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PHOTOINITIATING SYSTEMS AND THEIR USE IN POLYMER SYNTHESIS

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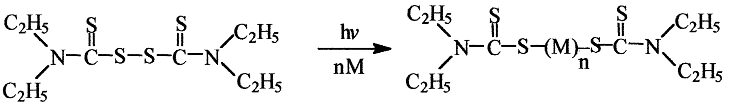
SUMMARY: This paper on recent developments in the use of photoinitiating systems in polymer synthesis concentrates on: (i) the possiblity of controlled//living polymerization by photopolymerization, (ii) major photoinitiating systems for both cationic and radical polymerization and (iii) preparation of block copolymers and functional polymers by photoinduced processes. Much progress has been made in the past ten years in preparation of block copolymers by photoinduced reactions of either chromophoric groups incorporated into polymers or low-molecular-weight compounds with suitable functional groups present in polymer chains.

INTRODUCTION

The control of polymerization is extremely important from the synthetic point of view. During the past five decades, the use of living polymerization processes has revolutionized the synthesis of polymers with well defined structures. Controlled/living polymerization techniques in anionic, cationic, metathesis and group transfer polymerizations have been developed [1]. Recent approaches to achieve controlled/living polymerization in ionic and also radical systems are based on the stabilization of unstable growing species by the reversible formation of the corresponding covalent and dormant species that rapidly exchange [2,3]. To our knowledge, no effort has been devoted to the extension of such control to polymerization conducted photochemically. However, the earlier approach based on reversible combination of growing radicals with a scavenging radical can be applied in thermal and photoinitiated radical polymerization. According to Otsu [4], photochemical polymerization of vinyl monomers with alkyl dithiocarbamates, referred to as iniferter (*ini*tiator-trans*fer*-*ter*minator) is characterized by the initial rapid growth and an increase in molecular weight with the conversion.



$$(C_2H_5)_2N-\overset{S}{\overset{\|}{C}}-S-S-\overset{S}{\overset{\|}{C}}-N(C_2H_5)_2 \xrightarrow[nM]{h\nu} (C_2H_5)_2N-\overset{S}{\overset{\|}{C}}-S-(M)_n-S-\overset{S}{\overset{\|}{C}}-N(C_2H_5)_2 \qquad (1)$$

However, this system deviates from the truly controlled/living conditions [5] and suffers from poor photochemical initiation.

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By photolysis of existing radical and cationic initiators, a controllable amount of initiating species is formed. The concentration of initiating species and finally of growing polymer chains may be conveniently adjusted by choosing appropriate light intensities. On the other hand, the polymers formed by controlled//living polymerization or upon initiation with photoinitiators do often differ in molecular weight distribution. Since initiating species in photopolymerizations are generated continuously, growing polymer chains with large differences in chain lengths are present at the same time. Therefore, polymers usually have a broad molecular weight distribution. In the case of controlled/living polymerization, formation of polymer molecules with the same lengths gives rise to polydispersities close to unity, provided chain-breaking side reactions are of minor importance.

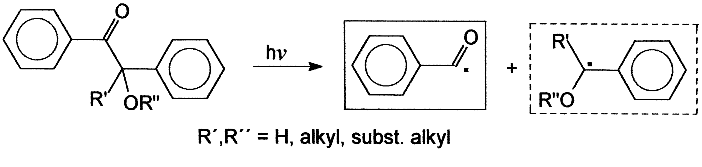
Although the available photoinitiating systems show lack of polymerization control, they still contribute to the macromolecular engineering of synthetic polymers. For example, block and graft copolymers can be prepared by using main-chain and side-chain polymeric photoinitiators, respectively. These systems consist in a photochemical reaction by which active sites are produced at the chain ends or side chains, which themselves initiate polymerization of a second monomer. Low-temperature conditions, usually room temperature, prevent side reactions leading to the formation of homopolymers and high block and graft yields are attained.

