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Photoinitiation of cationic polymerization by visible light activated titanocene in the presence of onium salts

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Summary

A visible light photoinitiating system for cationic polymerization of cyclic ethers such as cyclohexene oxide (CHO) and vinyl monomers such as n-butyl vinyl ether (BVE) and N-vinyl carbazole (NVC) has been developed, using a fluorinated titanocene free radical photoinitiator, Irgacure 784, together with an onium salt, such as diphenyl iodonium hexafluoro antimonate and N-ethoxy-2-methyl-pyridinium hexafluoroantimonate. Based on the reported photochemistry of fluorinated titanocenes, a mechanism for generating cationic species is proposed based on electron transfer between photoproducts of titanocene and onium salt. Evidence against the incorporation of an aromatic titanocene moiety in the resulting polymers is presented. Inhibition by a specific proton scavenger suggests that protons may initiate the polymerization.

Introduction

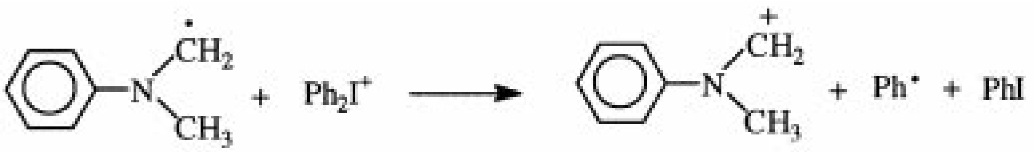
Photoinitiated cationic polymerization is an important industrial process used in a number of applications such as coatings, inks, adhesives and photolithography[1,2]. The process is based on the photogeneration of reactive cations or Bronsted acids which react with monomers such as vinyl ethers and cyclic ethers. Diaryliodonium[3,4] triarylsulphonium[5] and alkoxypyridinium[6-8] salts are technically useful onium type photoinitiators and their chemistry has been studied in detail. The spectral response of simple onium salts is usually below 300 nm and for their practical application it is often required to extend it to higher wavelengths. Besides chemical attachment of chromophoric groups, several indirect ways to overcome this problem have been described[10]. These pathways include electron transfer via exciplexes [11,12], oxidation of free radicals[13-16] and excitation of charge transfer complexes[17]. Among them free radical promoted cationic polymerization is particularly useful since free radical photoinitiators with a wide range of absorption characteristics are available. Many photochemically formed radicals can be oxidized by onium salts. The cations thus generated are used as initiating species for cationic polymerization according to the following reactions.

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}\cdot \qquad (1)$$

$$\mathrm{R}\cdot \xrightarrow{\mathrm{On}^{+}} \mathrm{R}^{+} + \mathrm{On}\cdot \qquad (2)$$

$$\mathrm{R}^{+} \xrightarrow{\mathrm{M}} \mathrm{Polymer} \qquad (3)$$

Although the use of many photoinitiators in free radical promoted cationic polymerization has been described, the sensitivity of the initiating system could be only rarely extended to the region of visible light. In a recent study[19], radicals formed by the irradiation system containing a xanthen dye and an aromatic amine, were oxidized by a diaryliodonium salt. By using the dye, the wavelengths of incident light chosen were between 500 and 650 nm. The initiation mechanism is assumed to involve the oxidation of α-amino radicals formed after hydrogen abstraction to the respective cations, which initiate the polymerization.



(4)

More recently, a novel visible light initiating system for the cationic polymerization of cyclic ethers such as cyclohexene oxide (CHO) and alkyl vinylethers such as butyl vinylether (BVE) was described[20]. This system consists of an organic halide, namely halogen containing solvents, dimanganese decacarbonyl, $Mn_2(CO)_{10}$ and an onium salts such as diphenyl iodonium salt, $Ph_2I^+PF_6^-$. Radical generation was achieved upon irradiation of $Mn_2(CO)_{10}$ in the presence organic halide at $\lambda = 436$ nm where the onium salt is transparent. A feasible mechanism involves oxidation of the carbon centered radicals to the corresponding cations capable of initiating cationic polymerization.

The proposed initiation mechanism, in which solvent methylene chloride and diphenyl iodonium salt were used as organic halide and oxidant, respectively, is shown below.

