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Photoinduced anionic polymerization of cyanoacrylates using substituted pyridine pentacarbonyl complexes of tungsten or chromium

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Photoinduced polymerization of cyanoacrylate monomers using a novel class of photoinitiators comprising Group VI metal carbonyl pyridine complexes is reported. Irradiation of a solution containing the monomer and photoinitiator, with visible light (436 nm), leads to a rapid exothermic polymerization reaction which is readily followed by calorimetric techniques. The photoinduced reaction exhibits the features expected of conventional amine initiated polymerization of cyanoacrylates consistent with photo-released pyridine acting as the initiating species. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

Photoinduced polymerization and crosslinking play a significant role in a range of technologies including lithography and photocuring. The vast majority of these systems involve a free radical or cationic mechanism[1,2]. While a considerable amount of work has been carried out on anionic polymerization in general, there have been few reports of photoinduced anionic polymerization. Electrophilic vinyl monomers such as cyanoacrylates (CAs) are characterized by their high reactivity to anions such as OH^- and NCS^-, and to Lewis bases such as amines and phosphines. Photogeneration of thiocyanate, a known initiator, from Reinecke's salt $(K^+[Cr(NH_3)_2(NCS)_4]^-$, abbreviated to K^+R^-) in neat CA was found to lead to polymerization[3]. We wish to report here that Group VI metal carbonyl pyridine complexes are very efficient photoinitiators for the anionic polymerization of CAs and can be used under a wider range of conditions than Reinecke's salt.

Results and discussion

The exothermic nature of the polymerization reactions of CA monomers means that they are readily followed by calorimetry. The heat evolved during the course of the reaction was measured using a thermistor and Wheatstone bridge circuit according to the method outlined by Pepper and co-workers[4,5], with the monomer concentration, $[M]_t$, being derived from the thermistor trace. In order to develop further this class of photoinitiators it is essential to study the kinetics in detail, and for this reason we have carried out most of our work in dilute tetrahydrofuran (THF) solution. This also allows us to compare the results of our photoinduced reactions to conventional amine initiated polymerizations where a solution containing the initiator is added to the monomer. Pepper[6] developed the SINT

(slow initiation, no termination) kinetic scheme for anionic polymerization of CAs (in dilute THF solution) using amine or phosphine initiators (see *Scheme 1*). The basis of the SINT scheme is that the rate of initiation of growing chains is slow compared to their propagation rate and in the absence of added acid there is no intrinsic termination process.

Working on the basis that pyridine, a well known initiator of CAs, is released from pyridine substituted transition metal carbonyls with a high quantum yield (>0.5) we have found that complexes of the formula $M(CO)_5L$ (where M = Cr or W, and L = pyridine or vinyl substituted pyridine) are very efficient photoinitiators of CAs. Irradiation of a solution containing a CA monomer and a $M(CO)_5L$ complex, with visible radiation, leads to a rapid exothermic polymerization reaction. By contrast, in the dark, solutions containing both monomer and photoinitiator, components are stable for over 1 h.

The behaviour of $W(CO)_5py$ (py = pyridine), its Cr analogue and the complexes $W(CO)_52\text{-vp}$ and $W(CO)_54\text{-vp}$ (where 2-vp = 2-vinylpyridine and 4-vp = 4-vinylpyridine) was found to be qualitatively similar in each case. All of these complexes are efficient photoinitiators of ethyl cyanoacrylate (ECA) and butyl cyanoacrylate (BCA) when irradiated in the neat monomer or in dilute THF solution. *Figure 1* shows the plots of $\ln[M]_0/[M]_t$ versus time for a series of photoinduced polymerizations having various initial concentrations of $W(CO)_5py$. All of the plots shown follow the characteristic pattern for amine initiated polymerization of CAs, exhibiting an initial inhibition and subsequent acceleration, followed by a linear portion in the later stages of the reaction. We have found that the overall rate of polymerization is dependent on the initial photoinitiator concentration (*Figure 1*) and the intensity of irradiation (1.2–$8.0 \times 10^{-8}\,E\,s^{-1}$ at 436 nm, determined by ferrioxalate actinometry). Both of these observations are explained in terms of the