The following sections will focus on recent developments in the application of light-induced reactions in polymer synthesis. Subjects to be discussed include: (i) major photoinitiating systems, (ii) block copolymers by photopolymerization, and (iii) polymer functionalization by photochemical methods.

PHOTOINITIATING SYSTEMS

Radical Polymerization

The most effective light-induced radical generation processes used in polymer synthesis are α-cleavage and hydrogen abstraction reactions. The main cleavable photoinitiators include benzil dimethyl ketal, benzoin ethers, alkyl hydroxyphenyl ketones, dialkoxyacetophenones, benzoylcyclohexanol, acylphosphine oxides and aminoalkyl ketones [6]. The cleavage takes place at carbon-carbon bonds upon photolysis to yield initiating radicals.



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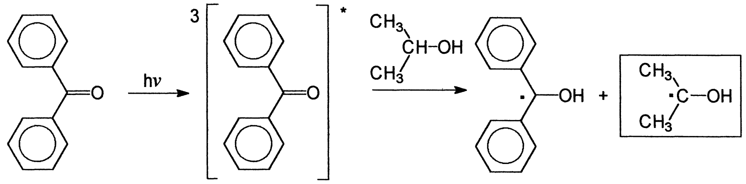
Another photoinitiating system consists of a photoinitiator such as a benzophenone or thioxanthone and a coinitiator such as an alcohol, tetrahydrofuran and amine [7]. Radicals are generated in a bimolecular process by the reduction of photoexcited aromatic carbonyl compound by hydrogen abstraction or electron transfer reactions as illustrated below for the benzophenone/isopropyl alcohol photoinitiating system.



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Notably, the radicals formed from the alcohol are considered initiating radicals while ketyl radicals were demonstrated to undergo radical coupling.

Cationic Polymerization

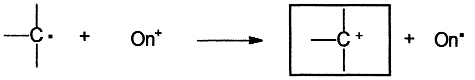
Upon photolysis, onium-salt-type initiators, namely diaryliodonium, triarylsulfonium and *N*-alkoxypyridinium salts, undergo irreversible photofragmentation to produce cation radicals and Brønsted acids capable of initiating cationic polymerization [8,9].

$$On^{+} \xrightarrow{h\nu} On^{+\bullet},\ H^{+} \qquad (4)$$

Photoinduced decomposition of the cationic photoinitiator can also be achieved by electron transfer reaction between photoexcited sensitizer and onium salt [10,11].

$$(PS^{*}) + On^{+} \longrightarrow PS^{+\bullet} + On\bullet \qquad (5)$$

The oxidation of photochemically formed radicals with onium salts is another way of producing reactive cations indirectly [12].



(6)

A key feature of this system appears to be the tunability of the irradiation wavelength by the choice of the radical photoinitiators employed.

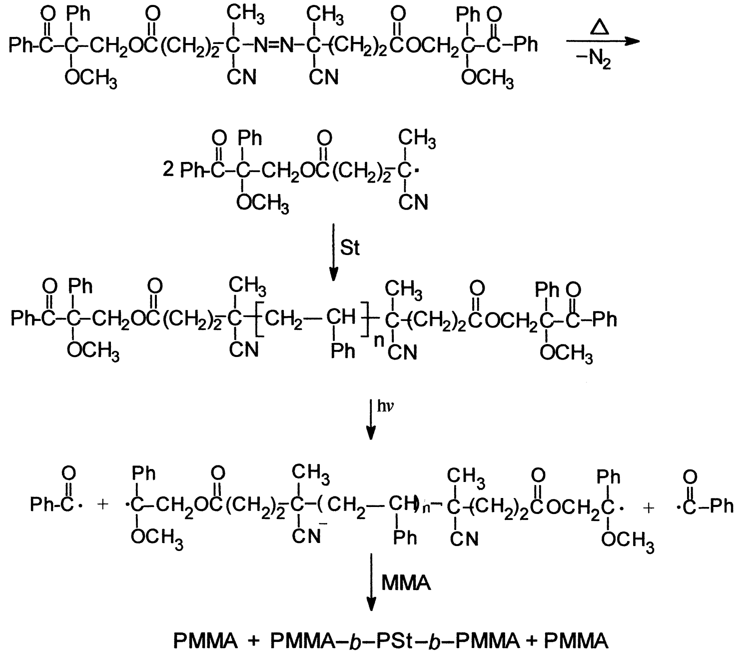
All the generic methodologies of photoinitiated polymerization described above have been succesfully used either in block copolymerization or in polymer functionalization.

