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Classical Metallocenes as Photoinitiators for the Anionic Polymerization of an Alkyl 2-Cyanoacrylate

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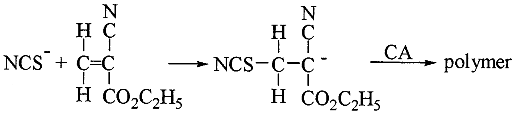
ABSTRACT: The classical metallocenes, ferrocene and ruthenocene, dissolve readily in neat ethyl 2-cyanoacrylate (CA) monomer. The electronic spectra of the resulting solutions display a near-ultraviolet absorption band assigned as a charge-transfer-to-solvent (metallocene → CA) transition. Irradiation into this band causes the one-electron oxidation of the metallocene to the corresponding metallocenium cation accompanied by reduction of CA to its radical anion. Addition of the latter species to CA initiates the anionic polymerization of the electrophilic monomer. The progress of photoinitiated polymerization was monitored in real time by attenuated total reflectance infrared spectroscopy.

I. Introduction

Studies conducted in this and other laboratories have provided several examples of photoinitiated anionic polymerization. Effective photoinitiators for this process include inorganic complexes such as *trans*-$Cr(NH_3)_2(NCS)_4^-$ [1] and $Pt(acac)_2$ ($acac^-$ is acetylacetonate),[2,3] organometallic complexes such as 1,1′-dibenzoylferrocene[4−6] and $M(CO)_5L$ (M is Cr or W; L is pyridine or vinyl-substituted pyridine),[7] alkylaluminum porphyrins,[8,9] pyridinium[10] and phosphonium[11] salts, and leuco dyes.[12] Despite substantial differences in structure and chemical properties, these photoinitiators share in common the mechanistic trait of generating the active initiating species—whether an anion, uncharged Lewis base, or metal-coordinated enolate—by photoinduced cleavage of a bond in the parent compound.[13] For example, visible-light irradiation of *trans*-$Cr(NH_3)_2(NCS)_4^-$ dissolved in ethyl 2-cyanoacrylate (abbreviated CA) results in cleavage of a Cr−NCS bond (eq 1). Attack of the released NCS^- on the carbon−carbon double bond of the monomer yields a resonance-stabilized carbanion, from which chain-growth polymerization rapidly propagates by repetitive addition of CA units (eq 2).

$$\underline{\text{trans}}\text{-}Cr(NH_3)_2(NCS)_4^- \xrightarrow[CA]{h\nu} Cr(NH_3)_2(NCS)_3(CA) + NCS^- \qquad (1)$$



$$NCS^- + \underset{H}{\overset{H}{C}}{=}\underset{CO_2C_2H_5}{\overset{C\equiv N}{C}} \longrightarrow NCS{-}\underset{H}{\overset{H}{C}}{-}\underset{CO_2C_2H_5}{\overset{C\equiv N}{C^-}} \xrightarrow{CA} \text{polymer} \qquad (2)$$

Our search for new anionic photoinitiators led us to examine ferrocene and ruthenocene ($FeCp_2$ and $RuCp_2$, respectively; Cp is η^5-C_5H_5). These classical metallocenes dissolve in a wide range of nonaqueous solvents and exhibit good thermal stability in solution. Previous studies had revealed that both compounds are relatively photoinert in solvents such as cyclohexane, acetone, and methanol.[14] In carbon tetrachloride and other electron-accepting media, however, $FeCp_2$ and $RuCp_2$ form ground-state donor−acceptor (D−A) complexes with the solvent that are characterized by a charge-transfer-to-solvent (CTTS) absorption band in the near-ultraviolet region. Irradiation into this band causes the one-electron oxidation of the metallocene to the corresponding metallocenium cation accompanied by reduction of the solvent to its radical anion (eq 3).[15−20] We have observed that metallocene photooxidation also occurs in neat CA to produce an active initiating species for anionic polymerization. Reported here are spectral and photochemical results that elucidate the key steps in this charge-transfer mechanism for anionic photoinitiation.

$$FeCp_2 + CCl_4 \rightleftarrows \underset{\text{D−A complex}}{[FeCp_2,CCl_4]} \xrightarrow{h\nu} FeCp_2^+ + CCl_4^{\bullet-} \qquad (3)$$

II. Experimental Section

Ferrocene and ruthenocene (98% and 97%, respectively, from Aldrich) were further purified by vacuum sublimation. High-purity ethyl 2-cyanoacrylate (99.9% from Loctite Corp.) was used as received; the colorless liquid monomer contained hydroquinone and methanesulfonic acid as scavengers for adventitious radical and basic impurities, respectively. Ethyl 2-cyanopropionate (98.2% from TCI America) and tetrahydrofuran (reagent grade from Fisher) were used without further purification.

