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Initiation of Cationic Polymerization by Photoinduced Electron Transfer

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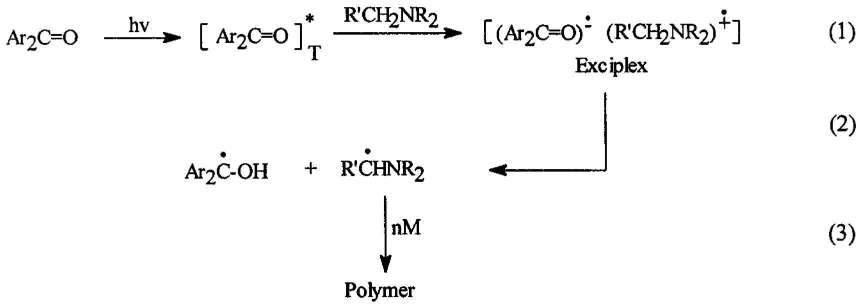
Abstract: The objective of this paper is to discuss: (i) the general approaches to the initiation of cationic polymerization by photinduced electron transfer reactions (ii) the use of photoinduced electron transfer reactions for block copolymer synthesis. For the first, it is concluded that three general methods are currently available which involve reduction of onium salts by (a) photogenerated radicals, (b) photoexcited sensitizers or (c) electron donor compounds in charge transfer complexes. According to this view, a variety of initiating systems are discussed. For the second, recent developments on the application of photoinduced electron transfer reactions to the synthesis of block copolymer of monomers polymerizable with different mechanisms are presented.

Introduction

Photoinduced electron transfer reactions are widely used in various synthetic applications [Ref. 1]. Many research effords have been devoted to use photoinduced electron transfer reactions in initiation of polymerization by radical and cationic mechanisms [Ref. 2,3]. Most of the bimolecular initiating systems for free radical polymerization are based on photoinduced electron transfer process. These systems include aromatic carbonyl/amine combinations, dye-coinitiators [Ref. 4] and transition metal organometallic complexes [Ref. 5]. The most recognized and practically used free radical initiating system is the reduction of aromatic carbonyls, usually ketones, by a large variety of electron donor molecules, particularly amines. The general mechanism is represented below.



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Photoinduced electron transfer reactions may also be used for the initiation of cationic polymerization [Ref. 6]. This approach involves the use of onium salts (iodonium, sulphonium, alkoxy pyridinium salts, etc.) in conjuction with co-iniators. It should be pointed out that these salts themselves can initiate cationic polymerizations upon irradiation. But, the spectral response of simple onium salts is only rarely acceptable for their practical application. The advantage of photoinduced electron transfer reactions, therefore, derives from the fact that many light sensitive compounds may be utilized, what enables an extension spectral sensitivity of onium salts to longer wavelengths where commercial lamp sources emmit the light.

Regarding photoinduced electron transfer initiation of cationic polymerization three modes of action concerning the formation of cationic species capable of reacting with monomers are distinguished;

i) Oxidation of free radicals. Many photolically formed radicals can be oxidized by onium salts [Ref. 7-9]. The cations thus generated are used as initiating species for cationic polymerization.

$$R^{\bullet} \xrightarrow{On^{+}} R^{+} \qquad (4)$$

ii) Electron transfer between a photoexcited molecule and an onium salt. Certain aromatic hydrocarbons are able 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 molecules to the onium salt giving rise to the generation of sensitizer radical cations [Ref. 10].

$$PS \xrightarrow{h\nu} PS^{*} \xrightarrow{On^{+}} \underset{\text{Exciplex}}{[PS^{*} + On^{+}]} \longrightarrow PS^{+\bullet} \qquad (5)$$

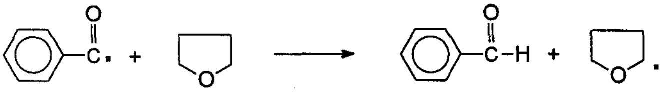
iii) Charge transfer complexes (CTC). Electronically excited charge transfer complexes of certain onium salts, namely pyridinium salts, and aromatic electron donors (D) undergo electron transfer resulting in the formation of aromatic radical cations [Ref. 11].

$$D + On^+ \longrightarrow \underset{\text{CTC}}{[D + On^+]} \xrightarrow{h\nu} D^{+\bullet} \qquad (6)$$

It should be noted that all species formed in above mechanisms are able to react with monomer molecules directly or produces protonic acids thus initiating cationic polymerization. In the following sections, typical examples of the three modes of electron transfer reactions for the initiation of cationic polymerization will be presented. Special emphasis will be given to alkoxypyridinium salts which undergo all modes of electron transfer reactions. At the end of the paper also the possibilities for preparing block copolymers by photoinduced eletron transfer processes will be dealt.

