoles of the surrounding medium; see Scheme 1.¹³ In the ground state (GS) the solvent molecules surrounding the organometallic complex will be oriented to accommodate its dipole moment. For a substituted metal carbonyl species, such as $W(CO)_4(4\text{-Me-phen})$, the dipole moment of the 3MLCT excited state is understood to be reversed from that of the ground state,^{18b,20} in accordance with the charge-transfer nature of the transition. Thus, immediately following excitation the excited-state dipole moment will be destabilized by its environment, until the solvent molecules reorient to permit a more favorable electrostatic interaction. In the case of a nonrigid solution this relaxation process will occur readily, but in a more rigid situation the solvent rearrangements will be restrained. The net result will be a destabilization of the 3MLCT excited state in the rigid environment (see Figure 6) and a shift of the emission band to higher energies.

Through a series of recent experiments involving $fac\text{-}XRe(CO)_3L$ in thermosetting diepoxide resins, the rigidochromic shift in the emission has been directly correlated with the viscosity changes taking place in the environment around the metal complex.⁸ In the case of the $W(CO)_4(4\text{-Me-phen})$ system, it is the lowest energy 3MLCT emission band (assigned above as the $b_2 \rightarrow b_2^*$ transition) which displays this distinctive energy shift as the polymer is formed. The upper emission band of the $W(CO)_4(4\text{-Me-phen})$ complex may also be moving, but it is a weak emission and becomes masked by the scattered light from the sample surface during photopolymerization.

The observed change in the lowest energy band from 750 nm in the unexposed thin film to 715 nm in the

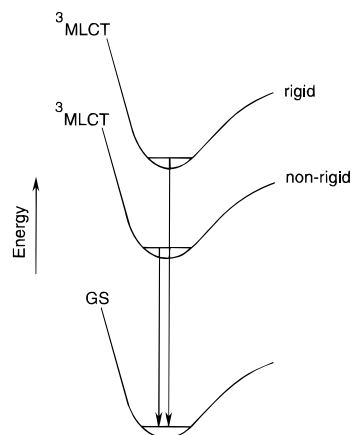


Figure 6. Schematic representation of the emission from the 3MLCT excited state in rigid and nonrigid environments.

UV-irradiated material is equivalent to a hypsochromic shift of 653 cm^{-1} . This is considerably greater than the corresponding shift of 432 cm^{-1} observed from the $fac\text{-}ClRe(CO)_3(4,7\text{-Ph}_2\text{-phen})$ ($4,7\text{-Ph}_2\text{-phen} = 4,7\text{-diphenyl-1,10-phenanthroline}$) complex in the identical TMPTA/PMMA (1:1 by weight) thin film.⁹ Clearly, the acrylate cross-linking reaction is able to impart a substantial "rigidochromic effect" on the lowest energy $b_2 \rightarrow b_2^*$ luminescence feature of $W(CO)_4(4\text{-Me-phen})$. Significantly, the 3MLCT emission band is positioned in the red region of the spectrum and well removed from the spectral properties of the acrylate resin and photoinitiators. Thus, the $W(CO)_4(4\text{-Me-phen})$ complex is useful as a spectroscopic probe in monitoring the extent of photopolymerization taking place in these thin films.

Summary

The complexes $W(CO)_5(4\text{-CN-py})$ and $W(CO)_4(4\text{-Me-phen})$ have been incorporated in UV-curable trimethylolpropane triacrylate/poly(methyl methacrylate) thin films and investigated as luminescent probes of acrylate polymerization. The $W(CO)_5(4\text{-CN-py})$ complex undergoes significant thermal degradation in the resin and was not found to be useful as a spectroscopic probe. In contrast, the $W(CO)_4(4\text{-Me-phen})$ complex was determined to be soluble and thermally stable in the acrylate photoresist, and it exhibits a number of desirable molecular probe characteristics. These include an intense metal-to-ligand charge-transfer absorption band envelope which is situated in the visible region and removed from the photoinitiator absorption. Hence, only low concentrations of the complex need to be employed. Also, the complex exhibits low-lying triplet-centered excited states which readily undergo luminescence in solution and facilitates detection in the red region of the spectrum. Significantly, the position of the lowest energy emission band of $W(CO)_4(4\text{-Me-phen})$ is subject to an environmental effect and undergoes a distinctive hypsochromic shift as the acrylate cross-linking reaction progresses.

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