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Communications

The Luminescent *fac*-ClRe$(CO)_3$(4,7-Ph_2phen) Complex as a Spectroscopic Probe in Monitoring Photochemical Polymerization of Epoxy Resins

Epoxy resins which are cured with the aid of UV light have found a wide range of commercial applications ranging from offset inks and adhesives to photoresist materials used in the microelectronics industry.[1] In each of these applications, it is desirable to have a knowledge of the physical state of the material as the cure of the epoxy resin progresses, yet it is experimentally difficult to obtain this information from thin-film and coating materials. Previous studies have employed various fluorescent probe materials to monitor the thermal cross-linking of epoxy resin materials with some success.[2] However, few studies have concentrated on probing photochemical cross-linking reactions using luminescent probes. In 1986 Meijer and Zwiers 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 utilized a fluorescence polarization technique to determine the cure state of a photopolymer.[4]

Previous work in our laboratory has focused on the use of transition-metal complexes that emit visible light to monitor the thermal cure of epoxy resins and the photocure of various acrylate-based polymers.[5,6] The present report deals with a new approach to monitoring the cure of photoinitiated cationic epoxy polymerization in thin films using a rhenium organometallic complex which acts as a luminescent probe; this complex has intense absorption and emission features in the visible region which are well removed from those of the photoinitiator, a triarylsulfonium hexafluoroantimonate salt. Metal complexes with the general formula *fac*-XRe$(CO)_3$L [X = Cl, Br, I; L = 1,10-phenanthroline (phen) or a substituted phen] have been previously shown to be strongly emissive in room-temperature solution and in organic glasses at 77 K. The emission features are associated with the lowest lying triplet-centered metal-to-ligand charge-transfer (MLCT) excited state in which electronic transitions take place between a metal-centered molecular orbital and a π^* orbital centered on the phen ligand.[7] An interesting feature of these complexes is that the luminescence characteristics are greatly affected by solvent polarity and the rigidity of the surrounding matrix, the latter being referred to as "luminescence rigidochromism".[5,7,8] In general, a more intense, longer lived, and hypsochromically shifted emission is observed as the environment becomes more rigid. Here, we demonstrate that the complex *fac*-ClRe$(CO)_3$(4,7-Ph_2phen) (4,7-Ph_2phen = 4,7-diphenyl-1,10-phenanthroline) exhibits luminescence upon incorporation into thin films of a UV-curable mixed-epoxy coating and that this can be employed as a spectroscopic probe in the visible region to monitor the extent of this important photochemical curing reaction.

The organometallic probe, *fac*-ClRe$(CO)_3$(4,7-Ph_2phen), was synthesized by refluxing ClRe$(CO)_5$ with an excess of ligand in benzene according to a literature method.[7] The photosensitive mixed-epoxy system was formulated by adding 10 g of bisphenol A-novolac resin (SU8, Interz, Inc.) as a 50 wt % solution in methyl amyl ketone to 20 g of the diglycidyl ether of bisphenol-A (DGEBA, Aratronics 5001, Ciba-Geigy). To this were added 2.5 g of a 50 wt % propylene carbonate/triarylsulfonium hexafluoroantimonate photoinitiator (Cyracure UVI-6974, Union Carbide) and 0.002 g of the probe complex. Samples for luminescence studies were prepared by coating the epoxy/probe mixture onto 0.051 mm thick polyester sheeting using a coating knife with a 0.254-mm gap. 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. After coating, the epoxy samples were air-dried for 1 h followed by a preexposure bake for 10 min at 348 K. The resulting films were exposed in air using a 350-W Oriel mercury lamp for the specified irradiation times. Typical lamp intensities were 3.5 mW/cm^2 as measured using an International Light Model IL7000 radiometer. Following light exposure, the epoxy films were again heated at 348 K for 10 min.

