Cure monitoring of a photosensitive polymer using the luminescent organometallic complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen)

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The organometallic complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) exhibits a bright yellow–orange phosphorescence centred at 576 nm in poly(methyl methacrylate)/trimethylolpropane triacrylate (PMMA/TMPTA) solutions. This luminescence feature is shown to be a useful spectroscopic probe of the acrylate crosslinking reactions in the u.v. photochemical curing of a model PMMA/TMPTA thin film system.

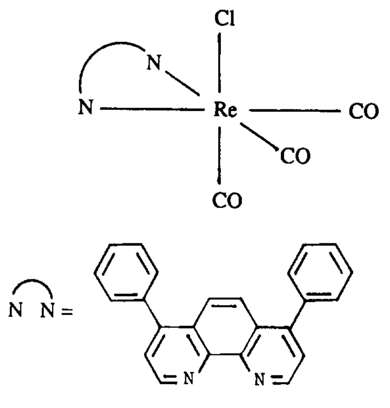
(Keywords: photosensitive polymer; acrylate; curing; luminescence; phosphorescence; organometallic)

Introduction

Photoreactive polymers form the basis of photoresist technology which constitutes an important part of the microelectronics industry[1]. Additionally, u.v. curable coatings are increasingly being used in the graphic arts, packaging, medical and dental industries. In all of these applications it is desirable to have a knowledge of the cure state of the polymer in order to insure proper material performance. Fluorescent probes have shown great utility in monitoring the cure kinetics of a variety of thermally curing systems[2–4]. In 1986 Scarlata and Ors reported a fluorescence polarization method to monitor cure in a photosensitive acrylate system[5] but, apart from this, fluorescent probes have been underexploited in photoactive systems. This is largely due to the fact that traditional fluorescent probes have intense absorption features in the u.v. spectral region which interfere with the cure process.

We wish to report here the cure monitoring of a model photosensitive system using an organometallic luminescent probe with absorption and emission features that are in the visible region and well removed from the wavelengths involved in the photoinitiator chemistry. Complexes of the type *fac*-XRe(CO)$_3$L [X = Cl, Br, I; L = 1,10-phenanthroline (phen) or a substituted phenanthroline] have been found to be strongly luminescent in the visible region in both room temperature fluid solution and low temperature glassy solutions at 77 K[6,7]. The emissions of the materials are, in each case, associated with a low lying metal-to-ligand Re(dπ) → (π^*)phen charge transfer (MLCT) excited state that is of a predominantly 'triplet' character†; these phosphorescence features have been shown to be particularly sensitive to changes in the surrounding matrix[6]. Recently, a series of these complexes have been used to monitor the thermal cure process of a model epoxy system[8].

In this communication we demonstrate that the organometallic complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) [4,7-Ph$_2$-phen = 4,7-diphenyl-1,10-phenanthroline] readily exhibits phosphorescence while incorporated in thin films of a model u.v. curable system and that this can be used as a spectroscopic probe in the visible region to monitor the extent of the photochemical crosslinking reaction. Previously, spectroscopic information of this nature has been experimentally difficult to obtain from thin film and coating materials. The probe molecule used in this study is shown below:



4,7-Ph$_2$-phen

Experimental

The organometallic complex *fac*-ClRe(CO)$_3$(4,7-Ph$_2$-phen) was synthesized according to a previously outlined method[6]. The model photosensitive system was formulated by mixing trimethylolpropane triacrylate (TMPTA; Celanese) and medium molecular weight poly(methyl methacrylate) (PMMA; Aldrich) in a 1:1 wt% ratio and then dissolving this mixture in a solution of methylene chloride:xylenes (5:2 wt%). To this was added 0.01% by weight of the probe material and 1.0% by weight of the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (Ciba-Geigy Irgacure® 651). The samples were then coated onto 0.051 mm (2 mil) thick polyester sheet using

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† The large degree of spin-orbit coupling in these rhenium carbonyl complexes precludes a 'pure' triplet designation

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a coating knife with a 0.254 mm (10 mil) gap and then dried at 85°C for 10 min. The resulting films were exposed with light from a 350 W Oriel mercury lamp and the samples were maintained under a gaseous dry nitrogen environment throughout photolysis. Typically, excitations were performed with a lamp intensity of 3.5 mW cm^{-2} as measured by an International Light Model IL7000 radiometer with a 365 nm filter.

