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Ferrocenes as Anionic Photoinitiators

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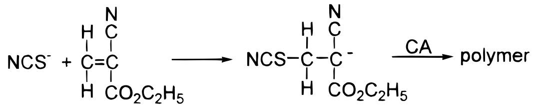
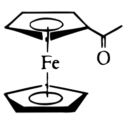
Photopolymerization reactions play a prominent role in important technologies such as the ultraviolet curing of protective coatings, the optical storage/output of visual information, and the photolithographic patterning of electronic components.[1] The light-sensitive compositions used for these purposes generally contain a photoinitiator system which, upon irradiation, releases a radical and/or an acid.[2] In a subsequent thermal step, these reactive species initiate polymerization of a monomer via radical and/or cationic pathways. The possibility that photoinitiated polymerization can occur by an anionic mechanism had been largely overlooked prior to our recent studies[3,4] of *trans*-$Cr(NH_3)_2(NCS)_4^-$ and $Pt(acac)_2$ ($acac^-$ is acetylacetonate) dissolved in neat ethyl α-cyanoacrylate (abbreviated CA). We observed that photolysis of each complex generates a species (NCS^- in the case of the *trans*-$Cr(NH_3)_2(NCS)_4^-$) that rapidly attacks the carbon−carbon double bond of the electrophilic monomer to yield a resonance-stabilized carbanion (eq 1). Polymerization then proceeds via the repetitive addition of CA units to the growing anionic chain.

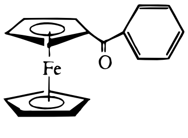


$$NCS^- + H_2C{=}C(CN)CO_2C_2H_5 \longrightarrow NCS{-}CH_2{-}C^-(CN)CO_2C_2H_5 \xrightarrow{CA} \text{polymer} \qquad (1)$$

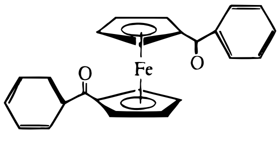
Our search for new classes of anionic photoinitiators led us to examine several members of the ferrocene family, **I**−**III**. These organometallic sandwich complexes dissolve in a broad range of nonaqueous solvents,



I



II



III

possess excellent thermal stability in the solid state and solution, and absorb strongly in the ultraviolet and, in some cases, in the visible wavelength regions (Figure 1). Ease of synthesis, modest cost, and low environmental impact are further attractive features. Ferrocene complexes have a long history of use in photoinitiator systems that generate radical or cationic initiating species.[5,6] Our studies of **I**−**III** provide the first evidence that ferrocenes also can function as effective anionic photoinitiators.[7]

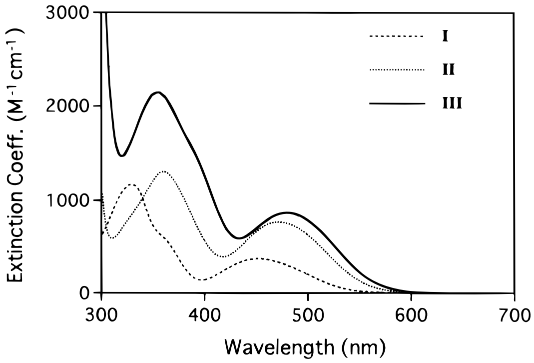


Figure 1. Electronic absorption spectra of **I**−**III** in room-temperature ethyl α-cyanopropionate.

Commercially available samples of **I**−**III** were further purified by sublimation or recrystallization from *n*-hexane. Neat CA (99.9% purity) was obtained from Loctite Corp. as a colorless liquid that contained hydroquinone and methanesulfonic acid as scavengers for adventitious radical and basic impurities, respectively. The monomer is unaffected by prolonged (>6500 s) exposure to the Pyrex-filtered output (>290 nm) of a 200-W high-pressure mercury-arc lamp. Solutions of CA containing $(1.1-1.9) \times 10^{-3}$ M **I**−**III** exhibit no visible change in viscosity for several days to several weeks when stored in the dark at room temperature. Upon exposure to light, however, these solutions polymerize to a viscous syrup, which then solidifies. Data summarized in Table 1 reveal that this photoinitiated process occurs most rapidly for samples containing the benzoyl-substituted ferrocenes (compare runs a, b, and d). 1,1′-Dibenzoylferrocene, **III**, is a particularly effective photoinitiator that functions at wavelengths well into the visible region (runs e and f).