Electronic absorption spectra were recorded at room temperature (21 ± 3 °C) on a Varian DMS spectrophotometer. Continuous photolysis experiments were conducted with an Illumination Industries 200 W high-pressure mercury-arc lamp. The 365 nm line was isolated with a narrow band-pass (10 nm at half-height) interference filter, and light intensity at this wavelength was measured by ferrioxalate actinometry.[21] Polychromatic light of wavelengths >290 nm was obtained by passing the full output of the lamp through Pyrex glass. Photolyzed samples were analyzed by gas chromatography−mass spectrometry on instrumentation described previously.[5]

Studies of the rate of photoinitiated polymerization were conducted on freshly prepared solutions of CA and the metallocene photoinitiators. In one set of experiments, 2 mL samples were placed in 1 cm rectangular, optically transparent methacrylate plastic cuvettes containing a magnetic stirring bar. In most runs, no special precautions were taken to exclude air or ambient moisture. Samples were irradiated at 23 ± 1

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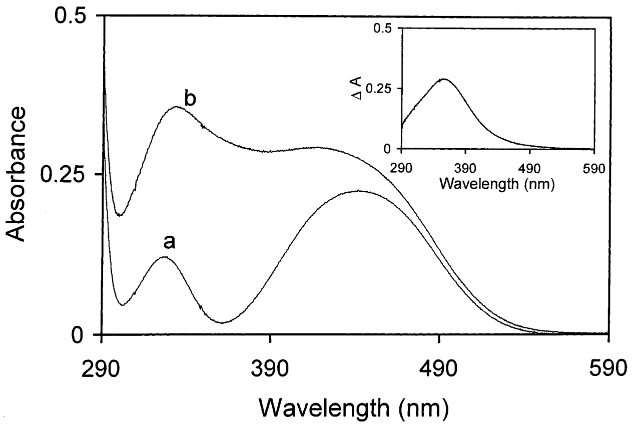


Figure 1. Electronic absorption spectrum of $FeCp_2$: (a) in pure THF; (b) in a 2:3 (v:v) mixture of CA and THF. Inset shows the difference spectrum of (a) and (b).

°C, and t_{poly}, the time required for solution viscosity to increase to the point that the stirring bar ceased to spin, was recorded. For a series of samples run under identical conditions of incident light intensity and stirrer speed, t_{poly} values provide a simple, yet reliable, measure of the relative rates of photoinitiated polymerization.

In another, more quantitative set of experiments, attenuated total reflectance infrared (ATR-IR) spectra of irradiated samples were acquired with a Bio Rad FTS-60 spectrometer equipped with a narrow band HgCdTe detector. A small volume (~0.3 mL) of the sample solution was placed on a germanium ATR crystal mounted in a horizontal ATR accessory (CIC Photonics) within the sample chamber of the spectrometer. Assuming a refractive index of 1.5 for CA and 4.0 for Ge and a 45° angle of incidence, we calculate that the electric field of the monitoring IR beam penetrated the sample to a depth of 2−3 μm.[22] Polymerization of CA commenced upon irradiating the sample with the polychromatic output of the mercury-arc lamp. Incident light intensity was measured with a Coherent Radiation model-10 power meter. Infrared absorbance spectra were collected every 1.5 s using the following parameters: one co-added scan, triangular apodization with one level of zero filling, and 4 cm^{-1} resolution. Spectra were analyzed with the Grams 32/AI spectral software package (Galactic Industries). Peak heights, frequencies, and areas were calculated with a center-of-gravity algorithm[23] using a program written by R. A. Dluhy. The area of the C=O stretching band of CA at 1734 cm^{-1} was assumed to remain constant during polymerization and used as an internal standard to correct the area of the C=C stretching band at 1616 cm^{-1} for changes in sample thickness.

