Photoinitiated Cationic Polymerization of Unconventional Monomers

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Summary: Photoinitiated cationic polymerization of unconventional monomers namely, benzoxazines, monothiocarbonates and macromonomers of poly(ε-caprolactone) and poly(ethylene oxide) is described. Ring opening polymerization of benzoxazines and thiocarbonates by direct and sensitized photoinitiation using onium salts was studied. The structures of the resulting polybenzoxazine were complex and related to the ring opening process of the protanated monomer either at through oxygen or nitrogen atoms. In the case of monothiocarbonate, the polymerization was accompanied with isomerization of thiocarbonate group. The potential use of macromonomers in photoiniated cationic polymerization to design complex macromolecular structures such as graft copolymers, water-borne photoresist materials and networks with dangling chains was presented. Photoinduced oxidative polymerization of thiophene, precursor for conducting polymers, using onium salts was also demonstrated.

Keywords: benzoxazine; cationic polymerization; macromonomer; monothiocarbonate; Photopolymerization; thiophene

Introduction

Photoinitiated polymerization is an important industrial process widely used in different applications. For instance, UV curing of coatings, inks, adhesives and photolithography can be performed without the use of solvents, so potential source of air and water pollution is eliminated[1–3]. In addition to UV initiated free radical polymerization, the corresponding cationic polymerization holds considerable promise in future, particularly as a means of overcoming volatile emissions, toxicity and molecular oxygen inhibition limitations. The types of general monomers which may undergo photoinitiated cationic polymerization, are vinyl and alkoxy vinyl monomers, heterocyclic monomers involving sulphur, oxygen, nitrogen atoms. Obviously, in UV curing applications bifunctional monomers based on epoxides and alkyl vinyl ethers are used to yield insoluble networks. The structure of the monomers has a great influence on the physical and mechanical properties of the cured products. A large variety of the monomers is now available, allowing for the design of networks with tailor-made properties according to the specific end uses. Newly developed monomers carrying different functional groups may lead to a high conversion and improved properties.

The objective of this article is to present the photoinitiated cationic polymerization of new monomers, namely benzoxazines, monothiocarbonates and macromonomers possessing cationically polymerizable end groups. At the end of the paper, special emphasis will be given to photoinitiated polymerization of thiophene as a new initiating system for the synthesis of conducting polymers.

Before dealing with the polymerization of particular monomers, it is essential to first review briefly the types and character-

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$$Ph_2I^+\,X^- \xrightarrow{h\nu} PhI^{\stackrel{+}{\bullet}}\,X^- + Ph\bullet \qquad (1)$$

$$PhI^{\stackrel{+}{\bullet}}\,X^- + R{-}H \longrightarrow H^+X^- + PhI + R\bullet \qquad (2)$$

$X^- = SbF_6^-, PF_6^-, AsF_6^-$ *etc.*
$R{-}H$ = *Monomer or Solvent*

Scheme 1.

istics of the photoinitiated cationic polymerization. Among the various types of photoinitiators that can lead to the formation of cations as a result of UV light induced fragmentation, onium salts such as diaryl iodonium and triaryl sulphonium salts have found considerable application in UV curing and photoresist technology. The photochemistry of these novel classes of cationic photoinitiators is well documented [4–7].

i) Direct Initiation

Upon photolysis, these thermally and hygroscopically stable initiators undergo irreversible photofragmentation to produce cation radicals and Brønsted acids as presented below on the example of iodonium salts.

Both species produced photochemically with cationic photoinitiators initiate the cationic polymerization of suitable monomers. Onium salts used in cationic photopolymerization mainly absorb at wavelengths of light between 225 and 350 nm. Alkoxy pyridinium salts[8], are also treated as onium salts since the chemistry of these salts resembles that of classical onium salt initiators, and initiate the polymerization in the same manner. For practical applications, onium salts should absorb light appreciably at wavelengths longer than 350 nm where the commercially available medium and high pressure mercury lamps emit much of their radiation. Since this requirement is not fulfilled for certain easily available onium salts several systems were developed to extend the applicability of the onium salt photoinitiators. In these cases additives are present which participate in the reaction sequence to yield reactive species capable of initiating the cationic polymerization. Depending on the role played by the additives in the initiation of the polymerizationthree modes of indirect initiation are possible.