BLOCK COPOLYMERS VIA PHOTOINITIATED RADICAL POLYMERIZATION

The posibility of incorporation of a wide range radical-generating photochromophoric groups into polymers has led most studies to focus on radical polymerization. Both α-cleavage and hydrogen abstraction type photoinitiations have been shown to yield block copolymers under proper conditions.

Photoblocking by α-Cleavage

A way to incorporate photolabile groups into polymers is the use of the functional azo initiator approach [13]. For example, the initiation of polymerization with azo-benzoin initiators yields polymers with one or two benzoin groups depending on the termination of the monomer involved [14,15].



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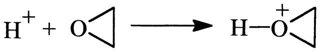
UV irradiation fragments the resulting polymer to generate both a carbonyl and polymeric alkyl radical. The process has an inherent problem involving competitive initiation by both radicals. Addition of the monomer to the polymeric radical leads to the block copolymer structure while homopolymers are formed from the low-molecular-weight radical fragments. In fact, this is the case of most of the α-cleavage-type photoinitiator groups incorporated into polymer chain ends. However, more nucleophilic radicals will preferentially react with more electrophilic monomers and vice versa. By manipulating the monomer structure and polymerization sequences, neat block copolymer formation is possible [16].

Benzoin groups can also be incorporated into polymers by ionic polymerization methods such as by the activated monomer polymerization. Penczek et al. [17] reported that cationic polymerization of oxiranes may proceed in the presence of hydroxy compounds by the AM mechanism:



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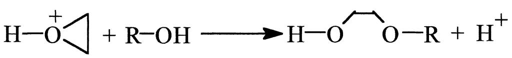
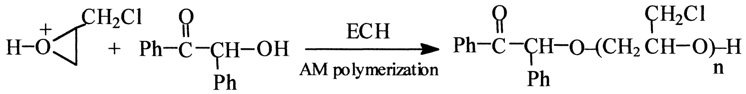


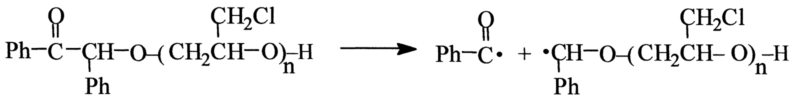
(12)

In our recent work, benzoin derivatives containing hydroxy groups were used as initiators of activated monomer (AM) polymerization of epichlorohydrin [18]. The polymerization was carried out by slow addition of an oxirane monomer, epichlorohydrin (ECH), to a solution of benzoin derivative in methylene chloride, in the presence of a catalyst.



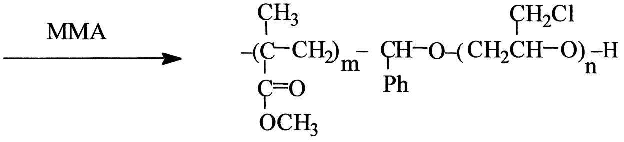
(13)

The resulting polymers contain photoactive benzoin terminal groups. Photoinduced blocking would then proceed in the same manner as described above [19].



$$\mathrm{Ph{-}\overset{O}{\overset{\|}{C}}{-}\underset{Ph}{CH}{-}O{-}(CH_2\overset{CH_2Cl}{CH}{-}O)_n{-}H \longrightarrow Ph{-}\overset{O}{\overset{\|}{C}}\bullet + \bullet\underset{Ph}{CH}{-}O{-}(CH_2\overset{CH_2Cl}{CH}{-}O)_n{-}H}$$

