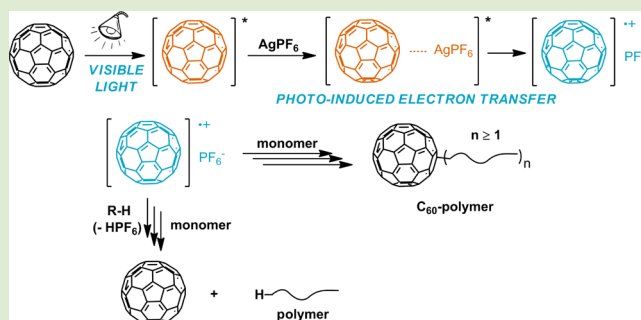


Visible Light-Induced Cationic Polymerization Using Fullerenes

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Supporting Information

ABSTRACT: A novel visible light sensitive photoinitiator system for the cationic polymerization of typical monomers, for example, of oxiranes, such as cyclohexene oxide, vinyl ethers, such as iso-butyl vinyl ether, and other vinyl monomers, such as *N*-vinylcarbazole, using fullerene derivatives is described. The cationic polymerization of these monomers was initiated at room temperature upon irradiation in the visible region ($\lambda_{\text{inc}} > 400$ nm) in bulk or chlorobenzene solutions with polystyrene- C_{60} (PS- C_{60}) adduct or bare C_{60} , respectively, in the presence of oxidizing salts such as silver hexafluorophosphate (AgPF_6) and diphenyliodonium hexafluorophosphate ($\text{Ph}_2\text{I}^+\text{PF}_6^-$). A feasible mechanism, as correlated with optical absorption measurements, free energy changes (ΔG), and proton scavenging studies, involves formation of exciplex by the absorption of light in the first step. Subsequent electron transfer from excited C_{60} or PS- C_{60} to oxidizing salt yields radical cations of the fullerene derivatives. Both radical cations and a strong Brønsted acid derived by hydrogen abstraction initiate the cationic polymerization of a variety of monomers.



Solar energy is the basis of all natural chemistry. In nature, a variety of electron transfer reactions such as photosynthesis are promoted by visible light.^{1,2} Artificially, many organic reactions are also driven by solar energy, affording important advantages meeting the actual objectives of green chemistry.^{3–7} The most common organic and polymeric compounds are transparent in the visible region (400–800 nm), which accounts for about 43% of the incoming solar spectrum. As a result, there has been great interest in developing soluble and processable organic and polymer-based catalysts absorbing efficiently in the visible region of the spectrum.^{8–13}

Photoinitiated polymerization is a well-known technique exploited in many industrially important areas.¹⁴ Both free radical and cationic polymerizations have been used, and the mechanisms of initiation have been studied in detail.^{15–24} The free radical mode is in a more advanced state due to not only its applicability to a wide range of monomers but also availability of photoinitiators with a broad spectral sensitivity, including the visible range.^{22,25,26} Such photoinitiators are widely used in many targeted applications such as dental filling materials, photoresists, printing plates, integrated circuits, laser-induced 3D curing, holographic recordings, and nanoscale micro-mechanics. The most prominent cationic photoinitiators are iodonium²⁷ and sulphonium salts,²⁸ which absorb the light in the far and mid-UV regions. Extension of the spectral sensitivity of cationic polymerization to near UV and visible ranges is realized by the activation with light-sensitive additives, which do not directly initiate the polymerization.^{29,30} Three different modes can be distinguished to externally stimulate the activity

of the onium salts in the visible range: (i) oxidation of free radicals by onium salts (also called free radical promoted cationic polymerization),^{31–33} (ii) electron transfer between the photoexcited sensitizer and an onium salt,^{34,35} and (iii) electron transfer in photoexcited charge transfer complexes of certain onium salts.³⁶ Among them, photosensitizer and onium salt combinations give rise to the unique initiating systems through electron transfer within the exciplex formed, consequently, becoming a useful tool to adjust the absorption characteristics and initiation efficiency. The excellent photosensitizers of aromatic compounds include several requirements, such as suitable solubility in monomers, excitation and oxidation energy levels well-matched with the acceptors, and absorption bands in the near UV and visible ranges. Electron-rich polynuclear aromatic compounds such as anthracene, perylene, pyrene, and phenothiazine appear to be efficient photosensitizers fulfilling these requirements. In our previous studies, we reported that several conjugated thiophene derivatives with extended conjugation can also act as electron-transfer photosensitizers in the near UV and visible regions for the photoinitiated cationic and free radical polymerization using onium salts.³⁷