ii) Initiation by Photosensitization[9–11]

Many aromatic hydrocarbons such as anthracene, phenothiazine and perylene are able to sensitize the decomposition of onium salts via electron transfer. The irradiation of the sensitizer (PS) 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 cation as a result of homolytic cleavage of the corresponding onium salt. The radical cations themselves initiate the polymerization of appropriate monomers or, alternatively, interact with hydrogen donor constituents of the polymerization mixture (such as solvent or monomer) resulting in the release of Brønsted acid. For this type cationic

$$PS \xrightarrow{h\nu} PS^* \xrightarrow{Ph_2I^+\,X^-} [PS^*\text{----}Ph_2I^+\,X^-] \longrightarrow PS^{\stackrel{+}{\bullet}}X^- + PhI + Ph\bullet \qquad (3)$$

$$PS^{\stackrel{+}{\bullet}}X^- + R{-}H \longrightarrow H^+X^- + PS + R\bullet \qquad (4)$$

$$\mathrm{PI} \xrightarrow{h\nu} \mathrm{R}\bullet \xrightarrow{\mathrm{Ph_2I^+X^-}} \mathrm{R^+X^-} + \mathrm{PhI} + \mathrm{Ph}\bullet \qquad (5)$$

Scheme 3.

initiation, the following general scheme holds;

iii) Initiation by Free Radical Oxidation[12–13]

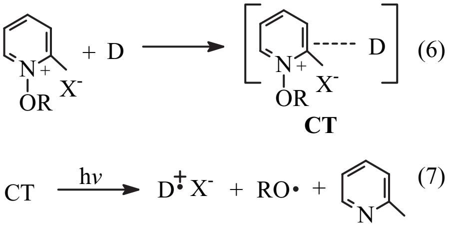
Many photochemically formed radicals can be oxidized by onium salts according to the following reaction:

The cations thus generated are used as initiating species for cationic polymerization. This process is usually termed as the free radical promoted cationic polymerization. This so-called free radical promoted cationic polymerization is an elegant and fairly flexible type of indirect initiation of cationic polymerization.

iv) Initiation Via Charge Transfer Complexes[14]

Alkoxy pyridinium salts are capable of forming charge transfer (CT) complexes with electron rich donors such as methyl- and methoxy-substituted benzene[14]. Notably, these complexes absorb at relatively high wavelengths, where the components are virtually transparent. It was found that the CT complexes formed between pyridinium salts and aromatic electron donors (D) act as photoinitiators for the cationic polymerization. The mechanism illustrated in equations 6 and 7 for the initiation has been suggested[12].

The following section concerns photoinitiated cationic polymerization of several unconventional monomers by using above described initiation systems.



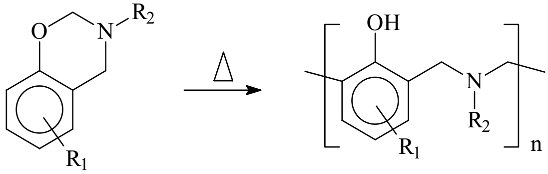
Scheme 4.

Photoinitiated Cationic Polymerization of Benzoxazines

Among various high performance materials[15–18], polybenzoxazines, as recently developed phenolic resins, have received much interest because they possess typical characteristics of traditional phenolic resins such as heat resistance, good flame retardance and stable dielectric constants. In addition, they provide low absorption of water and also excellent dimensional stability due to the low shrinkage upon cure, which cannot be found in the traditional phenolic resins. Polybenzoxazines are obtained by ring opening polymerization of the corresponding monomers at elevated temperatures without catalysts.

We have recently examined whether benzoxazine monomers would undergo photoinitiated cationic polymerization by onium salts[19]. Application of the onium salt photoinitiation outlined in Scheme 1, would involve the photoinduced formation of protons and subsequent protonation of the monomer. The spectral analysis of the photopolymerization products shows that polymers possessing the following complex structures in the chain are obtained due to different possibilities of the reaction to proceed.