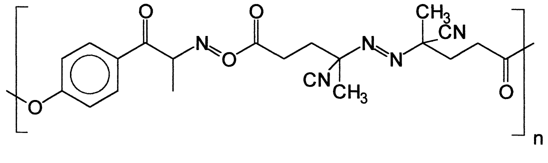
(14)



$$\xrightarrow{\mathrm{MMA}} \mathrm{-(\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}{-}CH_2)_m{-}\underset{Ph}{CH}{-}O{-}(CH_2\overset{CH_2Cl}{CH}{-}O)_n{-}H}$$

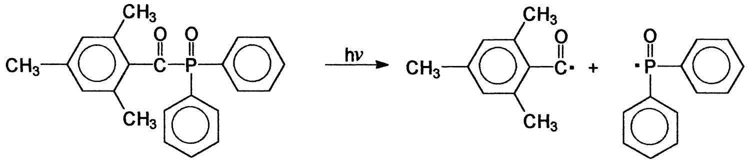
(15)

Polymers containing acyloxime moieties in the main chain can act as photochemical macroinitiators for block copolymerization [20]. It seemed, therefore, appropriate to apply again the functional azo initiator approach for such incorporation. The thermal initiation of polymerization using an azo-acyloxime ester initiator of the following structure yields polymers with photolabile groups in the main chain as was demonstrated by optical absorption measurements.



Recent studies concerning their photolysis in the presence of a second monomer revealed that acyl oxime groups may also degrade during thermal treatment in the first step and give relatively low block yields [21].

Acylphosphine oxides have been used as photoinitiators for radical-initiated photopolymerization [22]. Long-wavelength absorption characteristics make these compounds particularly useful for the polymerization of TiO_2-pigmented formulations containing acrylate- or styrene-type monomers and of glass-fiber-reinforced polyester laminates with reduced transparency [23]. Extensive investigations on the photochemistry of acylphosphine oxides revealed that they undergo α-cleavage with fairly high quantum yields [24-26].



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Furthermore it was found that the phosphinoyl radicals formed are highly reactive towards vinyl monomers [27].

We have recently demonstrated [28] that phenylbis(2,4,6-trimethylbenzoyl)phoshine oxide (BAPO) can be used for block copolymer synthesis. As shown in Figure 1, the absorption of BAPO at 420 nm and that of a monoacylphosphine oxide such as diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TMDPO) at 380 nm make this compound a bifunctional photoinitiator when photolysed sequentially.

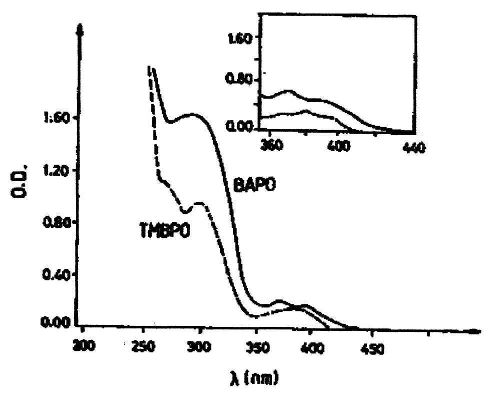
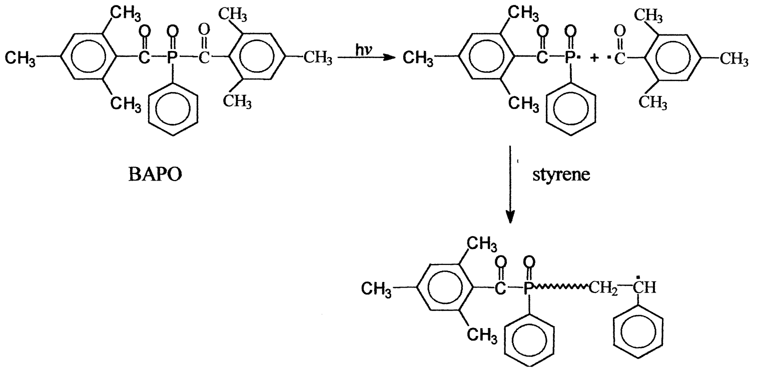


