A New Photoinitiator for Anionic Polymerization

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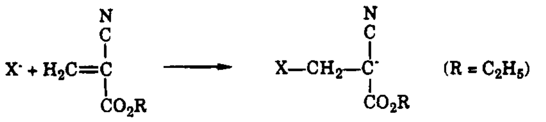
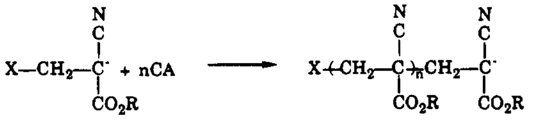
Photoinitiated polymerization has become an increasingly popular technique for the curing of adhesives and sealants, resin/glass fiber composites, lacquer surface coatings, printing inks, and electronic packaging materials.[1] Most of the commercially important photoinitiators are organic or organometallic compounds that, upon exposure to light, initiate polymerization via a radical or cationic mechanism.[2] Recently, we reported the first example of an attractive strategy for photoinitiating anionic polymerization.[3] In brief, visible-light irradiation of *trans*-$Cr(NH_3)_2(NCS)_4^-$ dissolved in ethyl α-cyanoacrylate (CA) results in the controlled release of a thiocyanate ion from the metal complex. Subsequent addition of NCS^- to the carbon−carbon double bond of the acrylate monomer yields a resonance-stabilized carbanion (eq 1; X^- is NCS^-). Polymerization then proceeds rapidly by the repetitive addition of monomer units to the active anionic center (eq 2).



$$X^- + H_2C{=}\underset{CO_2R}{\overset{\overset{N}{C}}{C}} \longrightarrow X{-}CH_2{-}\underset{CO_2R}{\overset{\overset{N}{C}}{C^-}} \quad (R = C_2H_5)$$

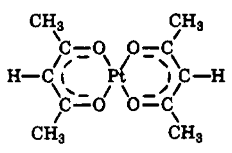
(1)



$$X{-}CH_2{-}\underset{CO_2R}{\overset{\overset{N}{C}}{C^-}} + nCA \longrightarrow X{+}CH_2{-}\underset{CO_2R}{\overset{\overset{N}{C}}{C}}{+}_nCH_2{-}\underset{CO_2R}{\overset{\overset{N}{C}}{C^-}}$$

(2)

Our search for new anionic photoinitiators led us to investigate $Pt(acac)_2$ (structure shown below; $acac^-$ is the anion of acetylacetone). This uncharged, square-planar β-diketonate complex dissolves in a variety of nonaqueous solvents, exhibits excellent thermal stability in solution, and absorbs strongly in the ultraviolet region (Figure 1). Photoexcitation of the complex to a ligand field or a ligand-to-metal charge-transfer excited state should weaken the Pt−O bonds[4] and thereby facilitate the production of a free acetylacetonate anion. Reported here are results which demonstrate that $Pt(acac)_2$ functions as a highly effective photoinitiator for the anionic polymerization of CA.



$Pt(acac)_2$

High-purity (99.9%) CA was obtained from Loctite Corp. The colorless liquid monomer contained hydroquinone and methanesulfonic acid as scavengers for adventitious radical and basic impurities, respectively. Analytically pure $Pt(acac)_2$ was purchased from Alfa Chemical and used as received. Solutions of CA containing (0.51−1.5) × 10^{-3} M $Pt(acac)_2$ undergo no discernible change in viscosity when kept in the dark for 1 week at room temperature. In contrast, the addition of 1 drop of a 6.9 × 10^{-3} M solution of Tl^+acac^- in acetonitrile to 1 mL of CA causes instantaneous solidification. This observation establishes $acac^-$ as a potent initiator for the polymerization of CA.