Oxidation of Free Radicals

As mentioned above, onium salts may be used to oxidize free radicals according to reaction (4) thus generating reactive cations. This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of initiation mode. Free radicals may be produced by various modes: photochemically, thermally or by irradiating the systems with high energy rays. The photochemicall generation of radicals can be applied even at low temperatures. Being photolyzed with high quantum yields, benzoin derivatives are so far the most effective photoinitiators for the free radical promoted cationic polymerization [Ref. 12]. The other suitable free radical promoters include benzilketals [Ref. 12], acylphosphineoxides [Ref. 13-14], azo compounds [Ref. 12], benzophenone and certain dyes in conjuction with hydrogen donor compounds [Ref. 15] and substituted vinyl halides [Ref. 16]. In addition to direct generation of electron donating compounds, non-nucleophilic radicals such as benzoyl and phosphonyl radicals, formed from the photolysis of the photolabile compound, may react with the monomer molecules producing electron donating radical, as described on the example of benzoyl radical in reactions (7) and (8).



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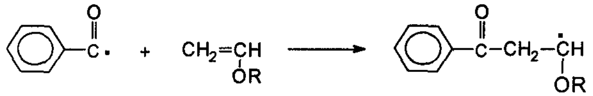


(8)

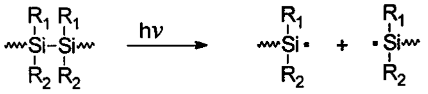
Thus formed, these radicals can easily be oxidized by onium salts yielding initiating species. For efficient electron transfer, the free energy (ΔG), which may be estimated from equation (9), must be negative [Ref. 17].

$$\Delta G = F[E_{ox}^{1/2}(R^{\cdot}) - E_{red}^{1/2}(On^{+})] \qquad (9)$$

where F is Faraday constant.

However, the calculation of ΔG is usually not feasible since the exact oxidation potentials, $E_{ox}^{1/2}(R^{\cdot})$ of most radicals involved in radical polymerizations are unknown. The efficiency of onium salts as oxidizing agent is related to their electron affinity. The higher the oxidation power of the onium salt, the higher (more positive) is the reduction potential $E_{red}^{1/2}(On^{+})$. The efficiency of onium salts in this mode of polymerization rises in the order of trialkyl sulphonium sats ($E_{red}^{1/2}$=-1.2V) [Ref. 18] < alkoxy pyridinium salts ($E_{red}^{1/2}$=-0.7V) [Ref. 12]< diaryliodonium salts ($E_{red}^{1/2}$=-0.2V) [Ref. 19] < aryldiazonium salts ($E_{red}^{1/2}$=-1.2V) [Ref. 20]. The radical promoted cationic polymerization has been known for more than a decade. Therefore, only recent examples will be described below.

Polysilanes are decomposed [Ref. 21] upon irradiation with relatively high quantum yields producing silyl radicals and silylene biradicals.



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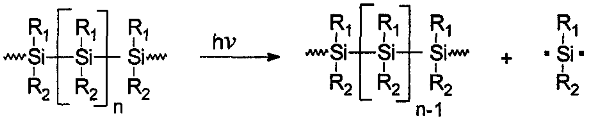
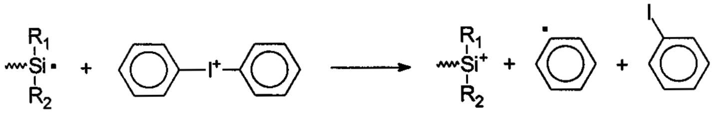


(11)