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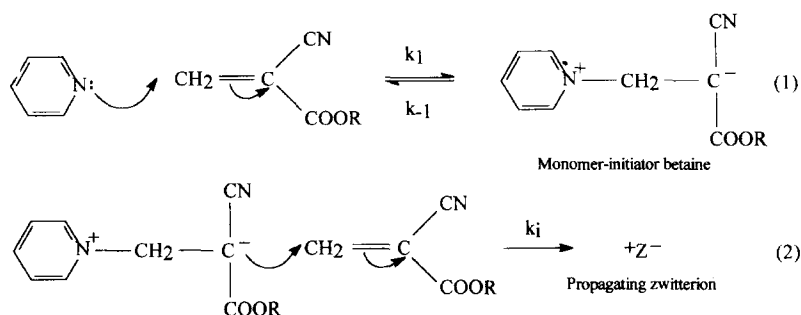
**Scheme 1** SINT mechanism for the initiation of polymerization in CA monomers by pyridine
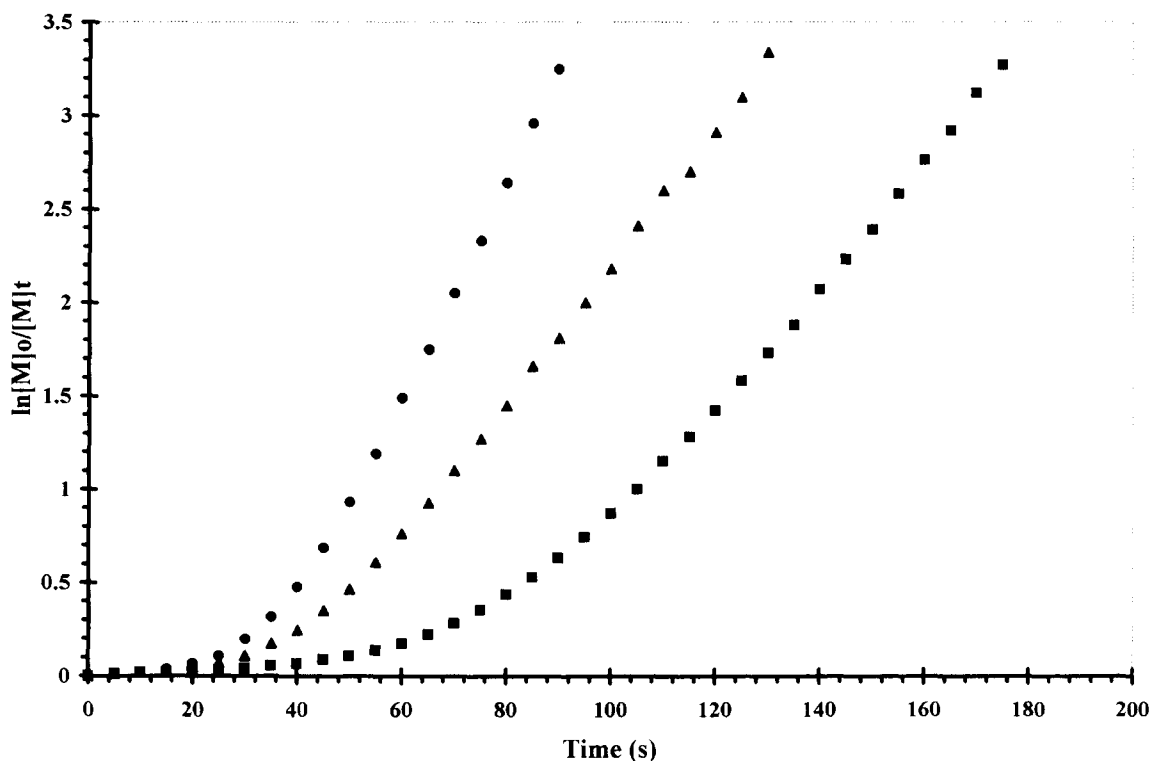
Figure 1 Variation of the overall rate of polymerization with photoinitiator concentration. $[BCA]_o = 0.074$ M (1% v/v) in THF; $[W(CO)_5py]_o$: (●) 7.47×10^{-5} M; (▲) 3.74×10^{-5} M; (■) 1.87×10^{-5} M. In each case p-toluenesulfonic acid (1.94×10^{-7} M) was added to increase monomer stability. All experiments were carried out at 18°C; irradiation was at 436 nm with $I_o = 8.0 \times 10^{-8}$ E s^{-1}

greater amount of light absorbed by the photoinitiator, resulting in an increased concentration of pyridine being released.