Emission spectra were collected on a SLM Instruments Model 8000/8000S spectrometer that incorporates a red-sensitive Hamamatsu R928 photomultiplier tube. Spectra were obtained by orienting the epoxy film at an angle of 20° to the incident light and by excitation at 420 nm (note: the photoinitiator does not absorb light at this wavelength). Infrared spectra were recorded as absorbance spectra on an IBM Instruments IR/98 FTIR spectrometer. The reaction was monitored by observing the

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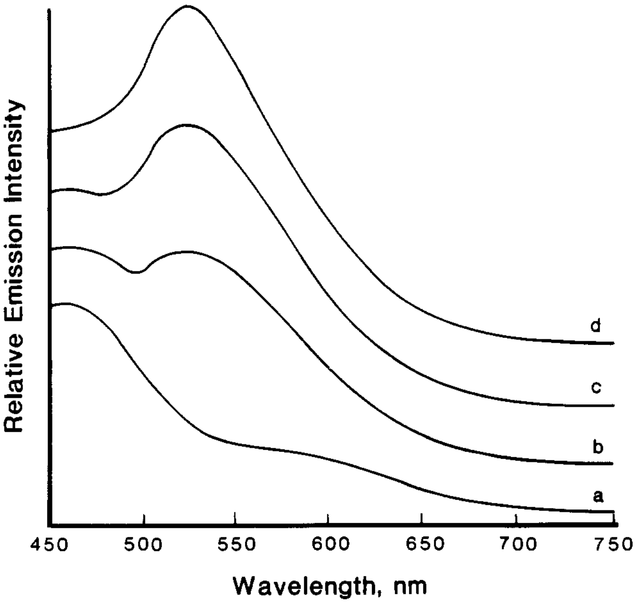

Figure 1. Luminescence spectra of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in thin films of the mixed-epoxy/photoinitiator system at 293 K after (a) 0 s, (b) 15 s, (c) 30 s, and (d) 60 s of UV irradiation. The spectra are uncorrected for variations in photomultiplier tube response and were recorded with an excitation wavelength of 420 nm. The spectra are vertically displaced for clarity.

disappearance of the epoxy ring vibration at 916 cm^{-1}, using the phenyl absorbance at 1609 cm^{-1} as an internal calibrant.[9]

Irradiation of the photosensitive epoxy/probe mixture was carried out with the incorporation of the cationic photoinitiator. Figure 1 shows emission spectra from *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) in the photosensitive mixed-epoxy system recorded following various irradiation times. It is evident that in each case the epoxy/probe mixture gives rise to dual-emission features. The high-energy band at 460 nm is observed even with exclusion of the organometallic probe, and it is attributed to Raman-scattered light arising from the epoxy material itself. Indeed, this emission band was found to energy-shift concomitantly with variations in the excitation wavelength. In contrast, the low-energy band is observed only upon incorporation of *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) and is clearly due to the MLCT luminescence of the metal complex.[7,8,10] The MLCT emission band intensity increases by a factor of approximately 5.5 during the photolysis sequence; it appears initially as a shoulder at 581 nm, and it subsequently shifts to 522 nm after irradiation (this corresponds to a hypsochromic shift of 1945 cm^{-1}). The substantial increase in the MLCT emission intensity is attributed to a decrease in the nonradiative relaxation pathways of the metal complex during the photochemical cross-linking reaction of the epoxy material. Qualitatively, the changes in the vibrational and rotational nonradiative decay pathways are attributed to the increasing rigidity of the matrix and the corresponding reduction in the matrix free volume. Previously, this effect has been investigated for fluorescent probe systems by Loufty et al.,[11] who determined that the nonradiative decay rate constant (k_{nr}) decreases exponentially with decreasing polymer free volume. The large rigidochromic shift (1945 cm^{-1}) in the MLCT maximum of the probe complex can be attributed to the highly polar nature of the cured epoxy network [δ = 9.7–10.9 (cal/cm^3)$^{1/2}$][12] and the rearrangement of the local dipoles around the excited-state molecular probe species. As the cross-linking reaction proceeds and the microviscosity increases, there will be a reduction in the random solvent orientation in the polymer matrix and the rearrangement of the solvent molecules about the probe complex will be increasingly sluggish.

