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A Novel Visible Light Initiatiating System for Cationic Polymerization[†]

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Introduction

Photinitiated polymerization has gained much attention during the past two decades due to its application in various areas.[1,2] Both free radical[3] and cationic[4] polymerization have been used and the mechanisms of initiation have been studied in detail. Photoinitiated free radical polymerization is more developed because of its applicability to a wide range of formulations based on acrylates, unsaturated polyesters, and polyurethanes and the availability of photoinitiators having spectral sensitivity in the near-UV or visible range. Significant advances in the cationic polymerization has been achieved by the use of thermally stable but photochemically active onium salts,[5] pyridinium salts,[6] iron arene complexes[7, 8] and latent sulfonic acids.[9−11]

Regarding onium salts, which are the most prominent cationic photoinitiators, direct and indirect acting systems can be considered.[4,5]

In direct acting systems, these salts can themselves initiate cationic polymerization upon irradiation. However, the spectral response of simple onium salts is limited to the shorter region of the UV. On the other hand, in indirect systems many light sensitive compounds which do not directly initiate the polymerization may be utilized.[12,13] This enables the extension of the spectral sensitivity of onium salts to longer wavelengths where commercial lamp sources emit the light.

Regarding indirect initiating systems, three modes of action concerning the formation of cationic species capable of reacting with monomers can be distinguished:

(i) Oxidation of free radicals.[14,15] Many photolytically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization.

$$R^{\bullet} \xrightarrow{On^+} R^+ \tag{1}$$

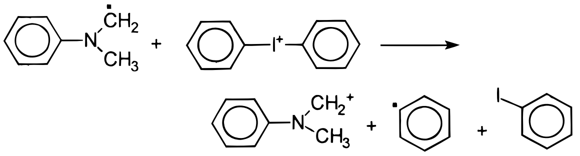
(ii) Electron transfer between a photoexcited molecule and an onium salt.[16−18] Certain aromatic hydrocarbons are capable to sensitize the decomposition of onium salts via electron transfer in an excited complex referred to as exciplex. In this complex, one electron is transferred from the sensitizer molecule to the onium salt, giving rise to the generation of sensitizer radical cations.

$$PS \xrightarrow{h\nu} PS^* \xrightarrow{On^+} \underset{\text{exciplex}}{[PS^* + On^+]} \rightarrow PS^{+\bullet} \tag{2}$$

(iii) Charge-transfer complexes[19] (CTC). Electronically excited charge transfer complexes of certain onium salts, namely pyridinium salts, and aromatic electron donors (D) undergo electron-transfer resulting in the formation of aromatic radical cations.

$$D + On^+ \rightarrow \underset{\text{CTC}}{[D + On^+]} \xrightarrow{h\nu} D^{+\bullet} \tag{3}$$

In a recent study,[20] radicals formed by the irradiation of a system containing a dye and an aromatic amine were oxidized by a diaryliodonium salt. By using the dye, the initiating system was extended to the region of visible light; the wavelengths of incident light were between 500 and 650 nm. Although the initiating mechanism is apparently complex, it is assumed to involve the oxidation of α-amino radicals, formed by hydrogen abstraction, to the respective cations, which initiate the polymerization.



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In another study,[21] dye-sensitized photodecomposition of polymeric iodonium salts was demostrated. Polyimidothioethers containing diaryliodonium salt groups in the main chain underwent degradation upon photolysis at $\lambda = 475$ nm in the presence of a sensitizing dye, benzoflavin.

In this paper, we shall report our preliminary results on the visible light cationic polymerization of cyclic ethers, vinyl ethers, and bisepoxides, initiated by a ternary system consisting of an alkyl halide, dimanganese decacarbonyl, and an onium salt.

Experimental Section

Materials. Cyclohexene oxide (CHO) was vacuum distilled from calcium hydride before use. *n*-Butyl vinyl ether was washed with water to remove alcohols and then dried with sodium and distilled under vacuum. Solvents were purified by conventional drying and distillation procedures. The commercial bisepoxide, 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (EEC) (Ciba Specialty Chemicals) was used as received. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$ (Merck), was purified by vacuum sublimation and stored in the dark in the refrigerator. *N*-Ethoxy-2-methylpyridinium hexafluorophosphate[22] ($EMP^+PF_6^-$), diphenyliodonium hexafluorophosphate[23] ($Ph_2I^+PF_6^-$), and triphenylsulfonium hexafluorophosphate[24] ($Ph_3S^+PF_6^-$) were prepared as described previously.