First, a proton (or carbocation) can add either to oxygen or to nitrogen. The adding of a new molecule can proceed with the formation of the new cation either at oxygen or at nitrogen. In the latter case there are two possibilities of breaking the ring (Scheme 6). The next step furnishes more possibilities of developing the reaction. If only one of the routes described in Scheme 7 is followed, a polymer with one of the repeating units presented in Scheme 6 (**a, b**) is obtained. If the phenolic mechanism is also implied, structures as in Scheme 6 (**c, d**) would be obtained, too. FT-IR and NMR spectral analysis and comparison of the thermal behavior of the polymers with



(8)

Scheme 5.

that formed by thermal polymerization confirmed that all structures were present in the polymer indicating phenolic mechanism and protonation both at carbon and nitrogen atoms proceed simultaneously.

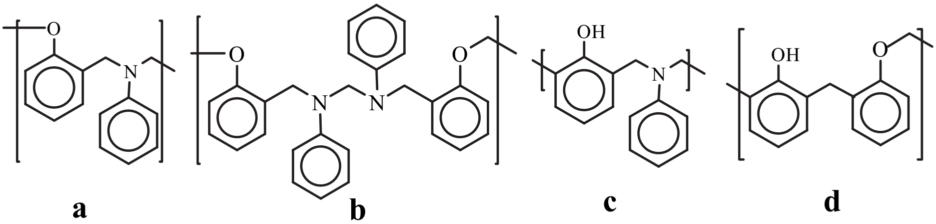
Notably, photosensitized and free radical promoted cationic polymerizations gave similar results.

Photoinitiated Cationic Polymerization of Monothiocarbonates

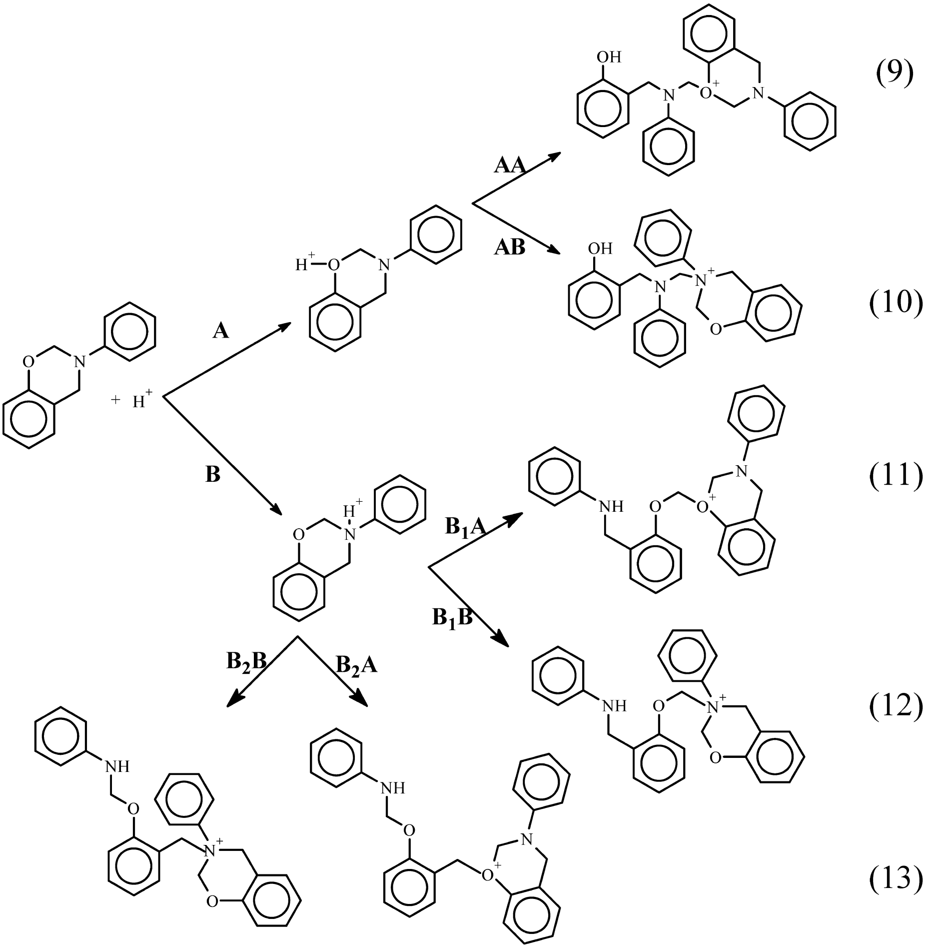
Cyclic carbonates are interesting class of monomers which undergo cationic and anionic ring-opening polymerization accompanied with volume expansion due to the difference in strength of intermolecular interaction between monomers and polymers. Recently, six membered cyclic thiocarbonates such as 5, 5-dimethyl-1, 3-dioxane-2-thione (DDT) have been introduced as the structurally related monomers to yield the corresponding polymonothiocarbonates by controlled cationic polymerization[20]. More recently, we have shown[21] that the photoiniated polymerization of the monothiocarbonate, DDT can be achieved by using onium salt type photoinitiators, namely diphenyliodonium, triphenyl sulphonium and N-ethoxy-2-methyl pyridinium salts. Both direct and indirect methods utilising either free radical sources such as 2, 2-dimethoxy-2-phenylacetophenone (DMPA) or photosensitizers such as perylene and anthracene were shown to be efficient in the photoinitiation process. It should be pointed out that in the case of indirect initiation, photoactivation was achieved at longer wavelengths, i.e., 350 nm. Structural investigations revealed that polymerization was accompanied with isomerization as it was observed with conventional cationic initiators. The overall process is depicted in Scheme 8 for the direct initiation where photochemiccaly produced protonic acids are the actual initiating species.