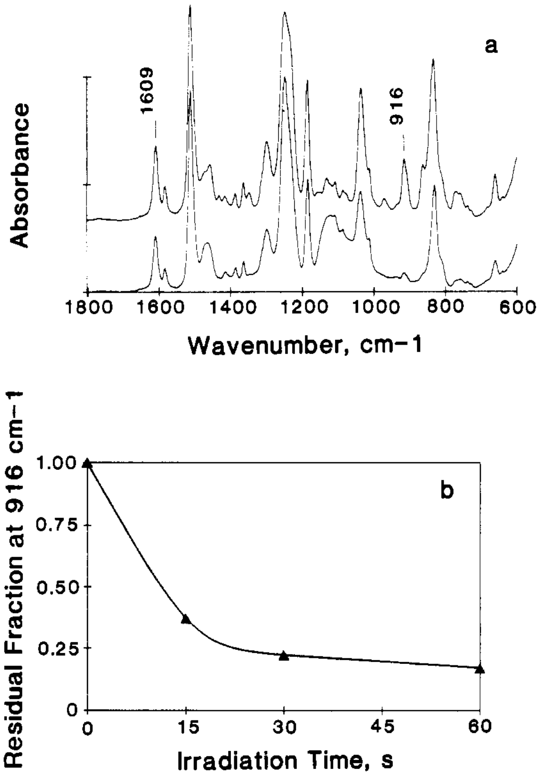

Figure 2. (a) FTIR spectra of thin films of the mixed-epoxy/photoinitiator systems at 293 K: top spectrum recorded before irradiation; bottom spectrum recorded after 60 s of UV irradiation. (b) Plot of normalized area of epoxy vibration at 916 cm^{-1} as a function of UV irradiation time in the thin-film mixed-epoxy/photoinitiator system.

Figure 2a shows FTIR spectral data obtained from 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. It is noteworthy that toward the end of the photolysis sequence the IR spectra show little change (see Figure 2b), whereas the emission band of the probe continues to grow. We note that while the IR spectra reflect the concentration of the epoxy functional groups, the luminescence results from the phosphorescent probe molecule may be providing a better representation of the degree of cross-linking and the microviscosity changes in these thin polymer films. This aspect is currently being further investigated.

In summary, we have found that the luminescence properties of the organometallic complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$phen) are most useful for monitoring the important photoinitiated cationic polymerization reactions of epoxy resin materials. These metal complexes lend themselves well to this application, as they are readily soluble in organic media of varying polarities, they are thermally and photochemically stable throughout the polymerization process, and they possess spectroscopic (absorption and emission) properties that enable them to be used as a probe material without interfering with the photoinitiator chemistry. Currently, we are further investigating the use of such visible-probe compounds in a wide range of polymerization reactions including both thermal-based and photobased systems.

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Is CrF_6 Octahedral? Experiment Still Suggests "Yes!"

The synthesis of CrF_6 was first reported in 1963 by Glemser et al.,[1] who prepared a volatile yellow material with a Cr:F atom ratio of ca. 1:6 from the reaction between chromium and fluorine at high temperature and pressure (400 °C/ca. 300 atm). This synthesis does not appear to have been successfully repeated, but in 1985, Hope et al.[2] prepared a very similar material (yellow, volatile, Cr:F = 1:5.7) from the fluorination of CrO_3 and obtained IR and UV/vis data consistent with those expected for octahedral CrF_6. Since this latter characterization, two papers have appeared which cast doubt on the existence of this molecule. The first of these was by Jacob and Willner[3] (J&W), who concluded that the yellow material was CrF_5, while a theoretical paper by Marsden and Wolynec[4] predicted that if CrF_6 were to exist, its ground-state geometry would be a trigonal prism. The purpose of this communication is to reaffirm our belief that the yellow volatile material is indeed CrF_6 and that it is almost certainly octahedral.

First, we examine the spectroscopic arguments put forward by J&W and suggest that their characterization of this material as CrF_5 is not consistent with the experimental data. Second, we examine whether the results may be interpreted on the basis of the predicted[4] prismatic structure for CrF_6.

Before embarking on this discussion however, it is important to stress the very satisfactory agreement between our original[2] spectroscopic data and the results subsequently reported by J&W.[3] Both research groups carried out matrix isolation studies on a volatile yellow fluoride of chromium and obtained IR spectra showing a single intense absorption in the Cr–F stretching region at ca. 760 cm^{-1}. Both groups observed chromium isotope structure on this feature, and J&W also reported a weaker absorption in the bending region close to the frequency predicted in the initial matrix study.[2] There is no question but that we are discussing the same species.

Our results[2] were obtained from a yellow volatile material with a stoichiometry of Cr:F = 1:5.7, but our assignment of the 760-cm^{-1} band as the T_{1u} stretch in octahedral CrF_6 is based primarily on the observed spectrum and does not rely upon the identity of the starting material. Figure 1a reproduces our high-resolution nitrogen matrix spectrum in which the experimental bandwidths for the ^{50}Cr, ^{53}Cr, and ^{54}Cr isotopic features are all ca. 0.5 cm^{-1}. Figure 1b shows the corresponding spectrum calculated for octahedral CrF_6 by assuming no coupling with the T_{1u} bend. The agreement is very satisfactory.