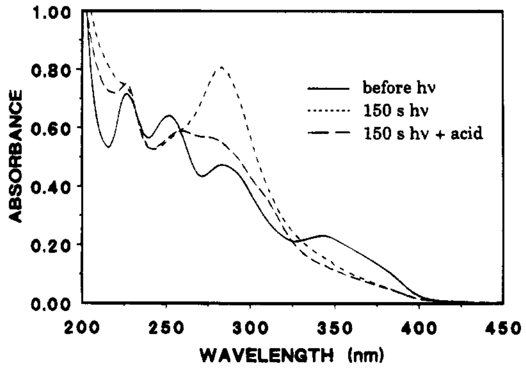


Figure 1. Electronic absorption spectrum of $Pt(acac)_2$ in Ar-purged acetonitrile at 10 °C: (—) before photolysis; (- - -) after photolysis at 365 nm for 150 s; (— —) after addition of ~0.15 mL of methanesulfonic acid to the photolyte.

Table 1. Studies of $Pt(acac)_2$ as a Photoinitiator for the Anionic Polymerization of CA

run[a]	$[Pt(acac)_2]$, M	λ_{ex}, nm	photopolymn time,[b] s
a	2.67×10^{-4}	>290	67
b	7.25×10^{-4}	>290	27
c	1.79×10^{-3}	>290	15
d	1.79×10^{-3} [c]	>290	56
e	1.5×10^{-3}	365[d]	95

[a] General conditions: a 3-mL sample of CA containing the indicated concentration of $Pt(acac)_2$ was irradiated with stirring in a 1-cm rectangular Pyrex 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 stirring bar ceased to spin. [c] Concentration of methanesulfonic acid in the monomer sample raised from 5 to 46 ppm. [d] Selective excitation at 365 nm was achieved by means of a narrow band-pass interference filter; light intensity = 3.57 × 10^{-8} einsteins/s.

Neat CA is unaffected by prolonged (>6500 s) exposure to light of wavelength >290 nm. When irradiated in the presence of $Pt(acac)_2$, however, CA undergoes rapid thickening and eventual solidification. Qualitative rate data summarized in Table 1 reveal that concentrations of $Pt(acac)_2$ at the 100 ppm (2.5 × 10^{-4} M) level cause visually-observable photoinitiated polymerization in about 1 min. Increasing the complex concentration decreases this time (runs a−c), owing to the absorption of a greater fraction of the incident radiation. Selective excitation of $Pt(acac)_2$ at 365 nm also triggers polymerization (run e), but the lower intensity that results from filtering the polychromatic light source lengthens the required time.

The nature of the active initiating species was probed in a series of scavenging experiments. Neither molecular oxygen nor added hydroquinone (up to 3500 ppm), both of which are radical scavengers, influences the rate of photoinitiated polymerization. In contrast, increasing the concentration of methanesulfonic acid in the monomer sample inhibits polymerization (Table 1, runs c and d). We attribute this inhibition to the ability of the strong protonic acid to scavenge a photogenerated anionic species (X^- in eq 1) and/or the active anionic center on the growing polymer chain (eq 2).

Spectroscopic evidence is consistent with the photochemical production of acac$^-$ from Pt(acac)$_2$. As seen in Figure 1, irradiation (λ_{ex} = 365 nm[5]) of the complex in acetonitrile causes the growth of an intense band at 283 nm attributable to the lowest spin-allowed $\pi-\pi^*$ transition of free acac$^-$. Subsequent addition of acid to the solution shifts this band to higher energy, owing to protonation of the anion.[6] The NMR spectrum of the photolyte confirms the presence of acac$^-$ among the photoproducts. Interestingly, these photoproducts react in the dark over a period of several hours to regenerate Pt(acac)$_2$. Efforts are underway to delineate the mechanism of this back reaction and to identify photogenerated platinum-containing intermediates.

The present study demonstrates that the ultraviolet photolysis of Pt(acac)$_2$ dissolved in ethyl α-cyanoacrylate initiates anionic polymerization of the acrylate monomer. Scavenging and spectroscopic evidence implicate photogenerated acac$^-$ as the active initiating species (X$^-$ in eq 1). Viewed in a broader context, our results expand the list of reported anionic photoinitiators to include a complex that photoliberates an oxy anion. Given the wide variety of β-diketonate ligands available,[7] the opportunity exists to develop a family of Pt(diketonate)$_2$ photoinitiators whose properties (solubility, absorption spectrum, nucleophilicity of released anion) can be tailored for specific applications. Our efforts in that direction will be described in future papers.

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References and Notes

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