Rates of photoinitiated polymerization were determined for CA solutions of **III** by real-time Fourier transform infrared spectroscopy.[8,9] The short sampling time (300 spectra collected per minute) and sensitivity to molecular structure of this technique allow the rapid and accurate measurement of monomer concentration during irradiation. The extent of polymerization in a sample is defined by eq 2, where A_o denotes the initial

$$\%\ \text{polymerization} = \frac{(A_o - A_t)}{A_o} \times 100 \qquad (2)$$

(dark) integrated absorbance of the C=C stretching band of CA at 1616 cm^{-1} and A_t is the integrated absorbance after irradiation for time *t*. As seen in Figure 2, polymerization commences within the first few seconds following exposure to light and reaches a plateau within 10−15 s at the highest photoinitiator concentration. The rate of photoinitiated polymerization, R_p, can be calculated from eq 3, where A_{t1} and A_{t2}

$$R_p = \frac{M(A_{t1} - A_{t2})}{A_o(t_2 - t_1)} \qquad (3)$$

represent the integrated absorbances of the 1616 cm^{-1}

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Table 1. Studies of I–III as Photoinitiators for the Polymerization of CA

run[a]	photoinitiator (PI)	PI concentration mol/L × 10^3 (ppm)	λ_{ex}, nm	photopolymerization time,[b] s
a	**I**	1.89 (404)	>290	552
b	**II**	1.46 (404)	>290	176
c	**II**	1.90 (523)	436[c]	>900
d	**III**	1.07 (403)	>290	3.1
e	**III**	1.61 (605)	436[c]	38
f	**III**	2.40 (902)	546[d]	31

[a] General conditions: a 2-mL sample of CA containing the indicated concentration of photoinitiator was irradiated with stirring in a 1-cm rectangular plastic (methacrylate) cell. The excitation source was a 200-W high-pressure mercury lamp. No attempt was made to exclude air from the sample. [b] Irradiation time required for the sample to become so viscous that the 8-mm stirring bar ceased to spin. [c] Sample absorbance = 1.0; light intensity = 7.8 × 10^{-8} einstein/s. [d] Sample absorbance = 0.7; light intensity = 1.2 × 10^{-7} einstein/s.

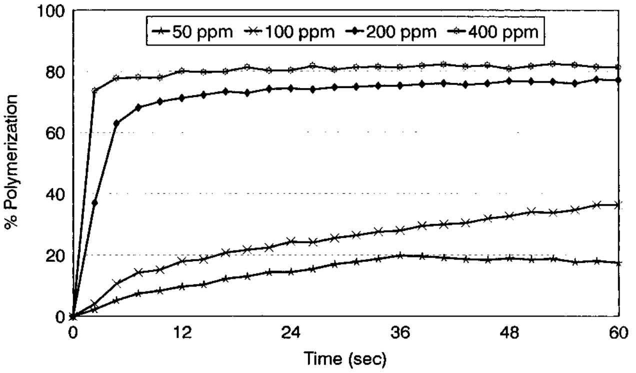

Figure 2. Plots of percentage polymerization vs time of irradiation for samples of CA containing the indicated amounts of **III** (400 ppm = 1.1 × 10^{-3} M). Thin films of these samples were coated onto acid-treated silicon wafers and irradiated with an unfiltered 100-W high-pressure mercury lamp having a power of 27 mW/cm^2 at 366 nm.

band at the indicated times, and *M* is the molar concentration of vinyl groups in CA. Maximum rates of 6.4, 3.4, and 0.8 M·s^{-1} result for samples containing 1.1 × 10^{-3}, 5.5 × 10^{-4}, and 2.8 × 10^{-4} M concentrations of **III**, respectively. The trend toward faster rates at higher photoinitiator concentrations reflects the greater fraction of light absorbed by the sample and the corresponding increase in the concentration of the photogenerated species responsible for initiating polymerization.