High-resolution (10 700 $m/\Delta m$ at $m/z = 1580.2691$) mass spectra of CA oligomers were acquired with a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an internal matrix-assisted laser desorption/ionization (MALDI) source.[24] A 10 μL aliquot of a freshly photolyzed solution of the monomer and $RuCp_2$ was mixed with 100 μL of the matrix solution (0.5 M 2,5-dihydroxybenzoic acid in tetrahydrofuran). The spectra were calibrated externally using poly(ethylene glycol) standards, and the repeat unit mass was determined from the slope of the linear regression analysis of the monoisotopic masses.[25,26]

III. Results and Discussion

A. Spectral Evidence for Donor−Acceptor Interactions. Figure 1 (spectrum a) displays the room temperature electronic absorption spectrum of $FeCp_2$ dissolved in tetrahydrofuran (THF). The weak bands at 442 and 325 nm correspond to spin-allowed ligand field transitions predominantly localized on the d^6 metal center.[27] Switching the solvent to a 2:3 (v:v) mixture of CA and THF results in the appearance of a band at 355 nm (spectrum b and inset), which is indicative of a ground-state donor−acceptor interaction between $FeCp_2$ and the monomer. Given the ease of oxidizing $FeCp_2$ [28] and the strong electron-acceptor character of CA,[29] we assign this new feature as a CTTS ($Cp_2Fe \rightarrow CA$) transition. As seen in Figure 2, the spectral change that occurs upon mixing $RuCp_2$ and CA likewise is consistent with a D−A interaction between these two components. The spin-allowed ligand field transition of the metallocene at 319 nm[30] (spectrum a) is overlapped by a new absorption following addition of the monomer (spectrum b and inset). We attribute this new feature to a CTTS ($Cp_2Ru \rightarrow CA$) transition.

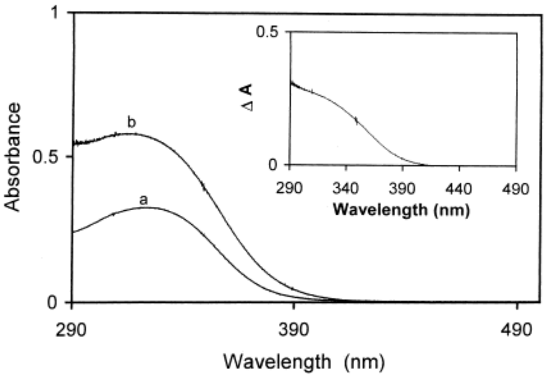


Figure 2. Electronic absorption spectrum of $RuCp_2$: (a) in pure THF; (b) in a 2:3 (v:v) mixture of CA and THF. Inset shows the difference spectrum of (a) and (b).

Table 1. Photoinitiated Polymerization Data

run	photoinitiator (PI)	[PI], mM	λ_{excit},[a] nm	t_{poly},[b] s
1	$FeCp_2$	7.96	>290	285
2	$FeCp_2$	7.78	365[c]	2094
3	$FeCp_2$	8.1	>290	292[d]
4	$RuCp_2$	12.1	>290	9
5	$RuCp_2$	11.4	365[c]	405
6	$RuCp_2$	2.42	>290	17
7	$RuCp_2$	2.42	>290	19[e]
8	$RuCp_2$	2.42	>290	>600[f]

[a] Excitation wavelength(s). [b] Irradiation time required for sample viscosity to increase to a point where the magnetic stirring bar in the photolysis cell ceased to spin. [c] Light intensity = 2.50×10^{-8} einstein/s. [d] Sample bubbled with argon for 10 min to remove O_2. [e] Hydroquinone (400 ppm) was added to sample. [f] Methanesulfonic acid (494 ppm) was added to sample.

B. Photoinitiated Polymerization Studies. Solutions of neat CA containing millimolar concentrations of $FeCp_2$ or $RuCp_2$ undergo no discernible change in viscosity for at least 24 h when stored in the dark at room temperature. Upon exposure to light, however, these solutions polymerize to a hard, plasticlike solid. Qualitative photopolymerization rate data compiled in Table 1 are expressed as t_{poly}, the irradiation time required for the sample to become so viscous that a magnetic stirring bar in the 1 cm rectangular photolysis cell ceases to spin. These results reveal that $RuCp_2$ is an especially effective photoinitiator for CA polymerization. Samples containing this metallocene solidify within seconds when irradiated with the Pyrex-filtered output (>290 nm) of the mercury lamp (run 4), and even a low-intensity monochromatic (365 nm) light beam causes solidification within a few minutes (run 5). Samples containing $FeCp_2$ generally require longer irradiation times (compare runs 1 and 4 and runs 2 and 5) and, at the point defined by t_{poly}, possess a viscosity akin to a syrup. Solidification of this material occurs over a 2−3 h period of storage in the dark. Neither molecular oxygen (runs 1 and 3 in Table 1) nor hydro-