Emission spectra and lifetime (τ_e) data were obtained on an SLM model 8000/8000S spectrometer which incorporates a red sensitive Hamamatsu R298 photomultiplier tube and photon counting capabilities[9]. Spectra were obtained by orienting the samples at 20° with respect to the incident light. Emission lifetimes were recorded in an identical experimental configuration on a PRA system 3000 time-correlated pulsed single-photon counting apparatus[9]. Samples for i.r. 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° attenuated total reflection crystal. The acrylate band at 808 cm^{-1} was determined[10] at a penetration depth of 0.75 μm. Samples were placed in a 4X beam condenser accessory from Harrick Scientific Corp. and i.r. spectra were obtained on an IBM Instruments model 98 Fourier transform infra-red (*FT*i.r.) spectrometer.

Results and discussion

Irradiation of the photosensitive PMMA/TMPTA/probe mixture was carried out using the free radical producing photoinitiator. *Figure 1* shows the emission spectra recorded from the organometallic probe *fac*-ClRe$(CO)_3$(4,7-Ph_2-phen) in the photoresist system at various photolysis times. It is evident that the intensity of the MLCT emission band increases by a factor of ~2.5 during the irradiation. Also, the emission band maximum is observed to undergo a hypsochromic shift from 576 to 562 nm (~430 cm^{-1}); this is attributed to the 'luminescence rigidochromic effect' that is recognized to occur for a number of organometallic complexes exhibiting MLCT emission in solution upon cooling through their glass transition point[6,11–13]. In general this phenomenon produces a blue shifting in the emission band maxima as the matrix viscosity increases and it is understood to arise from the variations that take place in the local solvent dipole interactions of the surrounding medium with the polar excited molecular probe species[11].

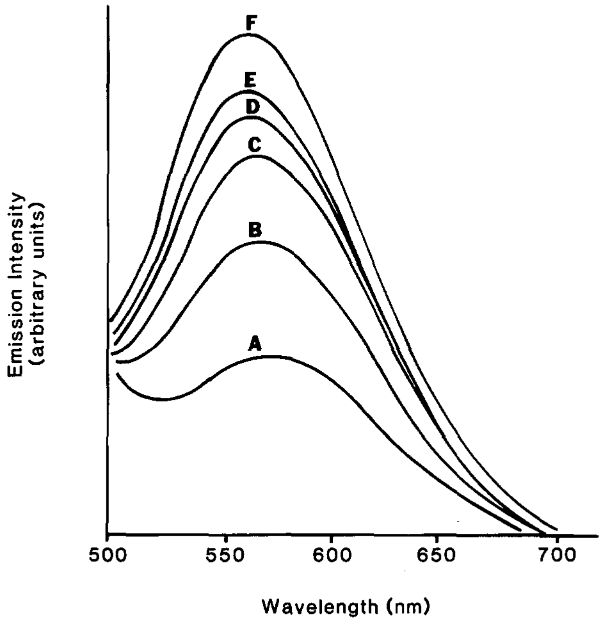

Figure 1 Emission spectra of *fac*-ClRe$(CO)_3$(4,7-Ph_2-phen) in the model PMMA/TMPTA photosensitive system as a function of irradiation time: (A) 0; (B) 5; (C) 10; (D) 20; (E) 30; (F) 60 s. The emission spectra are uncorrected for variations in photomultiplier response and the excitation wavelength is 420 nm