The nature of this reactive species was probed in a series of scavenging experiments. Neither molecular oxygen nor added hydroquinone (up to 0.032 M), known radical scavengers, affect the rate of photoinitiated polymerization in CA solutions containing **I**–**III**. Initiation by photogenerated radicals thus appears to be unlikely in these systems. In contrast, methanesulfonic acid strongly inhibits polymerization. This effect is clearly depicted in Figure 3, where increasing acid concentrations are seen to lengthen the induction period and lower the polymerization rate. We attribute this inhibition by strong acid to the ability of protons to scavenge photogenerated anions and/or anionic sites on the growing polymer chain.

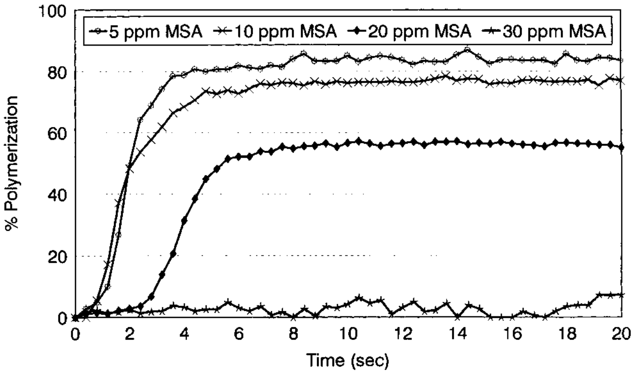

Figure 3. Effect of added methanesulfonic acid (MSA) on the photoinitiated polymerization of CA in the presence of 400 ppm (1.1 × 10^{-3} M) of **III**. See the caption to Figure 2 for experimental details.

Further information about the anionic initiating species was obtained by photolyzing **III** in ethyl α-cyanopropionate (abbreviated CP), a nonvinylic analogue of CA that cannot undergo polymerization. A 3-mL solution of CP containing 1.08 × 10^{-3} M **III** was irradiated at 546 nm for 480 s. Thereupon, a 0.5 g aliquot of the photolyte was added to 2.0 g of CA and the time required for polymerization determined. Repeating this experiment for a second aliquot of the photolyte that had sat in the dark for 24 h prior to addition to CA yielded the identical polymerization time (17 min). This finding, when coupled to the scavenging results described above, demonstrates that the photolysis of **III** generates a long-lived anionic initiator. While the identity of this species is currently unknown, one possibility is a carboxylate anion. Thus, precedent exists for the generation of benzoate from **II** via the photoaquation of the carbonyl group accompanied by ring-metal and ring-carbonyl cleavage (eq 4; S is solvent).[10] In support of this suggestion,

$$\mathbf{II} \xrightarrow[H_2O]{h\nu,\ S} (\eta^5\text{-}C_5H_5)Fe(S)_3^{+} + C_6H_5COO^{-} + C_5H_6 \quad (4)$$

we find that benzoate effectively initiates CA polymerization, as evidenced by the immediate solidification that occurs when a suspension of sodium benzoate in acetonitrile comes in contact with the monomer.[11] A second possibility, electron transfer from the photoexcited ferrocene complex to CA, appears less likely on grounds that we find no evidence for a charge-transfer-to-solvent band in the electronic absorption spectrum of **III**/CA solutions, nor do we observe spectral changes consistent with the photogeneration of a ferricenium complex.[12]

Disappearance quantum yields (ϕ_{dis}) were determined for **II** and **III** in CP solutions irradiated at 546 nm. The extent of photolysis was calculated from the decrease in intensity of the long-wavelength absorption band of each complex (Figure 1). The finding that **III** (ϕ_{dis} = 0.28) is considerably more photosensitive than **II** (ϕ_{dis} = 0.035) implies that the greater effectiveness of the former complex as an anionic photoinitiator (Table 1) arises from its more efficient photochemical generation of the active initiating species.

In summary, **I**–**III** comprise an interesting new class of anionic photoinitiators that can be added to the short but growing list of transition metal complexes that function in this role.[3,4,13] Further studies of these and related members of the ferrocene family are underway with the goal of elucidating the key photochemical and thermal steps responsible for anion formation.

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(10) Ali, L. H.; Cox, A.; Kemp, T. J. *J. Chem. Soc., Dalton Trans* **1973**, 1468−1475. In our experiments, no attempt was made to remove trace amounts of water from CA.

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