Two other observations support an anionic mechanism for this reaction. Firstly, the addition of a strong acid to the reaction mixture prior to irradiation was found to cause well defined inhibition periods, proportional to the amount of acid added (*Figure 2*), after which polymerization took place at a rate approximately equal to that of acid-free polymerization. Such inhibition periods, where the acid kills off the chains as fast as they are generated by the initiator[4,5], can only be explained in terms of an anionic mechanism. Secondly, the overall rate of photopolymerization using $W(CO)_5py$ was found to increase with decreasing temperature consistent with conventional amine initiation. According to the SINT model, in the case of amine initiation the first monomer addition is reversible (*Scheme 1*), and the reverse reaction is favoured at higher temperatures, leading to a negative temperature dependence for the overall rate of polymerization[4,5].

The photochemistry of $W(CO)_5py$ has been extensively studied[7] and irradiation with visible light is found to cause negligible loss of carbonyl[8]. Therefore, the initiating species must be either of two photoproducts, i.e. pyridine or $W(CO)_5$, the latter being rapidly coordinated by THF[9]. The possibility of initiation by the $W(CO)_5$ fragment is ruled out by the observation that the addition of a solution of $W(CO)_5THF$ [formed by the irradiation of a THF solution of $W(CO)_6$ with u.v. light] to a solution of BCA causes no polymerization. Further, it seems unlikely that the polymerization is of a free radical nature in view of the observations that the reaction continues until all of the monomer has been consumed even after irradiation has ceased, and that the overall rate of polymerization is found to be unaffected by the presence of hydroquinone (a known free radical quencher).

The calorimetric technique used for monitoring $M(CO)_5L/CA$ reactions was found to be unsuitable for reactions using Reinecke's salt as the photoinitiator because of the slow evolution of heat in that case. For
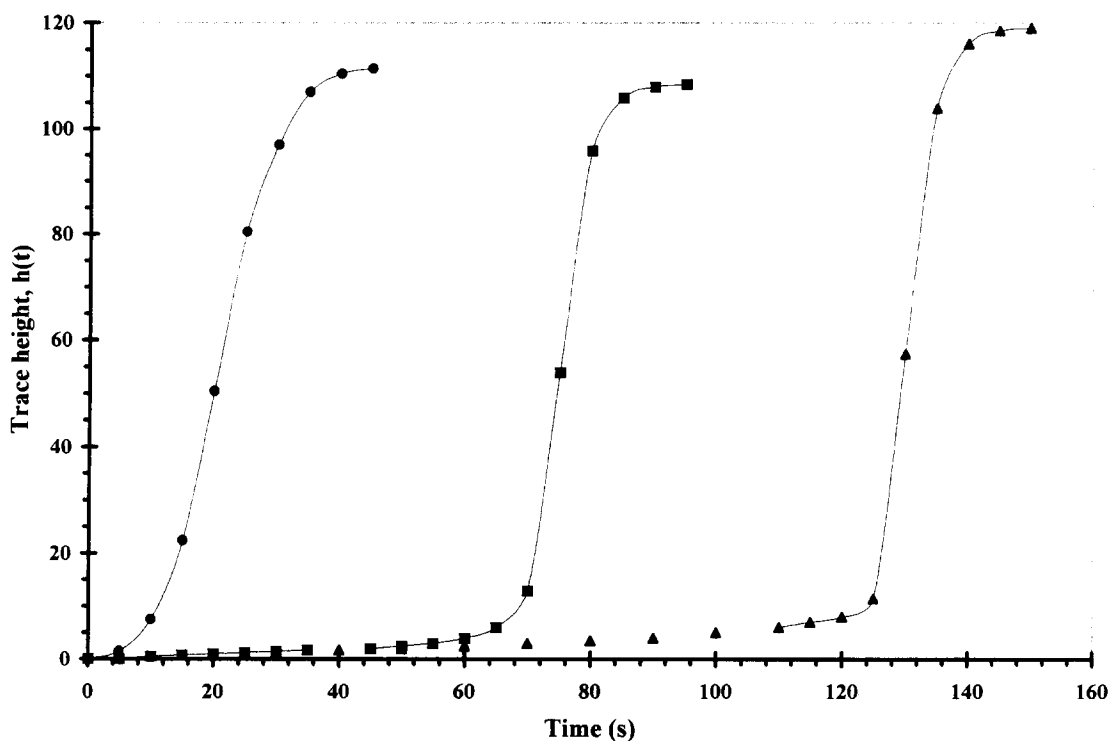
Figure 2 Inhibition of polymerization induced by addition of p-toluenesulfonic acid. In each case irradiation was started at $t = 0$ and $[ECA]_o = 0.082$ M; $[W(CO)_5py]_o = 1.15 \times 10^{-3}$ M [TSA]: ($\bullet$) 0 M; ($\blacksquare$) (4.50×10^{-5} M; ($\blacktriangle$) 9.81×10^{-5} M
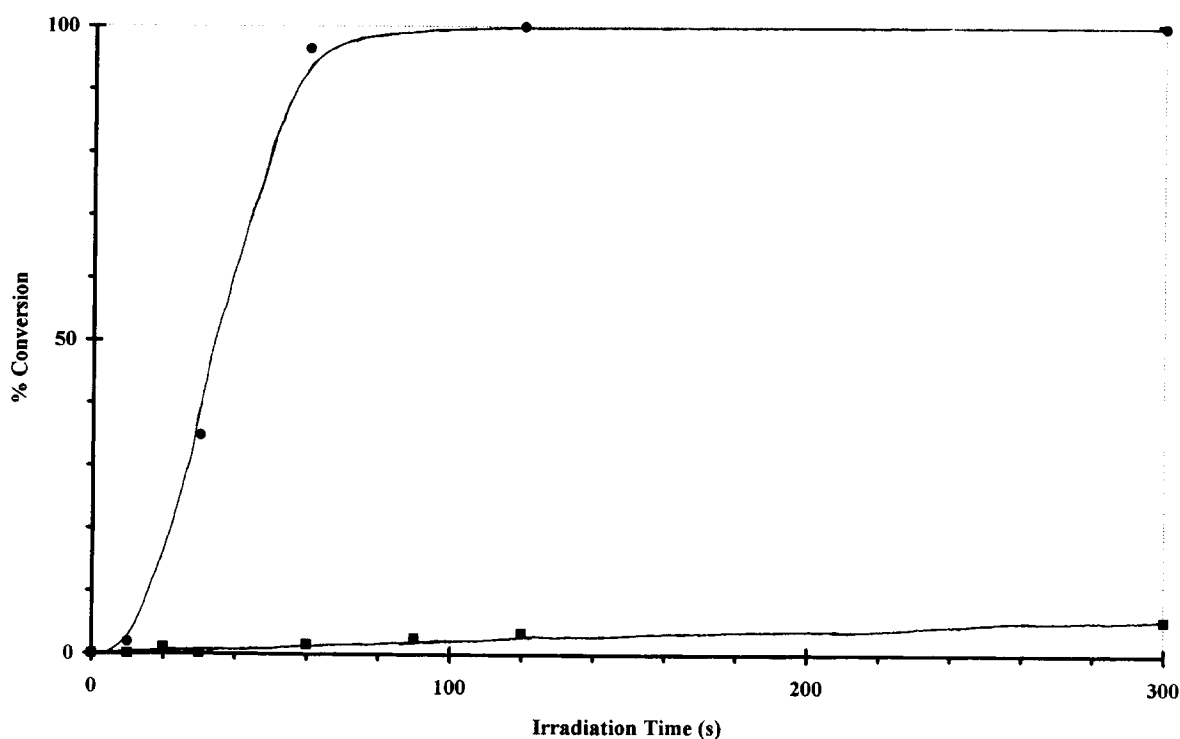
Figure 3 Photoinduced polymerization of ECA in THF solution (5% v/v); comparative performance of $W(CO)_5py$ (1.48×10^{-5} M), ($\bullet$); and potassium Reineckate (1.78×10^{-4} M), ($\blacktriangle$); irradiation at 436 nm