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

$$\mathrm{CH_2Cl_2} + \mathrm{Mn(CO)_5} \longrightarrow \dot{\mathrm{C}}\mathrm{H_2Cl} + \mathrm{Mn(CO)_5Cl} \qquad (6)$$

$$\dot{\mathrm{C}}\mathrm{H_2Cl} + \mathrm{Ph_2I^{+}PF_6^{-}} \longrightarrow \overset{+}{\mathrm{C}}\mathrm{H_2Cl\ PF_6^{-}} + \mathrm{PhI} + \mathrm{Ph}\cdot \qquad (7)$$

Both systems consisted of three components for the generation reactive cations and the initiation mechanisms are rather complex. In fact, for free radical polymerization, many visible light photoinitiating systems have been proposed and shown to be efficient[1]. Among them titanocene derivatives represent one of the few examples that are directly activated upon photolysis to initiate the free radical polymerization[21].

In this paper, a commercial titanocene type photoinitiator, namely Irgacure 784, was tested for its suitability as the visible light free radical source in free radical promoted cationic polymerization.

Experimetal

Materials

Titanocene photoinitiator, Irgacure 784, obtained from Ciba Specialty Chemicals was used as received. 2, 6-Di-tert-butyl-4-methyl pyridine (DBMP) was purchased from Aldrich and used as received. Cyclohexene oxide (CHO) was vacuum distilled from calcium hydride before use. n-Butyl vinyl ether (BVE) was washed with water to remove alcohols and then dried with sodium and distilled under vacuum. N-Vinyl carbazole (NVC) was crystalized from ethanol. 3',4'-Epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC), obtained from Ciba Specialty was used without further purification. Dichloromethane (CH_2Cl_2) (Lab-scan) was washed with conc. H_2SO_4 until the acid layer remained colourless, then washed with water, aq. %5 NaOH and then water again. It was pre-dried with $CaCl_2$ and distilled from CaH_2. Diphenyliodonium hexafluorophosphate[10] ($Ph_2I^+PF_6^-$), triphenylsulfonium hexafluorophosphate[1] ($Ph_3S^+PF_6^-$) and N-ethoxy-2-methylpyridinium hexafluorophosphate[10, 11] ($EMP+PF_6^-$), were prepared as described previously.

Photopolymerization

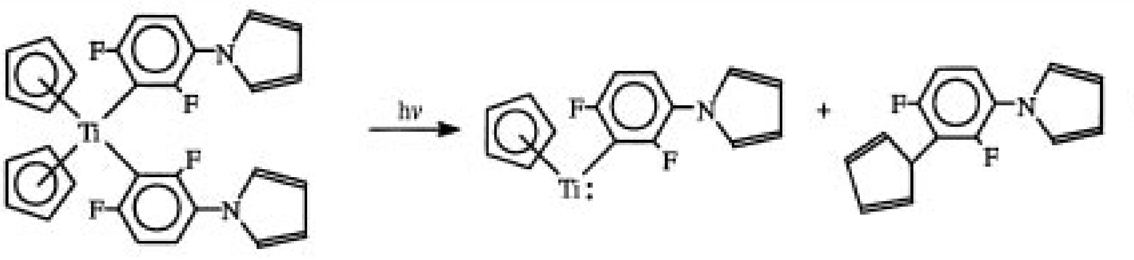
Photopolymerizations were carried out under nitrogen atmosphere. Prior to irridation, the appropriate solutions of monomers containing given amounts of Irgacure 784, onium salts, and dichloromethane (solvent) was placed in pyrex tubes previously heated with a heat gun and flushed with dry nitrogen and irradiated at λ=460 nm in an AMKO Ltd. photoreactor equipped with a HBO 100 W xenon lamp and a monochromator. The viscous polymer solutions formed during the irradiation were poured into methanol. The precipitated polymers were then filtered off and dried in vacou.

Characterization of Polymers

Molecular weight and molecular weight distrubition of the polymers were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with R410 differential refractometer and 600E pump using monodisperse polystyrene standards.THF was used as the eluent at a flow rate of 1.0 mL/min. ^{1}H-NMR measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz instrument. UV spectra were recorded on a Perkin-Elmer Lambda spectrophotometer.

Results and Discussion

Cyclohexene oxide (CHO) was polymerized with combination of Irgacure 784 and an onium salt. Polymerizations were performed at λ=460 nm where all onium salts are transparent and all the light emitted is absorbed by the titanocene initiator. This can be seen from Figure 1, where absorption spectra of Irgacure 787 and onium salts employed in this study are presented. CHO was deliberately chosen as cationically polymerizable monomer since it is not prone to undergo hydrogen abstraction nor can be polymerized by a radical mechanism. As can be seen from Table 1, CHO was polymerized effectively with iodonium and N-alkoxy pyridinium salts. Simple triaryl sulphonium salts do not undergo radical induced decomposition due to the unfavorable redox potentials. Notably, the two components of the initiating system are indispensable for the polymerization to occur; no polymer is formed in the absence of one of the compounds under our reaction conditions. When DBMP, a typical proton scavenger, was present in the reaction mixture, no polymer was formed during irradiation indicating that protons act as initiators. Photodecomposition behavior of titanocene derivatives is related to their structure. Radical trapping experiments revealed that non-fluorinated diary titanocenes photodecompose via homolytic cleavage of the metal-aryl-ligand bond to generate aryl and titanocene radicals[10, 11]. However, the corresponding fluorinated titanocene derivatives such as Irgacure 784 yield no primary organic radicals but titanium centered diradicals according to the following reaction[10, 11].