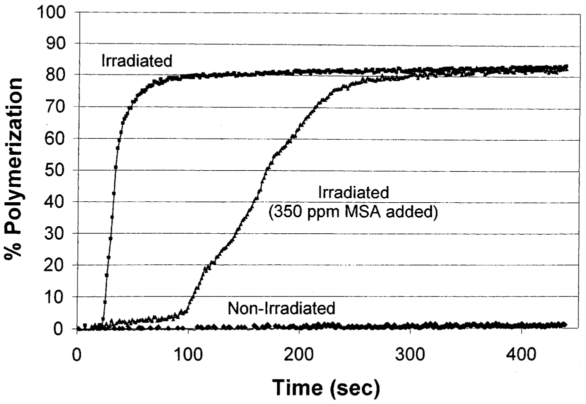


Figure 3. Plots of percent polymerization vs time for samples of CA containing 10.0 mM ruthenocene. Irradiated samples were exposed to 33 mW/cm^2 of polychromatic light from a high-pressure mercury lamp. MSA is methanesulfonic acid.

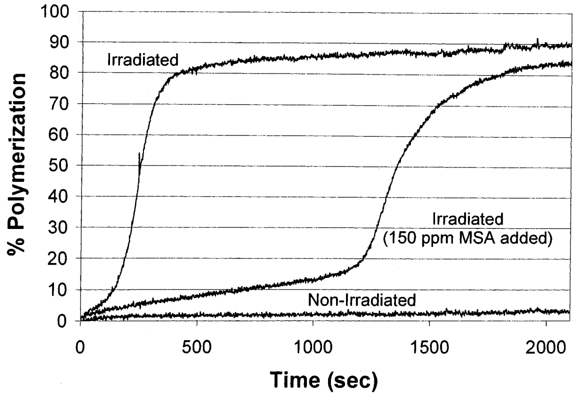


Figure 4. Plots of percent polymerization vs time for samples of CA containing 9.6 mM ferrrocene. Irradiated samples were exposed to 110 mW/cm^2 of polychromatic light from a high-pressure mercury lamp. MSA is methanesulfonic acid.

quinone (runs 6 and 7), known radical scavengers, influences the rate of photoinitiated polymerization. In contrast, methanesulfonic acid exerts a strong inhibiting effect on this process (runs 6 and 8). We infer from these findings that polymerization proceeds by an anionic rather than a radical mechanism. Protons inhibit this process by scavenging the photogenerated initiating species and/or reactive anionic sites on growing polymer chains.

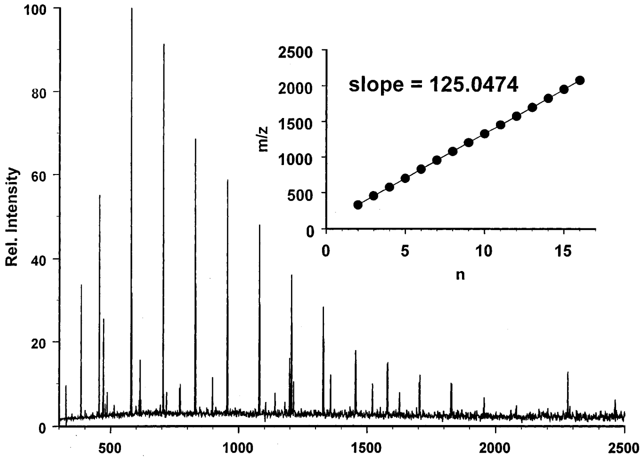


Figure 5. High-resolution MALDI/FTICR mass spectrum of a photolyzed THF solution of CA and RuCp$_2$. Inset shows the regression analysis (R^2 > 0.9999) of the measured monoisotopic mass-to-charge (m/z) ratios vs the number of monomer units (n). The slope of the line equals the mass of the repeat unit.