J&W obtained a very similar neon matrix spectrum[5] and also obtained isotope structure on the bending mode at ca. 332 cm^{-1}, but as they were unable to derive a unique force field for the T_{1u} block, they rejected our O_h CrF_6 model. However, in so doing, they neglected to take account of the possible effects of anharmonicity on the chromium isotope shifts, and when due allowance[6] is made for this, it may be shown[7] that rejection of the O_h model is premature.

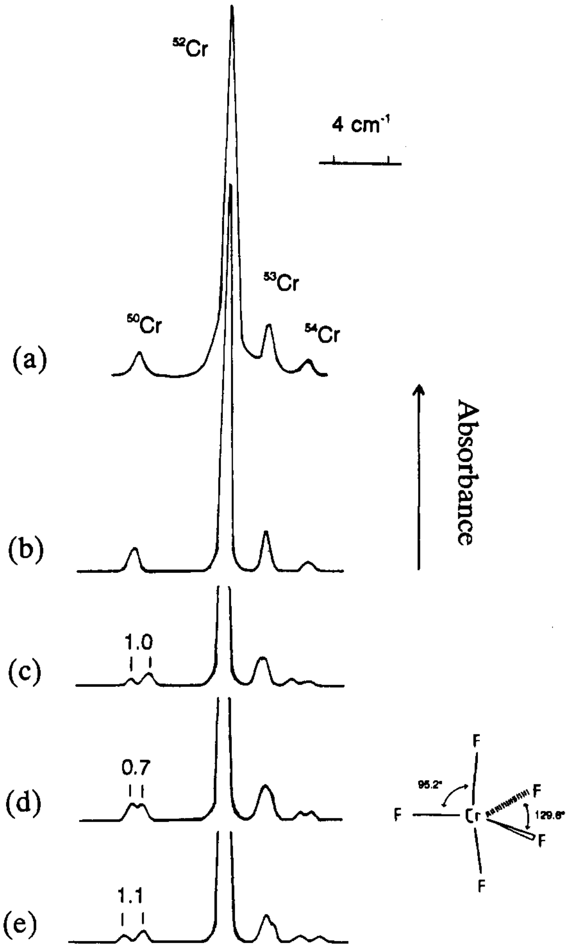

Figure 1. Observed and calculated Cr isotope patterns for the band at ca. 760 cm^{-1}, showing the effect of differential shifts: (a) high-resolution N_2 matrix IR spectrum, assigned to ν_3 O_h CrF_6; (b) spectrum calculated for ν_3 O_h CrF_6; (c) spectrum calculated for D_{3h} CrF_5 by assuming overlap of E′ and A_2'' stretching modes; (d) spectrum calculated for C_{2v} CrF_5 (model inset) by assuming overlap of B_1 and B_2 stretching modes; (e) spectrum calculated for D_{3h} CrF_6 (trigonal prism) by assuming overlap of E′ and A_2'' stretching modes.

As an alternative to O_h CrF_6, J&W propose that CrF_5 is the species responsible for the single IR-active stretch at ca. 760 cm^{-1}. Following normal convention, we therefore consider whether there is a reasonable structural model for CrF_5 which yields *one* intense IR feature in the Cr–F stretching region and also exhibits the observed isotope structure (Figure 1a). The D_{3h} trigonal bipyramid and the C_{4v} square pyramid clearly deserve consideration, and lower symmetry structures such as the C_{2v} model favored by J&W must also be examined. However, group theory predicts that all these structures will show at least *two* IR-active Cr–F stretching modes, and we must therefore consider the likelihood that two ^{52}Cr–F modes of different symmetries are separated by less than ca. 1.0 cm^{-1}.

In D_{3h} VF_5, the IR-active E′ and A_2'' stretches lie[8] at ca. 810 and 784 cm^{-1}, while, in UF_5, ClF_5, and BrF_5 (all C_{4v}), the two most intense stretches[9] are similarly separated by over 20 cm^{-1}. In view of this, we believe it to be most unlikely that there would be a near overlap of fundamentals if CrF_5 had either of these

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