this reason the effectiveness of potassium Reineckate and $W(CO)_5$pyridine as photoinitiators was compared by measuring gravimetrically the amount of polymer formed after various irradiation times. The concentrations of each photoinitiator were calculated so as to give equivalent light absorption at 436 nm. *Figure 3* shows that upon irradiation in dilute THF solution

$W(CO)_5$pyridine causes rapid polymerization of the monomer, with approximately 100% conversion being attained in approximately 1 min. On the other hand, potassium Reineckate was found to be a poor photoinitiator under these conditions, when the reaction is carried out in dilute solution in a non-polar solvent such as THF.

Conclusions

The reported results are consistent with the photolysis of W(CO)$_5$py in a CA monomer solution leading to the generation of free pyridine and initiating a polymerization reaction which proceeds via an anionic propagation mechanism similar to that described by the SINT theory. The efficient loss of the unique ligand from M(CO)$_5$L complexes upon irradiation, coupled with the relative ease of synthesis of pentacarbonyl complexes with a wide range of ligands, makes this class of compounds ideal photoinitiators of reactive vinyl monomers such as CAs. They are of particular interest because of their ability to initiate polymerization when irradiated with visible light. Work is continuing on a full kinetic analysis of this novel photo-induced polymerization reaction and we are investigating several other potential photoinitiators.

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