Photoinitiated Cationic Polymerization of Macromonomers

We also considered that the photoinitiated polymerization of macromonomers possessing vinyl ether[22]- and cyclohexene oxide[23]-end-functional polymers might be particularly interesting since photochemically generated cationic species are quite reactive towards these groups. A novel well-defined macromonomer of epoxy end functionalized poly(ε-caprolactone) (PCL) was synthesized and its reactivity in photoinitiated cationic polymerization was examined.[22]



Scheme 6.

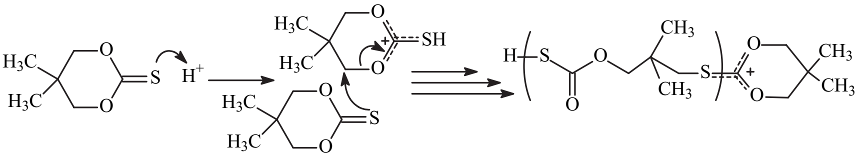


Scheme 7.

Table 1 shows photopolymerization of PCL macromonomer with various types of photoinitiation. Homopolymerization of macromonomers provides comb-shaped polymers with a very high branch density. All types of photoinitiation systems yielded polymers with high conversion (>99%) and basically the same structure. Expectedly, molecular weight distributions of the obtained polymers were slightly higher than that of the macromonomer. PCL macromonomer was also used as a comonomer in the copolymerization with (cyclohexene oxide) CHO under similar conditions that applied for the polymerization of PCL macromonomer itself (Table 2).

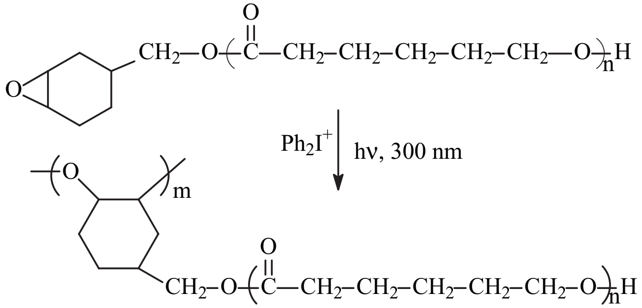
PCL macromonomer as the comonomer allowed for a rather simple incorporation of PCL side chains into poly(cyclohexene oxide) backbone. This way poly(cyclohexene oxide)-*g*-poly(ε-caprolactone) graft copolymer with random sequences of the following structure is formed (Scheme 10).