Buckminster fullerene (C_{60}) exhibits excellent photochemical, superconducting, electrical, and magnetic properties due its

Received: September 10, 2012

Accepted: September 27, 2012

Published: October 2, 2012

aromatic-like character.^{38–40} Each carbon atom of its skeleton is connected to the others by 3 σ -bonds and carries a single electron at the outer shell to yield highly conjugated π -bonds at the surface. However, due to the s character in the π system induced by the curvature, the oxidation potential of C_{60} is high (~ 1.7 V vs saturated calomel electrode). Generally, C_{60} has a strong tendency to be reduced in multiple single-electron transfer steps (from 0 to a maximum of -6) and to react with nucleophiles, as it is said to be an “electrophile par excellence”.^{41–44} However, recent studies showed that C_{60} can be oxidized to its respective cations. Reed et al. described the synthesis and taming of $C_{60}^{\bullet+}$ and HC_{60}^+ in solution by treating C_{60} with superacids.⁴⁵

In virtue of all these points, we decided to focus our attention on the possibility of the oxidation of fullerenes by photo-induced electron transfer reactions and its use in synthetic polymer chemistry. Herein we introduce a novel visible light method for the initiation of cationic polymerization of oxirane and vinyl monomers such as cyclohexene oxide (CHO) and *n*-isobutyl vinyl ether (IBVE) and *N*-vinyl carbazole (NVC), respectively. The components used for the initiation consist of a fullerene derivative (bare C_{60} or polystyrene- C_{60}) as the light absorbing molecule and an oxidizing agent, namely, silver hexafluorophosphate ($AgPF_6$) or diphenyl iodonium hexafluorophosphate ($PhI^+PF_6^-$). Experimentally, the photopolymerization of these representative monomers was conducted by exposing bulk or chlorobenzene solutions in visible light at different experimental conditions. At the irradiation wavelength, $\lambda > 400$ nm, the light emission is well matched with the absorption of C_{60} (Figure 1) and oxidants are transparent.

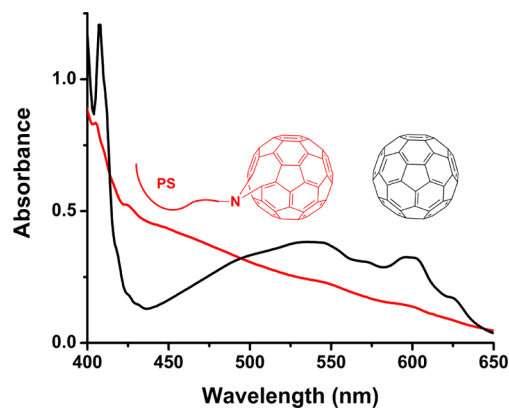


Figure 1. Visible absorption spectra of C_{60} and PS- C_{60} at equal concentrations in chlorobenzene (5.6×10^{-4} M).

In the polymerizations, chlorobenzene was used as the aromatic reaction solvent because C_{60} is not soluble in monomers. Compare to the other possible C_{60} dissolving solvents (benzene, toluene, etc.), chlorobenzene has a lower nucleophilicity due to the negative inductive effect of the chloro-substituent. Thus, its interference with the cationic species is restricted. Typical results are collected in Table 1. It should be pointed out that no polymerization took place in the control experiments in which either of the components was missing.