It was found that photolysis of solutions containing polysilanes and an onium salt (iodonium or alkoxy pyrdinium salts) in the presence of cationically polymerizable monomer readily initiates the polymerization [Ref. 22, 23]. Although not entirely elucidated, the initiating mechanism is assumed to involve both silyl radical and silylene biradical oxidation yielding initiating silicon centered cations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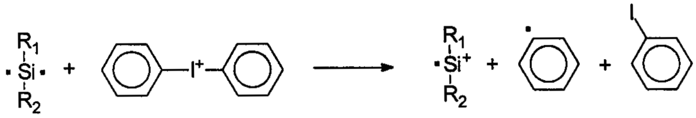
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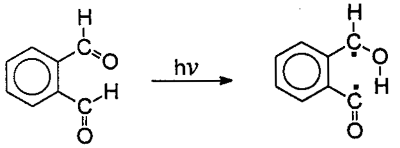
Recently, various pyridinium salts have been used in conjunction with *o*-phthaldehyde to create an efficient cationic photoinitiating system for wavelengths of c. 350 nm [Ref. 24]. The mechanism proposed involves the formation of a biradical of *o*-phthaldehyde after an intramolecular hydrogen transfer occurring in the excited triplet state. The carbon centered radical sites are oxidized by the pyridinium derivatives and finally, Brønsted acid initiating the polymerization is released from *o*-phthaldehyde molecules. The initiation efficiency has been demonstrated on the example of monomers such as cyclohexene oxide, butylvinyl ether and N-vinyl carbazol.



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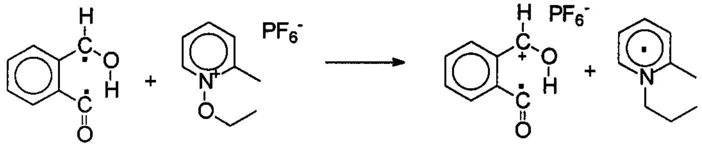

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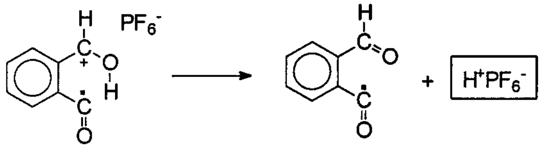
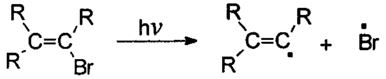


(17)

In a recent study [Ref. 16] it was found that substituted vinyl bromides in conjuction with sulphonium or alkoxy pyridinium salts initiated the polymerization of cyclohexene oxide upon photolysis at 350 nm. The photochemically formed vinyl radicals are probably oxidized by the onium salt yielding vinyl cations.



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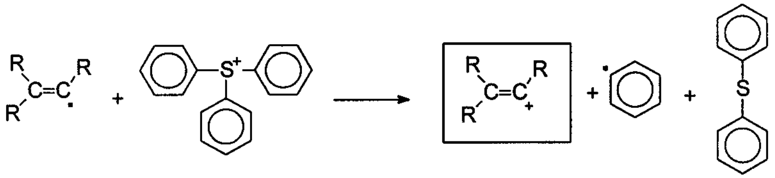
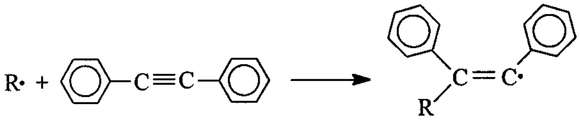


(19)

Following the same strategy, cyclohexene oxide was polymerized by using a ternary system consisting of free radical photoinitiator, diphenyl acetylene and triphenylsulponium salt [Ref. 25]. In this case oxidizable vinyl radicals are obtained by the addition of free radicals to the acetylenic compound as depicted below.



(20)

Electron transfer between photoexcited molecule and onium salt

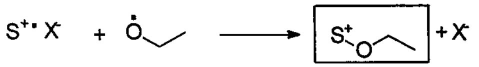
Many aromatic hydrocarbons are able to sensitize the decomposition of onium salts via electron transfer in an excited complex referred to as exciplex [Ref. 26]. For this type of cationic initiation, the following general scheme holds:

$$S \xrightarrow{h\nu} S^* \xrightarrow{On^+X^-} \left[S^* \cdots On^+X^-\right] \longrightarrow \boxed{S^{+\bullet}X^-} + \dot{O}n \qquad (21)$$

$$S^{+\bullet}X^- + R{-}H \longrightarrow HS^+X^- + \dot{R} \qquad (22)$$

$$HS^+X^- \longrightarrow \boxed{H^+X^-} + \qquad (23)$$

The excitation of the sensitizer is followed by the formation of a complex between excited sensitizer molecules and ground state onium salt. In this complex, one electron is transferred from the sensitizer to the onium salt giving rise to the generation of sensitizer radical cations. These can by themselves initiate the polymerization of appropriate polymers or, alternatively, interact with hydrogen containing constituents of the polymerization mixture (solvent, monomer) resulting in the release of Brønsted acid. In the case of alkoxy pyridinium salts, an additional mechanism has to be taken into account. Alkoxy radicals, which are generated by the decomposition of alkoxy pyridinium salts, react with sensitizer radical cations yielding initiating photosensitizer cations [Ref. 27].