Quantitative characterization of the rate of photoinitiated polymerization was obtained by attenuated total reflectance infrared spectroscopy (ATR-IR). This technique allows continuous monitoring of the polymerization occurring in a 2−3 μm layer of monomer immediately adjacent to the surface of the ATR crystal. The extent of polymerization is directly related to the decrease in the absorbance of the C═C stretching band of CA at 1616 cm^{-1}. This relationship is defined by eq 4, where A_0 denotes the initial (dark) area of the band and A_t is the area after irradiation for time t. Plots of percent polymerization vs irradiation time are displayed in Figures 3 and 4 for samples of neat CA containing RuCp$_2$ or FeCp$_2$. While significantly shorter irradiation periods are required for samples containing RuCp$_2$, both metallocene photoinitiators yield kinetic profiles with very similar characteristics. Polymerization exhibits an induction period, then accelerates rapidly, and finally approaches a plateau at 80−90% conversion. We attribute the induction period to the presence in the commercial monomer of 5−10 ppm of methanesulfonic acid (MSA), which serves as a scavenger for adventitious traces of basic impurities. Polymerization is inhibited until sufficient anionic species are photochemically generated to neutralize this acid, whereupon rapid consumption of monomer commences. Not surprisingly, addition of extra MSA to a sample lengthens the induction period and slows the ensuing anionic polymerization. Collectively, the ATR-IR results agree with our earlier observations (Table 1) that RuCp$_2$ is a more effective photoinitiator than FeCp$_2$ and that strong acid retards the polymerization process.

$$\%\ \text{polymerization} = \frac{A_0 - A_t}{A_0} \times 100 \qquad (4)$$

The rate of photoinitiated polymerization, R_p, can be calculated from eq 5, where A_{t_1} and A_{t_2} represent the areas of the 1616 cm^{-1} band at the indicated times and M is the molar concentration of vinyl groups in the monomer. Using the data in Figures 3 and 4, we obtain maximum rates of 0.5 and 0.060 M s^{-1} for the samples containing RuCp$_2$ and FeCp$_2$, respectively, and no added acid. Another important quantity is the polymerization chain length or number of monomer units reacted per photogenerated initiating species. Under the rather conservative assumption that each metallocene molecule photochemically produces one anionic initiator, we estimate a chain length of >700.

$$R_\mathrm{p} = \frac{M(A_{t_1} - A_{t_2})}{A_0(t_2 - t_1)} \qquad (5)$$

Information about the repeat unit in the polymeric product was obtained by MALDI/FTICR mass spectrometry. A THF solution containing 20% (v:v) CA and 12 mM RuCp$_2$ was bubbled with argon for 25 min prior to and during a 30 s exposure to the full output of the mercury-arc lamp. Then 10 μL of methanesulfonic acid was added to terminate polymerization. The mass spectrum of the photolyzed sample is displayed in Figure 5. Regression analysis (inset) of the measured monoisotopic mass-to-charge ratios vs the degree of polymerization yields a repeat unit mass of 125.0474 Da, which agrees with the calculated mass of 125.0479 Da for CA. This result confirms that irradiation of CA

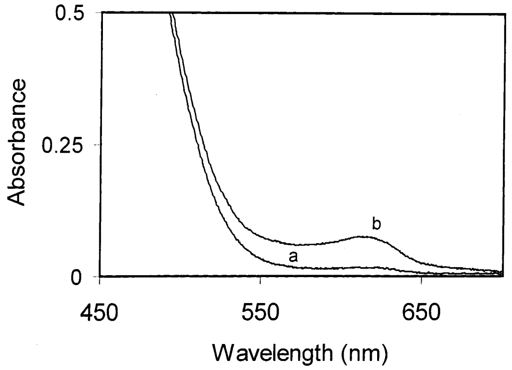


Figure 6. Spectral change that occurs upon irradiating 7.7 mM $FeCp_2$ in neat CA: (a) before irradiation, (b) after irradiation for 570 s with Pyrex-filtered (>290 nm) light from a mercury-arc lamp. Band appearing at 617 nm corresponds to $FeCp_2^+$.

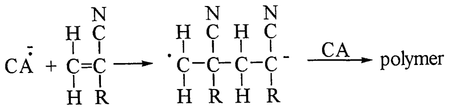
in the presence of the metallocene yields polycyanoacrylate. Number-average and weight-average molecular weights of 864 and 968, respectively, were obtained for this sample, which corresponds to a polydispersity of 1.14.