Photopolymerization. Photopolymerizations were carried out under nitrogen atmosphere. Bulk monomers containing given amounts of $Mn_2(CO)_{10}$, onium salt, and a halogenated solvent was placed in Pyrex tubes previously heated with a heat gun and flushed with dry nitrogen and irradiated at 435.8 nm in an AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and a monochromator. At the end of a given reaction time, solutions were poured into methanol; the precipitated polymers were filtered off and dried in vacuo.

Analysis of Polymers. Molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) on a Knauer M-64 instrument with a Hewlett-Packard column (Mixed-C PLgel, 5 μm)

[†] Dedicated to J. P. Kennedy on the occasion of his 70th birthday.

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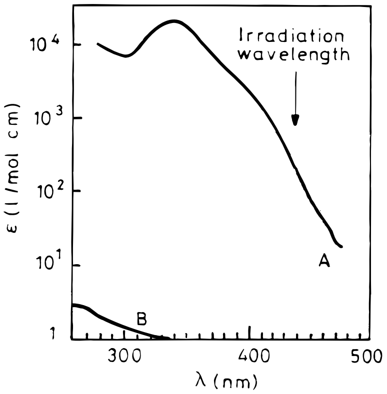


Figure 1. Optical absorption spectra of (a) $Mn_2(CO)_{10}$ and (b) $Ph_2I^+PF_6^-$ in methylene chloride.

using polystyrene standards. THF was used as the eluent at a flow rate of 1 mL min^{-1}, and detection was achieved with a differential refractometer.

Results and Discussion

The possibility of using metal carbonyls in combination with suitable co-initiators as a light initiating system for cationic polymerization was suggested by earlier studies on metal carbonyl initiation for free radical polymerization and studies on the high-energy initiation of cationic polymerization using alkyl halides and onium salts. Previously, it has been proposed by Bamford[25,26] that carbon-centered radicals were formed upon irradiation (λ = ca. 436 nm) of organic halides in the presence of dimanganese decacarbonyl, $Mn_2(CO)_{10}$. Upon absorption of light, $Mn_2(CO)_{10}$ decomposes to $Mn(CO)_5$. The latter reacts with the terminal halide group yielding initiating alkyl radicals.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5 \tag{5}$$

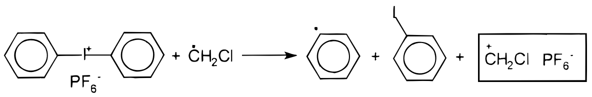
$$RX + Mn(CO)_5 \rightarrow R^{\bullet} + Mn(CO)_5\,X \tag{6}$$

$$R^{\bullet} + \text{monomer} \rightarrow \text{polymer} \tag{7}$$

It was found that both bromine and chlorine compounds were effective, and there was no initiation when no halide was present.

According to Teramato et al.,[27] cationic polymerization of monomers in methylene chloride solutions can be initiated by electron beam irradiation. The electrons present in the solution are absorbed virtually entirely by the solvent, and carbon-centered radicals thus formed are oxidized by suitable onium salts.

$$CH_2Cl_2 + e_s^- \longrightarrow \dot{C}H_2Cl + Cl^- \tag{8}$$



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It seemed therefore appropriate to trigger the cationic polymerization in a similar way by generating oxidizable radicals not by high energy irradiation but by the metal carbonyl photochemistry. Since the diphenyliodonium ion does not absorb at the irradiation wavelength, λ = 436 nm, all the light is absorbed by $Mn_2(CO)_{10}$ (Figure 1). As can be seen from Table 1, cyclohexene oxide was polymerized quite effectively with the ternary system consisting of manganese carbonyl, methylene chloride and diphenyliodonium salt. Experiments omitting any of these three components failed to produce polymer, which is consistent with the proposed mechanism. The proposed initiation mechanism is shown below.