Figure 1. UV absorption spectra of TMDPO (---) and BAPO (—) in methylene chloride

Photoinitiated polymerization of styrene (St) was carried out at λ = 420 nm. As shown in Table 1, conversion to polystyrene increased with the irradiation time. By irradiating selectively at 420 nm using a monochromator, BAPO undergoes α-scission to yield benzoyl and benzoylphosphinoyl radicals. Polymerization is expected to be initiated mainly by the phosphinoyl radicals since the bimolecular rate constant of the reaction of the phosphinoyl radicals with styrene monomer is two orders of magnitude higher than that of the reaction of benzoyl radicals with styrene ($k_{PO,St} = 5 \times 10^7$ l mol s^{-1}, $k_{Bz,St} = 2 \times 10^5$ l mol s^{-1}) [24,29].

Table 1. Photopolymerization of styrene with BAPO at λ = 420 nm

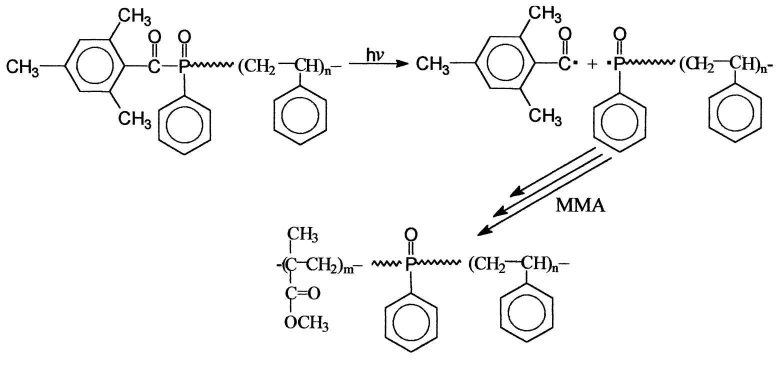
Code	[BAPO]/[St] mol/mol	Irradiation time min	Conversion %	M_n
PSt-1	0.0027	30	3.2	5000
PSt-2	0.0027	60	3.8	4700
PSt-3	0.0027	90	10.0	5800
PSt-4	0.0027	120	12.3	7200



(17)

(18)

Structurally, terminal acylphosphine oxide moieties mimic TMDPO photoinitiator. Thus, subsequent irradiation of the resulting polymer at 380 nm produces polymeric phosphinoyl radicals and low-molecuar-weight benzoyl radicals. In the presence of a second monomer such as methyl methacrylate (MMA), faster initiation with the phosphinoyl radicals ($k_{PO,MMA} = 6 \times 10^7$ l mol s^{-1}, $k_{Bz,MMA} = 1 \times 10^5$ l mol s^{-1}) [24] afforded formation of block copolymers by the following reactions.



(19)

(20)

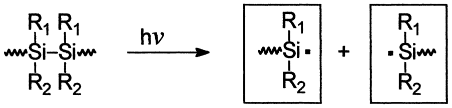
As can be seen from Table 2, conversion of MMA increased with increasing concentration of the prepolymer. Succesful blocking was confirmed by a marked increase in the molecular weight of the polymer as well by IR and NMR studies.

Table 2. Photoinitiated block copolymerization of MMA with PSt macrophotoinitiator at $\lambda = 380$ nm

Initiator[a]	[PSt]/[MMA] mmol/mol	Time min	Conversion %	M_n	M_n increase after blocking (%)
PSt-3	0.55	90	4.9	15 800	172
PSt-3	0.55	120	6.2	20 200	248
PSt-4	0.88	90	16.9	23 800	230
PSt-3	0.88	120	18.0	28 000	289

[a] [PSt] = 30 g/l

Upon irradiation, polysilanes undergo rapid cleavage yielding both silyl radicals and silylenes [30]. It has been reported [31] that polysilanes are effective photoinitiators for radical polymerization and it was assumed that the initiating process consists of the reaction of silyl-type radicals with vinyl monomers.