With all the monomers tested, rather low conversions were attained which may be due to poor solubility, the employment of a solvent and relatively less favorable thermodynamic conditions (vide infra). To increase the efficiency of the

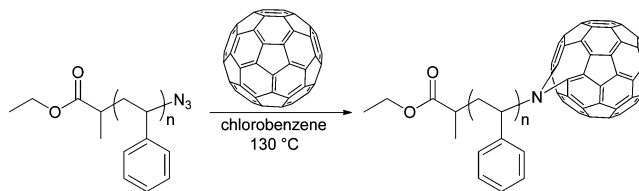
Table 1. Visible Light Induced Cationic Polymerization^a of Various Monomers Using C_{60} in the Presence of Oxidants in Chlorobenzene

oxidant	monomer ^b	conv. (%) ^c	M_n^d (g mol ⁻¹)	M_w/M_n^d
$AgPF_6$	CHO	4.2	3020	1.6
$AgPF_6$	IBVE	4.7	9480	1.1
$Ph_2I^+ PF_6^-$	CHO	<1	3200	1.2
$Ph_2I^+ PF_6^-$	IBVE	<1	9700	1.8

^a $[Monomer]/[oxidant]/[C_{60}] = 200/3/1$; $[C_{60}] = 1.7 \times 10^{-3}$ M; $\lambda > 400$ nm; light intensity = 45×10^{-3} W m⁻²; irradiation time = 2 h. ^bCHO, cyclohexene oxide; IBVE, isobutyl vinyl ether. ^cDetermined gravimetrically. ^dDetermined by gel permeation chromatography using polystyrene standards.

fullerene-based photosensitizing system by improving solubility and electrochemical properties, C_{60} , was modified by a simple conjugation process. Previously, several click strategies involving Cu(I)-mediated 1,3-dipolar Huisgen,⁴⁶ Diels–Alder coupling⁴⁷ and thiol–ene reactions⁴⁸ were successfully used to modify C_{60} . In the present work, the reaction of an azide terminal polystyrene with bare C_{60} readily afforded a monoaddition polymeric derivative of fullerene (PS- C_{60}) using a previously reported procedure (Scheme 1).⁴⁹

Scheme 1. Synthesis of a Polystyrene Derivative of Fullerene (PS- C_{60})



The visible light initiated polymerizations were conducted with the PS- C_{60} under similar experimental conditions to that of bare fullerene. The results are collected in Table 2.

Table 2. Visible Light Induced Cationic Polymerization^a of Various Monomers Using PS- C_{60} in the Presence of Oxidants in Chlorobenzene

oxidant	monomer ^b	conv. (%) ^d	M_n^e (g mol ⁻¹)	M_w/M_n^e
$AgPF_6$	CHO	78.0	4160	2.2
$AgPF_6$	CHO ^c	11.1	2720	1.3
$AgPF_6$	IBVE	46.6	10140	3.4
$AgPF_6$	NVC	70.1	3300	15.6
$Ph_2I^+ PF_6^-$	CHO	15.4	4010	3.1
$Ph_2I^+ PF_6^-$	IBVE	24.1	7200	4.2

^a $[Monomer]/[oxidant]/[C_{60}] = 200/3/1$; $[C_{60}] = 1.7 \times 10^{-3}$ M; $\lambda > 400$ nm; light intensity = 45×10^{-3} W m⁻²; irradiation time = 2 h. ^bCHO, cyclohexene oxide; IBVE, isobutyl vinyl ether; NVC, *N*-vinylcarbazole. ^cIn the presence of 2,6-di-*tert*-butylpyridine (5.0×10^{-3} M). ^dDetermined gravimetrically. ^eDetermined by gel permeation chromatography using polystyrene standards.

Although much higher conversions were obtained with all monomers, IBVE and NVC were polymerized more effectively due to their strong electron donating nature. Silver salt exhibited better activation efficiency than iodonium salt, which correlates well with their reduction potentials. It is also noted that although at much reduced rate, polymerization also

proceeds in the presence of a proton scavenger, 2,6-di-*tert*-butylpyridine, indicating reactive species other than a Brønsted acid are involved in the initiation process.

