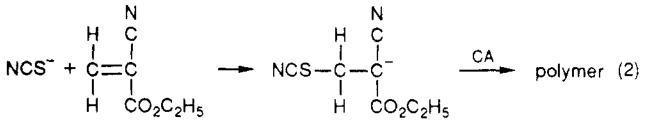
A Novel Strategy for Photoinitiated Anionic Polymerization

Photopolymerization has assumed an increasingly important role in the coatings, printing, and microelectronics industries.[1] Typically, the light-sensitive formulation contains a photoinitiator which, upon exposure to radiation, generates one or more of the following species: a radical, an uncharged or cationic Lewis acid, an uncharged Lewis base. Subsequent reaction of these species with the monomer initiates polymerization. Conspicuously absent from the current catalogue of photoinitiators are those that undergo photochemical release of an anionic initiating species. It occurred to us that properly selected coordination complexes could fill this void, and we have undertaken exploratory studies to test this premise. Reported here is the first example of an attractive strategy for photoinitiating anionic polymerization.

Transition-metal complexes generally undergo ligand substitution reactions upon irradiation of their ligand field absorption bands.[2] This photochemical process can be exploited for the controlled release of anions from an otherwise stable precursor. Several considerations suggest that *trans*-$[Cr(NH_3)_2(NCS)_4]^-$ (Reineckate anion, hereafter abbreviated R^-) should be an almost ideal anion source. Thus, K^+R^- dissolves readily in a variety of nonaqueous solvents, resists thermal substitution in nonhydroxylic media, and undergoes quantum efficient (>10%) release of NCS^- (eq 1) upon ligand field excitation with near-ultraviolet/visible light.[3] Addition of photogenerated NCS^- to a vinyl carbon atom of a monomer such as ethyl α-cyanoacrylate (CA), which contains electron-withdrawing substituents to stabilize the negative charge, should occur rapidly to initiate anionic polymerization (eq 2).

$$R^- \xrightarrow[\text{solvent}]{h\nu} Cr(NH_3)_2(NCS)_3(\text{solvent}) + NCS^- \qquad (1)$$



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

Neat CA (99.88% purity from Loctite Corp.) is a colorless liquid with a viscosity of 2.8 cP at 22 °C. The sample employed in this study contained hydroquinone and methanesulfonic acid as scavengers for adventitious radical and basic impurities, respectively. Commercially available $NH_4^+R^-$ (Alfa) was converted to the potassium salt by a published procedure.[3b] Solutions of CA containing K^+R^- ($(0.19-2.7) \times 10^{-3}$ M) undergo no change in viscosity when kept in the dark for 1 week at room temperature. In contrast, mixing one drop of a 5.2×10^{-3} M solution of K^+NCS^- in acetonitrile with 0.5 mL of CA causes immediate (<1-s) solidification accompanied by considerable evolution of heat. This dramatic response establishes NCS^- as an effective initiator for the polymerization of CA.

Pure CA is unaffected by prolonged (24-h) irradiation with light of wavelength >350 nm. The electronic absorption spectrum of K^+R^- dissolved in CA exhibits bands at 400 nm ($\epsilon = 89\ M^{-1}\ cm^{-1}$) and 528 nm ($\epsilon = 114\ M^{-1}\ cm^{-1}$) arising from spin-allowed ligand field transitions. Selective excitation (532 or 546 nm) of the lower energy transition causes the solution to thicken and eventually solidify. This behavior is the direct consequence of the photochemical release of NCS^- (eq 1),[4] which, as noted above, functions as an effective initiator for CA polymerization (eq 2).

Table I

Effects of K^+R^- Concentration and Light Intensity upon the Rate of Photoinitiated Polymerization of CA

run[a]	$[K^+R^-]$, M	λ_{ex}, nm	I,[b] einsteins/s	photopolymerization time,[c] s
a	2.1×10^{-3}	546	3.97×10^{-8}	880
b	2.1×10^{-3}	546	2.08×10^{-8}	1540
c	5.1×10^{-4}	546	3.97×10^{-8}	3380
d	2.0×10^{-3}	532	2.13×10^{-6}	6
e	6.0×10^{-4}	532	2.13×10^{-6}	12
f	2.0×10^{-4}	532	2.13×10^{-6}	45

[a] General conditions: a 2-mL sample of CA containing the indicated concentration of K^+R^- was irradiated (with stirring in runs a–c) in a 1-cm rectangular Pyrex cell. No attempt was made to exclude air from the sample. [b] Incident light intensity. Light at 546 nm was obtained by passing the output of a 200-W high-pressure mercury lamp through a narrow band-pass interference filter, while a Nd-YAG pulsed laser operated at 10 Hz was used for irradiations at 532 nm. [c] Irradiation time required for the sample to become so viscous that the stirring bar ceased to spin (runs a–c) or time required for the formation of a solid plug of polymer along the path of the 6-mm-diameter laser beam (runs d–f).