Apart from CHO, bifunctional monomer, 3, 4-epoxycyclohexylmethyl-3′,4′-epoxycyclohexane carboxylate (EEC) was also used as the comonomer. Because of the presence of two epoxide groups in EEC, an insoluble network polymer was readily formed upon irradiation in the presence of diphenyliodonium salt. The crosslinked polymer exhibited interesting swelling behavior in CH_2Cl_2. The higher swelling ratio



(14)

Scheme 8.



(15)

Scheme 9.

obtained with the network formed from the PCL macromonomer suggests that PCL segments stay out of the crosslinked domain. Penetration of the solvent into crosslinked region and the subsequent swelling must be therefore provided by these free segments.

More recently, we have described[23] novel hybrid PEO macromonomers carrying conventional but different vinyl end-groups of the following structure which can polymerize in different ways by a radical, cationic, and/or anionic mechanism.

Such hybrid macromonomers will be potentially attractive in controlled syntheses of network or gelled polymer materials with soft and hydrophilic domains or surfaces. One particularly interesting aspect of the use of these macromonomers deals with photopolymerization. Their reactivity in photoinitiated free radical and cationic systems was also studied[23] . The reactivity of the radical and cationic species formed upon photolysis of triphenylsulfonium tetrafluoroborate towards these end grous were studied by means of ^{1}H-NMR analysis following the disappearance of the respective olefinic groups.

Regarding the photolysis mechanism of triphenyl sulphonium salts, similar fragmentation to that described for iodonium salts occurs and a strong electrophilic Brønsted acid, corresponding diphenyl sulfinium radical cation and also radical species are produced. They react with the respective functional groups. It was also

Table 1.
Photoinitiated Cationic polymerization of Poly(ε-Caprolactone) Macromonomer (200 g L^{-1}, M_n = 1800) in the Presence of $Ph_2I^+PF_6^-$ (5×10^{-3} mol L^{-1}) at Room Temperature in CH_2Cl_2.

Photoinitiaton Type	Activator (mol L^{-1})	Irradiation Wavelength (λ, nm)	Irradiation Time (h)	Conversion (%)	M_n	M_w/M_n
Direct	—	300	5	>99	8650	1.60
Radical promoted	DMPA	350	5	>99	10600	1.39
Sensitized	Anthracene	300	5	>99	12500	1.71

Table 2.
Photoinitiated Cationic Polymerization of Poly(ε-Caprolactone) Macromonomer (200 g L^{-1}, $M_n = 1750$) with Cyclohexene Oxide (CHO) at Room Temperature in CH_2Cl_2 by Using $Ph_2I^+PF_6^-$ (5×10^{-3} mol L^{-1}).

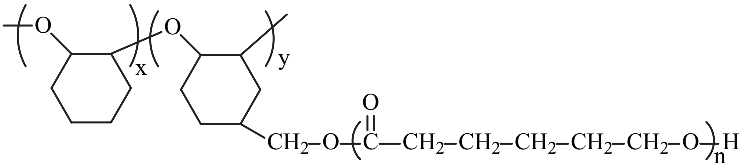
Run	CHO (mol L^{-1})	Irradiation Wavelength (λ, nm)	Irradiation Time (min)	Conversion[a] (%)	M_n	M_w/M_n	Copolymer Composition[b] (mol, %)	
							PCL	PCHO
A[c]	0.89	350	300	40	10700	1.51	58	42
B	0.89	300	20	40	7300	1.42	67	33
C	3.09	300	20	42	6500	2.14	26	74
D	4.94	300	20	50	4600	2.70	18	82
E[d]	9.89	300	20	36	5200	1.85	22	78

[a] CHO conversion.

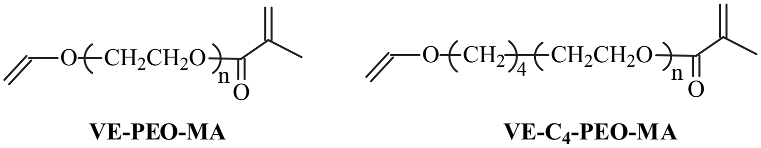
[b] Calculated from ^{1}H-NMR spectra of samples.