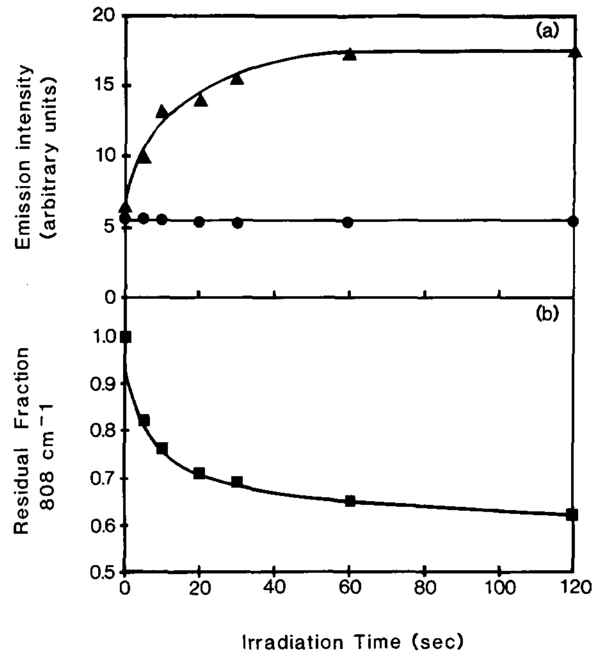

Figure 2 (a) Plots of the emission intensity (recorded at the MLCT emission band maximum) of *fac*-ClRe$(CO)_3$(4,7-Ph_2-phen) as a function of irradiation time in the model PMMA/TMPTA photosensitive system: (▲) with and (●) without added photoinitiator. The emission spectra are uncorrected for variations in photomultiplier response and the excitation wavelength is 420 nm. (b) Plot of normalized area of acrylate monomer *FT*i.r. band (recorded at 808 cm^{-1}) as a function of irradiation time in the model PMMA/TMPTA system

Figure 2a depicts the observed increase in MLCT emission intensity of the probe as a function of photolysis time. No further enhancement of the probe luminescence is observed after 60 s of irradiation has elapsed. In the absence of added photoinitiator the luminescence intensity of the probe in the PMMA/TMPTA mixture remains constant (*Figure 2a*) indicating that the probe does not undergo significant photodegradation or itself initiate polymerization in the film. *Figure 2b* reflects the change in intensity of the *FT*i.r. band at 808 cm^{-1} during this photochemical curing reaction. This band corresponds to the CH_2 wagging vibration of the residual fraction of the acrylate monomer and its intensity variation, therefore, monitors the extent of the crosslinking that takes place. Taken together, the data of *Figure 2* clearly demonstrate that there is a concomitant increase in the phosphorescence of the probe as the acrylate monomer is consumed and the crosslinking reaction proceeds.

Excited state lifetimes (τ_e) measured from the *fac*-ClRe$(CO)_3$(4,7-Ph_2-phen) complex increase by a factor of ~3 during curing, from 0.85 μs in the unirradiated sample to 2.5 μs in a sample that had been irradiated for 120 s. The radiative (k_r) and non-radiative (k_{nr}) rate constants can be interrelated with the experimental quantum yield (ϕ_e) and lifetime (τ_e) data, according to equations (1) and (2):

$$k_r = \phi_e/\tau_e \tag{1}$$

$$\tau_e = 1/(k_r + k_{nr}) \tag{2}$$

The observed changes in emission intensity and lifetime suggest that during the photochemical curing k_r changes very little and that the increase in the lifetime is mainly due to a decrease in k_{nr}. This relationship has been previously examined in the context of decreasing free volume during the polymerization of methyl methacrylate by Loufty[14]. In general, it was found that k_{nr} demonstrated an exponential dependence on polymer free volume, this parameter decreasing as the free volume is reduced. Thus, the present study appears to be analogous in that the observed increase in the emission intensity is a consequence of the microscopic changes in the free volume of the polymer matrix and their subsequent effects on the rotational and vibrational non-radiative decay pathways of the organometallic probe complex.

Conclusions

We have described a new technique which allows the reaction of u.v. curable acrylate monomers to be monitored as thin film materials. The phosphorescence properties of organometallic complexes make them useful spectroscopic probes of polymer viscosity and free volume without interfering with the absorption characteristics of either the acrylate, crosslinking agents or photoinitiator moieties.

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