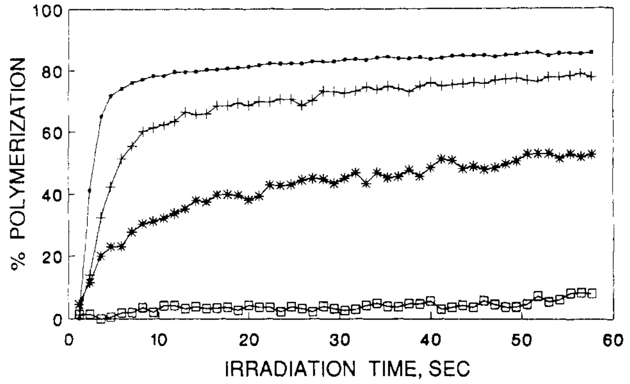


Figure 1. Plots of percentage polymerization vs time of irradiation for samples of CA containing the following concentrations of K^+R^-: (□) 0 M; (*) 2.2×10^{-4} M; (+) 5.4×10^{-4} M; (■) 2.0×10^{-3} M. Thin films of these samples were coated onto acid-treated silicon wafers and irradiated with a 500 mW/cm² polychromatic (254–630-nm) light source. Qualitatively similar results were obtained with UV-filtered (>385 nm) light.

Initiation by NH_3 or radicals can be discounted, since the photochemical release of these species from R^- only occurs at much shorter excitation wavelengths.[3b] The key role played by anionic species is underscored by the observation that increasing the level of methanesulfonic acid in the monomer sample from 10 to 98 ppm inhibits polymerization. We attribute this effect to the ability of the protonic acid to scavenge photogenerated NCS^- and/or anionic sites on the growing polymer chain. As summarized in Table I, the rate of photoinitiated polymerization depends upon the K^+R^- concentration and the incident light intensity. Thus, at constant intensity, polymerization proceeds more rapidly at higher complex concentration (compare runs a and c). Such behavior reflects the greater fraction of light absorbed by the more concentrated sample and the correspondingly higher photochemical rate of NCS^- release. An analogous explanation accounts for the faster polymerization observed upon increasing light intensity at constant K^+R^- concentration (compare runs a and b).

A more detailed kinetic characterization of the photoinitiated polymerization process was obtained by real-time Fourier transform infrared spectroscopy. This relatively new technique allows continuous monitoring (up to 204 infrared spectra collected per minute) of the sample during irradiation.[5] The extent of polymerization is

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directly related to the decrease in absorbance of the C=C stretching band of CA at 1616 cm^{-1}. This relationship is expressed in eq 3, where A_0 denotes the initial (dark) area

$$\% \text{ polymerization} = \frac{(A_0 - A_t)}{A_0} \times 100 \qquad (3)$$

of the band and A_t is the area after t seconds of irradiation. Plots of percent polymerization as a function of irradiation time are displayed in Figure 1. These results agree with earlier observations (Table I) that polymerization occurs more rapidly in samples containing higher K^+R^- concentrations. The rate of photoinitiated polymerization, R_p, can be calculated from eq 4, where A_{t1} and A_{t2} represent

$$R_p = \frac{M(A_{t1} - A_{t2})}{A_0(t1 - t2)} \qquad (4)$$

the areas under the 1616-cm^{-1} band at irradiation times $t1$ and $t2$, and M is the molar concentration of vinyl groups in CA. Maximum rates of 3.0, 1.3, and 0.60 M·s^{-1} result for CA samples containing 2.0×10^{-3}, 5.4×10^{-4}, and 2.2×10^{-4} M concentrations of K^+R^-, respectively.

Another important quantity is the polymerization chain length, or the number of monomer units reacted per photogenerated NCS$^-$. Under the rather conservative assumption that each R$^-$ in the CA sample undergoes photochemical release of one NCS$^-$, we calculate a chain length of $>10^4$ from the data in Figure 1. This multiplicative response of CA to NCS$^-$ constitutes chemical amplification[6] of the initial photochemical act and accounts for the high photosensitivity of the system.

In summary, we have demonstrated that visible-light irradiation of *trans*-[Cr(NH$_3$)$_2$(NCS)$_4$]$^-$ dissolved in ethyl α-cyanoacrylate initiates anionic polymerization. The initiation step involves addition of photoreleased NCS$^-$ to the carbon–carbon double bond of the acrylate monomer. More generally, our results suggest that ligand field excitation of judiciously selected transition-metal complexes represents a promising strategy for the controlled release of anionic initiators for polymerization reactions. Our continuing studies in this new area will be the subject of future reports.

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References and Notes

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(4) Attempts to measure the concentration of photogenerated NCS$^-$ in CA by the standard spectrophotometric method[3b] failed because the requisite analytical reagents triggered thermal polymerization. We can estimate, however, a value of 0.14 for the initial quantum yield of NCS$^-$ release (eq 1) in CA from the reported correlation between ϕ_{NCS^-} and solution viscosity.[3d]

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(6) Chemical amplification refers to a process in which a single photochemical event (e.g., release of NCS$^-$ in eq 1) initiates a cascade of subsequent chemical reactions (e.g., anionic polymerization in eq 2). See: MacDonald, S. A.; Ito, H.; Willson, C. G. *Microelectron. Eng.* **1983**, *1*, 269.

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