[c] DMPA was used as a free radical source.

[d] Bulk.



Scheme 10.



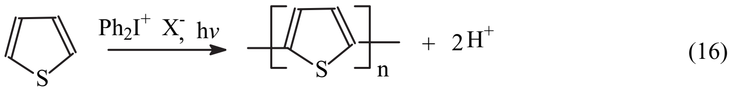
Scheme 11.

shown that vinyl ether moieties react more readily than the methacrylate. The rate for the disappearance of the vinyl ether double bond is about 50 times higher than that of the corresponding methacrylate bonds (Table 3). This may be due to the fact that vinyl ethers are strong electron donating monomers and readily react with the directly produced cationic species while radicals are only formed in a secondary reaction from the hydrogen donor present in the polymerization system. It is also interesting to note the influence of the spacer group between vinyl ether group and PEO chain. When the vinyl ether group is directly attached to PEO, **VE-PEO-MA**, the reactivity is higher with the sulfonium salt. This behavor may be atributed to stronger electron donating effect of CH_2CH_2O than the $(CH_2)_4$ spacer group.

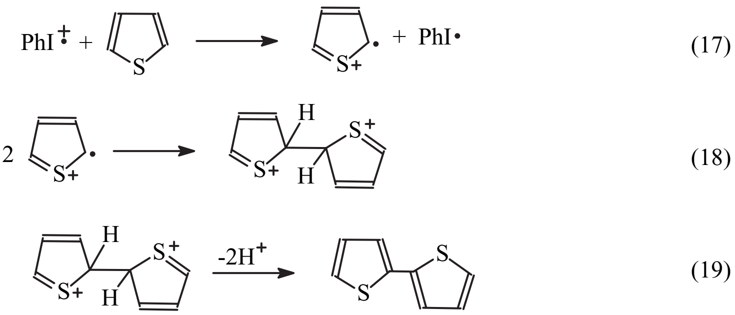
Table 3.
Rate of disappearance[a] of the double bonds of various hetero-functional macromonomers with $Ph_3S^+BF_4^-$

Macromonomer	$R_{dis.(VE)} \times 10^5$ (Mol l^{-1} s^{-1})	$R_{dis.(MA)} \times 10^5$ (Mol l^{-1} s^{-1})
VE-PEO-MA	4.8	0.16
VE-C_4-PEO-MA	2.7	0.17

[a] Determined by NMR.



Scheme 12.



Scheme 13.

Photoiniduced Polymerization of Thiophene

Among various conducting polymers polythiophenes have a special place due to their electrical properties, environmental stability in doped and undoped states, non-linear optical properties, and highly reversible redox switching.[24–29] Polythiophenes[30] can be obtained by chemical or electrochemical processes. Quite recently, we have demonstrated that thiophenes can also be polymerized by photochemical means. Upon irradiation of the solution containing thiophene and diphenyl iodonium salt, the solution becomes dark and films are deposited on the surface of the reaction tube. The free standing films of polythiophene with the shape of the tube are obtained after decantating the remaining solution and washing with methanol.

The photoinduced oxidative polymerization mechanism of thiophene is analogous to the already known electrochemical polymerization. Since the ground state iodonium salt does not undergo electron transfer reactions with thiophene, it is expected that the radical cations ($PhI^{+\bullet}$) formed from the photolysis of to the iodonium salt must be responsible for the polymerization. One electron transfer from the radical cation to thiophene results in the formation of thiophene radical cation (reaction 17).

Subsequent photoinduced electron transfer and chemical steps proceed until the oligomer becomes insoluble in the photolytic medium and precipitates onto the glass surface. In this connection, it should be pointed out that the black film formed on the surface screens the light penetration and the polymerization is ceased. However, irradiation of the remaining solution in another tube results in further polymerization and consequently in film formation providing that iodonium salt is available in the system. Apart from diphenyliodonium salt, the photooxidation capability of two other salts, namely triphenylsulphonium and *N*-ethoxy-2-methylpyridinium salts were also tested. All salts are capable of inducing oxidative polymerization of thiophene under similar experimental conditions.

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