As for the all-polynuclear aromatic compounds, electron transfer from the excited fullerene derivative to oxidant is feasible if the change in free energy (ΔG) is negative. On the basis of the oxidation potential (E_{ox}) and active excitation energy (E^*) of fullerene (C_{60}) and the reduction potential (E_{red}) of the oxidant (Ox), the free energy change (ΔG) for the photoinduced electron transfer process was estimated by Rehm–Weller equation constant according to eq 1 where f_c is the Faraday constant.

$$\Delta G = f_c [E_{\text{ox}}(C_{60}) - E_{\text{red}}(\text{Ox})] - E^*(C_{60}) \quad (1)$$

Table 3 summarizes the ΔG values of the free energy changes for the electron transfer from the singlet states of the fullerene

Table 3. Free Energy Changes for the Electron Transfer from Singlet Excited States of Fullerenes to Cationic Salts

fullerene	E_{ox}^a (V)	oxidant	ΔG (kcal/mol)
C_{60}	1.7	AgPF_6	-50.2
		$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	-27.3
PS- C_{60}	1.2	AgPF_6	-62.1
		$\text{Ph}_2\text{I}^+ \text{PF}_6^-$	-38.8

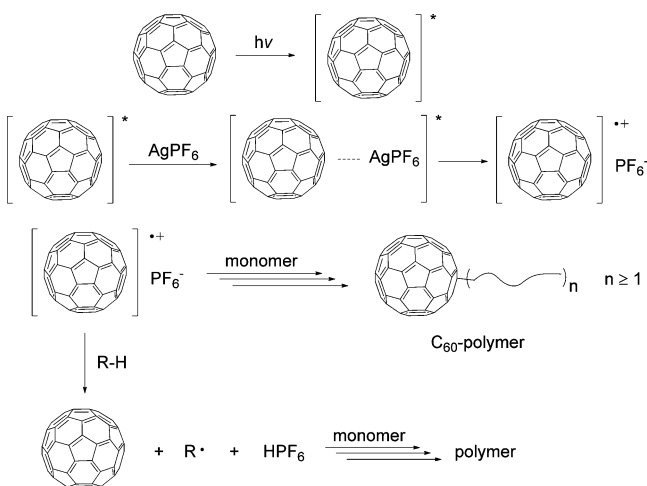
^aAs found by cyclic voltammetry measurements.

to the ground-state oxidant. E_{ox} and E_S^* for C_{60} and PS- C_{60} were determined by cyclic voltammetry and fluorescence measurements, respectively.

As can be seen from Table 3, electron transfer in singlet excited state of both fullerene compounds is thermodynamically favorable. A mechanism based on electron transfer concerning the reaction of excited C_{60} with oxidant is described in Scheme 2. The same mechanism may also be postulated for the PS- C_{60} .

The radical cations of C_{60} formed would be capable of initiating cationic polymerization since direct initiation by the species formed from polynuclear aromatic compounds is a well-known process, and because of the non-nucleophilicity of PF_6^- ions, cationic chain propagation would not be prevented.²⁰ Principally, polymerization could also be initiated by the

Scheme 2. Visible Light Induced Cationic Polymerization by Fullerene Sensitization



Brønsted acids formed via hydrogen abstraction. The polymerization proceeded even in the presence of a proton scavenger (see Table 2) indicates that both radical cations and Brønsted acids play an important role regarding the initiation of cationic polymerization.

In conclusion, a new visible light sensitive cationic photo-initiator system consisting of fullerenes and oxidizing salt has been designed. Key features of this initiating system are (i) the use of visible light, for example, $\lambda > 400$ nm, to excite fullerenes that undergo electron transfer reactions with the oxidizing salt, and (ii) the resulting radical cations and/or Brønsted acid formed from the hydrogen abstraction reaction initiate the polymerization. New initiating systems for cationic polymerization acting at visible range such as this will play an important role in emerging fields such as highly pigmented coatings, rapid setting inject inks, coatings for wood preservation, and three-dimensional imaging processes that require visible light sensitization. The initiation through the radical cations by preventing Brønsted acid initiation using proton scavenger may open a new pathway for the preparation of polymer–fullerene conjugates. Further studies in this line are now in progress.

■ ASSOCIATED CONTENT

Supporting Information

Additional experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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