(24)

The electron transfer is energetically allowed, if ΔG calculated by (25) (extended Rehm-Weller equation) is negative.

$$\Delta G = F\,[\,E^{ox}{}_{1/2}\,(S) - E^{red}{}_{1/2}\,(On^{+})] - E\,(S^*) \qquad (25)$$

F... Faraday constant

E (S*)... Excitation energy of the sensitizer (singlet or triplet)

Since the oxidation potentials of sensitizers, $E^{OX}{}_{1/2}$ (S), are easy to determine (in contrast to that of radicals), the calculation of ΔG can indeed be applied in order to predict whether or not an oxidation would take place (Table 1).

Table 1. Parameters related to photoinduced electron transfer reactions of photoexcited sensitizers and pyridinium salt.

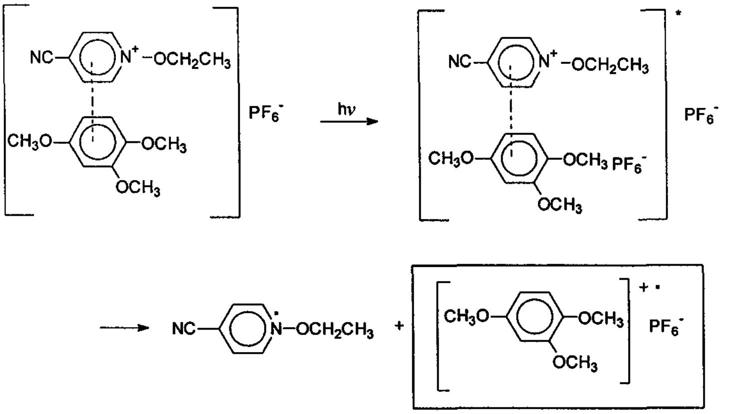
Sensitizer	E(S*) (kJ mol l^{-1})	$E^{ox}1/2$ (V)	ΔG (kJ mol^{-1})	λ_{max} , $S^{+\cdot}$ (nm)	Photosensitization
Benzophenone	290	2.7	+39.8	-	No
Acetphenone	308	2.9	+41.2	-	No
Thioxanthone	277	1.7	-44.2	430[a]	Yes
Anthracene	319	1.1	-144.4	715	Yes
Perylene	277	0.9	-121.8	535	Yes
Phenothiazine	239	0.6	-112.9	514	Yes

[a] Observed with iodonium salts [Ref. 28]

However, not all sensitizers are suitable in conjunction with onium salts. According to (25), the requirements are low oxidation potentials, $E^{OX}{}_{1/2}$(S), and relativley high excitation energies, E (S*), of the sensitizer. Besides that, only onium salts with high (low negative) reduction potentials $E^{red}{}_{1/2}$ (On^+) , such as diphenyliodonium or alkoxy pyridinium salts are easily reduced by the sensitizer.

Electron transfer within the photoexcited charge trasfer complexes

Pyridinium salts are capable of forming ground state CT complexes with electron-rich donors such as methyl- and methoxy-substituted benzene [Ref. 11]. Notably, these complexes absorb at relativley high wavelengths, where the components are virtually transparent. For example, the complex formed between N-ethoxy-4-cyano pyridinium hexafluorophosphate and 1,2,4-trimethoxybenzene possesses an absorption maximum at 420 nm. The absorption maxima of the two constituents are 270 nm and 265 nm for the pyridinium salt and trimethoxybenzene, respectively. It was found that the CT complexes formed between pyridinium salts and methyl- and methoxy-substituted benzene act as photoinitiators for the cationic polymerization of cyclohexene oxide and 4-vinyl cyclohexene oxide. The following mechanism for the initiation of the cationic polymerization has been suggested:

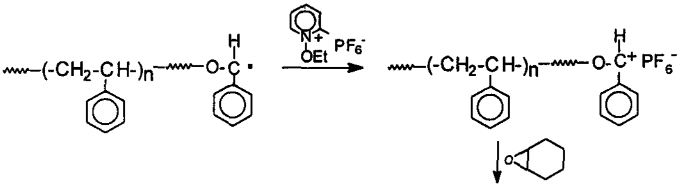


(26)

Since the proton scavenger 2,6-di-tert-butylpyridine did not noticeably influence the polymerization, the initiation by Brønsted acid that could be formed after an interaction with hydrogen containing components can be excluded. Notably, the CT complexes described above are applicable for the photoinitiation of epoxide monomers but not for the photoinitiation of vinyl ethers and N-vinyl carbazol. The latter monomers are already polymerized in a dark reaction upon addition of these complexes.

Preparation of block copolymers by photoinduced electron transfer reactions

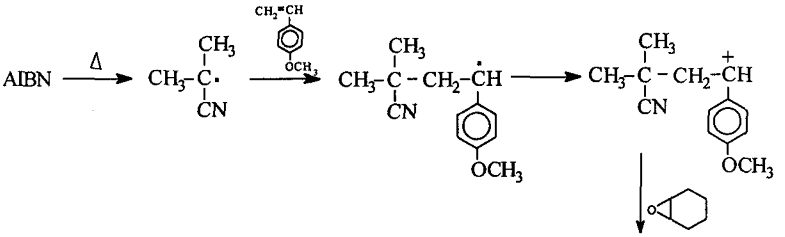
Polymers containing benzoin terminal groups can act as photochemical macroinitiators and are effective in photogenerating polymeric electron donor radicals. The initiation of polymerization by means of azo-benzoin initiators yields polymers with one or two benzoin end-groups according to the termination mode of particular monomer involved [Ref. 29, 30]. UV irradiation of the resulting prepolymers caused α-scission, and benzoyl and polymer bound electron donating radicals are formed in the same manner as for the low-molecular weigth analogoes. Electron donating polymeric radicals thus formed may conveniently be oxidized to carbocations to promote cationic polymerization of cyclic ethers. This way triblock copolymers of styrene and cyclohexene oxide were prepared [Ref. 31].



Styrene-cyclohexene oxide block copolymer

(27)

In some cases oxidizable macroradicals are formed by thermal means. For instance Guo et al. [Ref. 32] prepared *p*-methoxystyrene and cyclohexene oxide block copolymers by transforming polymethoxystyrene radicals, initiated by 2,2'-azobis(isobutyronitrile) (AIBN), to polymethoxystyrene cations.

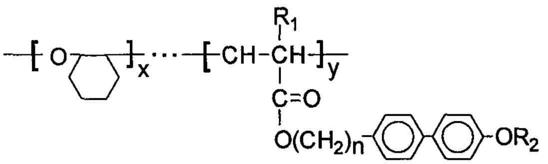


p-Methoxystyrene-cyclohexene oxide block copolymer

(28)

Side chain benzoin-containing polymers were also used as promoters to yield graft copolymers [Ref. 33].

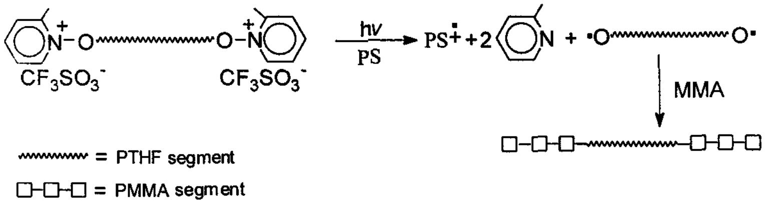
Free radical promoted cationic polymerization was successfully employed [Ref. 34] for the preparation of new classes of liquid ctystalline (LC) block copolymers comprising a semicrystalline block, (polycyclohexene oxide), and LC block of different structures:



(29)

The block copolymers obtained are essentially microphase seperated systems and form smectic mesophases, analogous to the corresponding LC homopolymers.

Another synthetic approach based on the electron trasfer reactions involves the use of alkoxy radical which are formed in sensitized decomposition of pyridinium ions. Polytetrahydrofuran with terminal N-alkoxy pyridinium ions can participate in photoinduced elctron transfer to yield photosensitizer radical cation and macroradical. The latter readily initiates polymerization of methyl methacrylate resulting in the formation of methyl methacrylate and tetrahydrofuran block copolymers with quantitative yields [Ref. 35].



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