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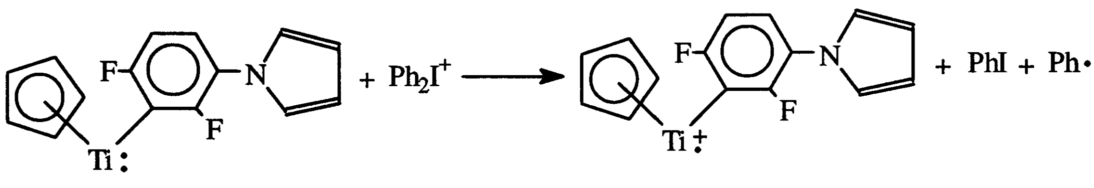
In the presence of suitable oxidants, such as onium salts, these biradicals may undergo electron transfer reaction to yield radical cations.



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The possibility of direct initiation by radical cations thus formed is precluded by spectroscopic investigations of the resulting polymer. As can be seen from the ^{1}H-NMR spectrum shown in Figure 2, aromatic moieties of the titanocene initiator were not covalently attached to polycyclohexene oxide. Similar observation was made by UV-Vis absorption measurements, i.e., absorptions arising from the aromatic chromophores are not detectable. Regarding the initiation mechanism, the experiment with the proton scavenger DBMP revealed that an important role is played by protons. Although the source of protons cannot be determined at present, the results suggest that they initiate the polymerization of CHO.

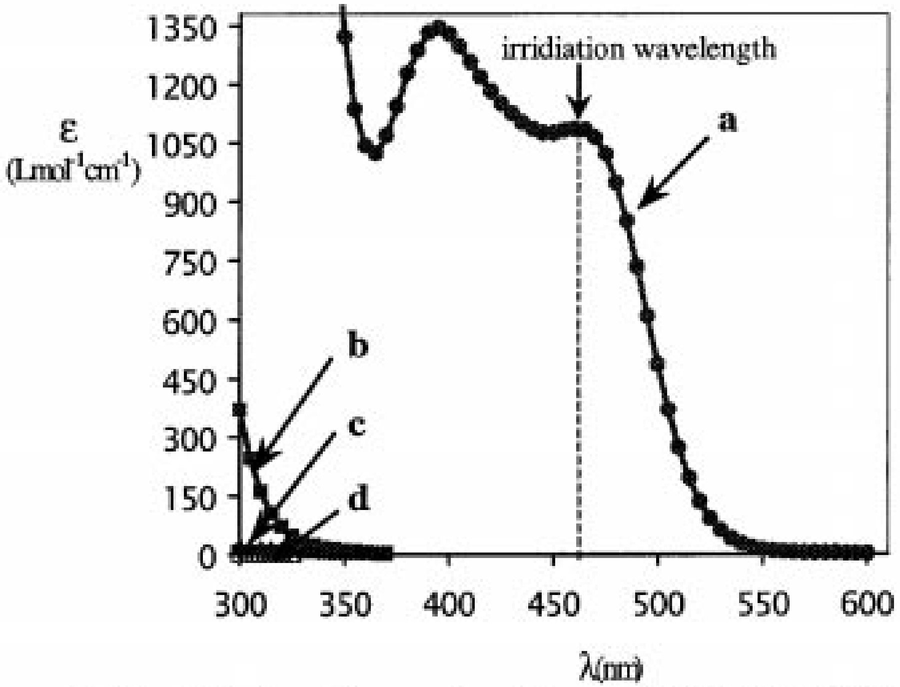

Figure 1. UV-visible absorption spectra of Irgacure 784 (**a**), $Ph_2I^+PF_6^-$ (**b**), $Ph_3S^+PF_6^-$ (**c**) and $EMP^+PF_6^-$ (**d**) in methylene chloride.

Table 1. Photoinitiated polymerization of CHO (4.55 mol l^{-1}) by using Irgacure 784 (5 x 10^{-3} mol l^{-1}) in methylene chloride, λ=460nm, room temperature.