Table 1. Photoinitiated Cationic Polymerization of Cyclohexene Oxide[a] by Using $Mn_2(CO)_{10}/CH_2Cl_2$ in the Presence of Onium Salts

onium salt	$E_{1/2}^{red}$ (V) vs SCE[b]	time (min)	conversion (%)	M_n[c]	M_w/M_n
Ph_2I^+	−0.2[28]	120	13	4090	1.48
EMP^+	−0.7[14]	120	0		
Ph_3S^+	−1.06[29]	120	0		

[a] [CHO] = 9.1 mol L^{-1}, [$Mn_2(CO)_{10}$] = 6.41 × 10^{-4} mol L^{-1}, [CHO]/[CH_2Cl_2] = 9/1 v/v, [onium salt] = 1.2 × 10^{-3}mol L^{-1}, λ= 435.8 nm. [b] Standard calomel electrode. [c] Determined by GPC based on a calibration with PSt standards.

Table 2. Photoinitiated Cationic Polymerization of Cyclohexene Oxide[a] by Using $Mn_2(CO)_{10}$ in the Presence of Various Halogen-Containing Solvents

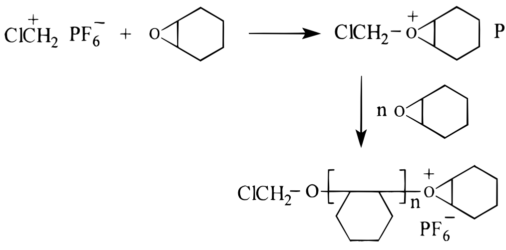
−C−Cl[b]	$\epsilon^{c,30}$	time (min)	conversion (%)	M_n[d]	M_w/M_n
C_4H_9Cl	7.27	120	5.5	4110	1.26
CH_2Cl_2	8.93	120	13	4090	1.48
$CHCl_3$	4.81	120	2	4603	1.33
CCl_4	2.24	120	<1		

[a] [CHO] = 9.1 mol L^{-1}, [$Mn_2(CO)_{10}$] = 6.41 × 10^{-4} mol L^{-1}, [Ph_2I^+] =1.2 × 10^{-3} mol L^{-1}, and λ= 435.8 nm. [b] [−C−Cl]/[CHO] = 1/9 v/v. [c] Dielectric constant. [d] Determined by GPC based on a calibration with PSt standards.

$$CH_2Cl_2 + Mn(CO)_5 \rightarrow \dot{C}H_2Cl + Mn(CO)_5Cl \tag{10}$$

$$\dot{C}H_2Cl + Ph_2I^+\,PF_6^- \rightarrow CH_2Cl^+\,PF_6^- + PhI + Ph^{\bullet} \tag{11}$$

The resulting cations can directly react with the monomer.



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(13)

In agreement with the proposed mechanism, the initiation efficiency of the ternary initiating system is related to redox potential of the onium salt, which acts as an oxidizing agent (Table 1). As can be seen, the diphenyl iodonium salt is the most suitable onium salt for the oxidation of radicals. On the other hand, alkoxy pyridinium and triphenyl sulfonium salts are not capable of initiating the free radical promoted cationic polymerization due to their low reduction potential.

Polymerization of cyclohexene oxide was also conducted in various solvents possessing halide atoms (Table 2). It is interesting to note that the efficiency of the organic halide in the metal carbonyl initiated cationic polymerization decreases in the order CCl_2 > CCl > CCl_3 > CCl_4. Notably, only negligible amounts of polymer are formed with CCl_4 after irradiating for 2 h under identical experimental conditions. This order differs from the reactivity of the halides in the manganese carbonyl initiated free radical polymerization.[26]

Table 3. Photoinitiated Cationic Polymerization of Various Monomers[a] by Using $Mn_2(CO)_{10}$/CH_2Cl_2 in the Presence of $Ph_2I^+PF_6^-$

monomer (mol L^{-1})	time (min)	conversion (%)	M_n[d]	M_w/M_n
CHO (9.1)	120	13	4090	1.48
n-BVE (3.1)	45	70	30630	1.8
EEC[b]	70	gel[c]		