C. Mechanistic Considerations. We considered the possibility that the active initiator for CA polymerization is the cyclopentadienide ion, $C_5H_5^-$, which would result from photoinduced metal-ring bond cleavage in the metallocene (eq 6; S is solvent). In one experiment, an acidified solution[31] of $RuCp_2$ was irradiated with polychromatic (>290 nm) light for 2 h. Analysis of the photolyte by gas chromatography−mass spectrometry failed to detect even a trace of C_5H_6 or higher homologues. In another experiment, a solution of $RuCp_2$ in ethyl 2-cyanopropionate, a nonvinylic analogue of CA, was irradiated with polychromatic light for 25 min without undergoing a change in its electronic absorption spectrum. These results reinforce earlier reports that $FeCp_2$ and $RuCp_2$ resist photodissociation of $C_5H_5^-$.[14]

$$RuCp_2 \xrightarrow[S]{h\nu} CpRuS_3^{\ +} + C_5H_5^{\ -} \qquad (6)$$

As an alternative to photoinduced bond cleavage, we propose that photoinduced charge transfer between the metallocene and CA generates the species responsible for initiating CA polymerization. By analogy to the behavior described in eq 3, irradiation into the CTTS absorption band of a ground-state metallocene−CA complex (Figures 1 and 2) should produce the metallocenium cation and CA radical anion (eq 7). Attack of the latter species on the monomer then initiates polymerization (eq 8; R = $COOC_2H_5$). Consistent with this charge-transfer mechanism, we find that irradiating $FeCp_2$ in neat CA results in the appearance of the characteristic 617 nm absorption band of the ferricenium ion, $FeCp_2^+$ (Figure 6).[15]

$$FeCp_2 + CA \rightleftharpoons \underset{\text{D-A complex}}{[FeCp_2,CA]} \xrightarrow{h\nu} FeCp_2^{\ +} + CA^{\bullet-} \qquad (7)$$



$$CA^{\bullet-} + \begin{array}{cc} H & \overset{N}{C} \\ | & | \\ C= & C \\ | & | \\ H & R \end{array} \longrightarrow {}^{\bullet}\begin{array}{cccc} H & \overset{N}{C} & H & \overset{N}{C} \\ | & | & | & | \\ C- & C- & C- & C^{-} \\ | & | & | & | \\ H & R & H & R \end{array} \xrightarrow{CA} \text{polymer} \qquad (8)$$

It is interesting to consider the difference between the two initiation steps represented by eqs 2 and 8. In the former, attack by the thiocyanate anion on CA yields a single, negatively charged site that then propagates by further addition of monomer units. In contrast, attack of the CA radical anion on the monomer generates two potentially reactive sites, one radical and one anionic, that become increasingly separated as polymerization proceeds. In principle, this difunctional species could initiate polymerization by both radical and anionic mechanisms, although our results show no evidence for operation of the former pathway. More likely, the radical site participates in one or more termination processes, such as reaction with radical scavengers (e.g., O_2, hydroquinone) present in the system. Alternatively, two radicals could undergo bimolecular disproportionation or coupling,[32] with the latter process yielding a dianion that could continue polymerization at both ends. Identification of polymer end groups is needed to distinguish between these possibilities.

IV. Concluding Remarks

Precedent for the involvement of a photosensitive D−A complex in the generation of an initiator for anionic polymerization can be found in the early studies of ionic photopolymerization by Irie et al.[33] These workers reported that irradiation of the complex formed between the electron-donor solvent, THF, and the electron-acceptor monomer, nitroethylene, yields the corresponding radical cation−radical anion pair. Attack of the photogenerated radical anion on the monomer initiates polymerization. An important distinction between this system and those described in the present study centers upon the relative concentrations of the electron donor and acceptor. In the THF−nitroethylene example, the solvent serves as the donor and is present in considerable molar excess over the acceptor monomer. In contrast, our results demonstrate that very low (millimolar) concentrations of $FeCp_2$ or $RuCp_2$ are sufficient for the photoinitiated polymerization of neat CA. The latter type of system is particularly attractive for the increasing number of applications in the coatings, adhesives, and reprographic industries that require solvent-free photosensitive formulations.

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