Onium salt (5 x 10^{-3} mol l^{-1})	$E_{red}^{1/2}$ V(SCE)	Irradiation time (min)	Conversion (%)	Mn[a] (g mol^{-1})	Mw/Mn[a]
Ph_2I^+	-0.2[10, 11]	30	76	7200	2.75
Ph_2I^{+b}	-0.2[10, 11]	90	0	-	-
Ph_3S^+	-1.0[10, 11]	180	0	-	-
EMP^+	-0.7[10, 11]	150	31	7600	2.34
-	-	200	0	-	-

[a] Determined by GPC according to polystyrene standards

[b] Polymerization was performed in the presence of DMTP (10^{-2} mol l^{-1})

Table 2. Photoinitiated polymerization of various monomers by using Irgacure 784 and $Ph_2I^+PF_6^-$ in methylene chloride at λ=460 nm at room temperature.

Monomer (mol l^{-1})	Irradiation time (min)	Conversion (%)	Mn^a (g mol^{-1})	Mw/Mn^a
CHO (4.55)	30	76	7200	2.75
BVE (3.87)	45	21	20000	2.62
NVC (1.05)	180	88	2500	1.42
EEC^a	250	0	-	-

[a]Determined by GPC according to polystyrene standards
[b]1/1, v/v in methylene chloride

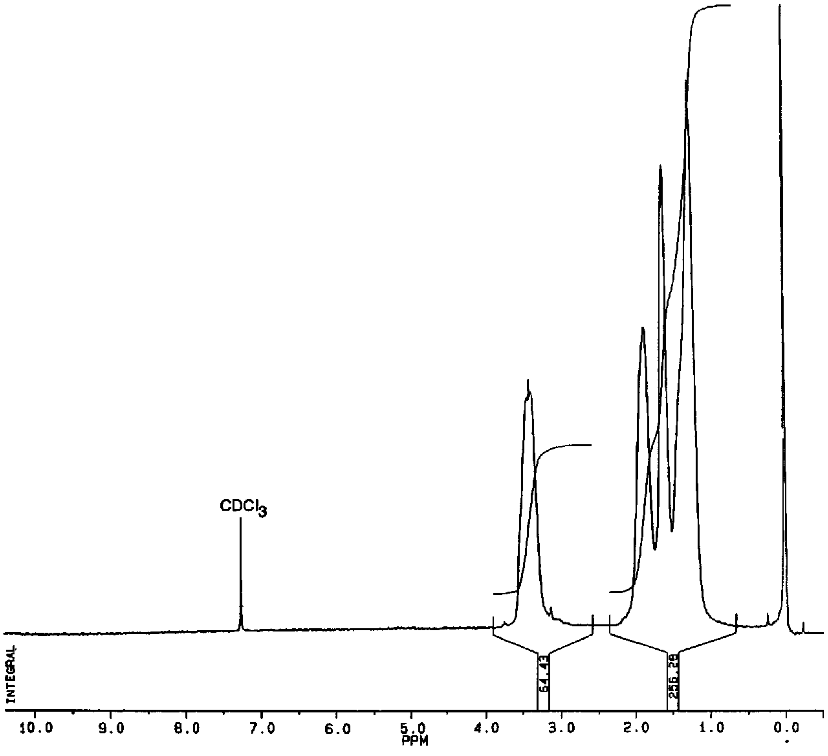

Figure 2. ^{1}H-NMR spectrum of polycyclohexene oxide initiated by Irgacure 784 in the presence of $Ph_2I^+PF_6^-$ at λ=460 nm (see Table 1 for the experimental conditions).

In addition to CHO, the polymerization of other cationically polymerizable monomers using this dual system was studied. Polymerization conditions and results are shown in Table 2. As can be seen, BVE and NVC polymerized very efficiently while bifunctional monomer, 3', 4'-epoxycyclohexyl-3',4'-epoxycyclohexene carboxylate (EEC) did not polymerize with this initiating system. It should be pointed out that NVC is also polymerizable via a free radical mechanism. However, attempts to polymerize NVC under the same absorptivity and experimental conditions by Irgacure 784 in the absence of onium salt failed to produce any polymer. This observation indicates that the mechanism of free radical polymerization initiated by titanocene derivatives is more complex than known in the literature and needs further studies for clarification. Interestingly, cationic polymerization of NVC is promoted by the addition of onium salts to the titanocene initiator, although the corresponding radical process is inefficient.

In conclusion, although mechanistic details are not as yet elucidated, it is clear that photoinitiation of cationic polymerization by using Irgacure 784 photoinitiator in combination with certain onium salts can be efficiently achieved in the visible spectral region. Work in progress is directed at further understanding mechanistic details, in particular, the initiation mechanism of individual systems containing titanocene derivatives.

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