[a] $[Mn_2(CO)_{10}] = 6.41 \times 10^{-4}$ mol L^{-1}, $[CH_2Cl_2] = 1.55$ mol L^{-1}, $[Ph_2I^+] = 1.2 \times 10^{-3}$ mol L^{-1}, and $\lambda = 435.8$ nm. [b] $Mn_2(CO)_{10} = 5 \times 10^{-3}$ mol L^{-1}; CY 179/CH_2Cl_2 = 2/1 (w/w). [c] Totally gelled. [d] Determined by GPC based on a calibration with PSt standards.

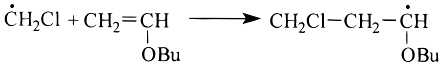
The reactivity increases in the latter process with multiple substitution in the order $CCl > CCl_2 > CCl_3 > CCl_4$. This difference in reactivity can be explained by the fact that, according to the proposed mechanism, the oxidizability of the radical is the major issue in the cationic polymerization. Provided the oxidation and reduction potentials of the free radical and onium ion, respectively are known, it can be estimated on the basis of the Rehm−Weller[31] equation whether a radical can be oxidized by a given salt or not

$$\Delta G = F[E^{ox}_{1/2}(R^{\bullet}) - E^{red}_{1/2}(On^+)]$$

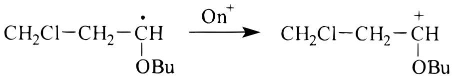
$$F \equiv \text{Faraday constant} \tag{14}$$

However, the calculation of ΔG is usually not feasible since the exact oxidation potentials $E^{ox}_{1/2}(R^{\bullet})$ of carbon-centered radicals formed from the organic halides are unknown. We believe that the electron-withdrawing effect of the chlorine atom plays an important role in the reactivity of the solvent in the oxidation process. Solvents possessing three and four halogen atoms at the same carbon atom hardly initiate the polymerization. Polarity of the solvent is also important. In methylene chloride, which is the most polar among the solvents tested and which forms a radical can be oxidized by the diphenyliodonium salt, the polymerization is very efficient, while in carbon tetrachloride which is both nonpolar and supposedly has a high oxidation potential, polymerization essentially does not occur.

In addition to CHO, butyl vinyl ether (BVE) and 3,4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (EEC) were also examined (Table 3). These monomers also polymerized readily in methylene chloride solutions containing dimanganese decacarbonyl and diphenyliodonium salt. In the case of the BVE monomer, in addition to direct oxidation, carbon-centered radicals react with the monomer molecules producing electron donor radicals. Thus formed, these radicals can easily be oxidized by the onium salt to the corresponding initiating species.



$$\dot{C}H_2Cl + CH_2{=}\underset{OBu}{CH} \longrightarrow CH_2Cl{-}CH_2{-}\underset{OBu}{\dot{C}H} \tag{15}$$



$$CH_2Cl{-}CH_2{-}\underset{OBu}{\dot{C}H} \xrightarrow{On^+} CH_2Cl{-}CH_2{-}\underset{OBu}{\overset{+}{C}H} \tag{16}$$

In the case of EEC, which possesses two epoxide groups, an insoluble network polymer was readily formed.

Conclusions

The dimanganese decacarbonyl−organic halide combination is an efficient co-initiator for visible light cationic polymerization when used in conjunction with suitable onium salts such as diphenyl iodonium hexafluorophosphate. Simple halogen-containing solvents can be used as organic halides. The mechanism follows free radical generation by the reaction manganese carbonyl photoproduct with the halide group and subsequent oxidation of thus formed carbon-centered radicals to yield reactive cations. The efficiency of the last step is controlled both by the polarity of the medium and by the redox potentials of the onium salt and the carbon centered radical.

The most striking advantage of this ternary initiating system is its applicability to pigmented systems in the visible range and preparation of polymers and copolymers with novel topologies. Hyperbranched, branched, and star polymers and block and graft copolymers may be prepared by using suitably selected low molecular weight and polymeric halides as part of the photoinitiation system. Further studies in this line are now in progress.

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