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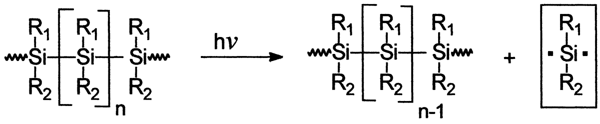


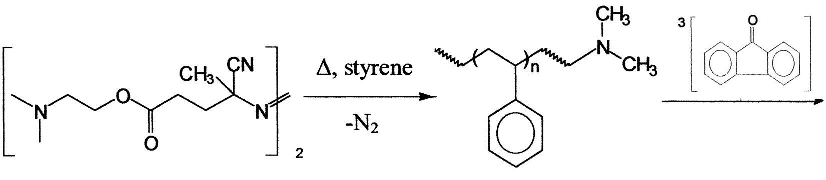
(22)

An elegant method for inserting polysilane fragments into vinyl polymers is to carry out polymerization by partial decomposition of polysilane in the presence of a monomer such as MMA [32]. The segment length of polysilane in PMMA is controlled by irradiation time; the resulting PMMA exhibits the polysilane absorption band. In the second stage, photoactive PMMA was used to initiate the styrene polymerization. Obviously, the initiating radicals are derived from silyl radicals as a result of photodegradation of polysilane moieties in the PMMA backbone. By adjusting the amount and position of polysilane segments in the initially formed PMMA, higher block yields may be obtained.

Other principal approaches utilizing α-cleavage-type photoinitiated radical polymerization for the synthesis of block copolymers have been described in the literature.

Photoblocking by Hydrogen Abstraction

Selective and efficient formation of block copolymers may be accomplished by UV irradiation of appropriate amino-containing prepolymers in the presence of aromatic ketones and vinyl monomers. An amino azo initiator, bis(2-dimethylaminoethyl) 4,4'-azodi(4-cyanopentanoate), facilitates the preparation of polymers with tertiary amine end groups [33].



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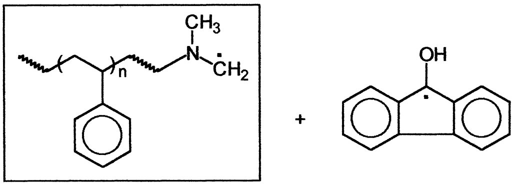

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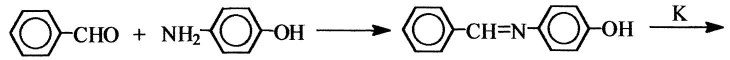
Polystyrene functionalized in this way was used in photoinduced polymerization of MMA in the presence of fluoren-9-one. The resulting polymer, presumed to contain a copolymer of poly(St-*b*-MMA), was completely soluble in acetonitrile, which is a non-solvent for styrene homopolymer. Semipinacol-type radicals produced by the reduction of aromatic ketones are not noticeably active in initiation of polymerization of MMA at room temperature as observed by Ledwith [34]. This behaviour reduces homopolymer formation in the block copolymerization via photoreduction of fluoren-9-one.

The amino-functionalized polymers are not prepared only by radical systems, but also by ionic routes. For example, a block copolymer composed of crystalline poly(ethylene oxide) and non-crystalline polystyrene was prepared by combination of anionic polymerization and photoinduced hydrogen-abstraction polymerization [35]. In this process, the amino-protected

4-aminophenol reacted with potassium metal. The phenoxy anion thus formed initiated the polymerization of ethylene oxide.



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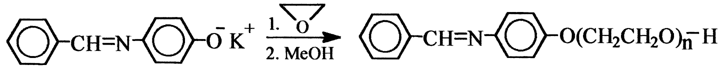

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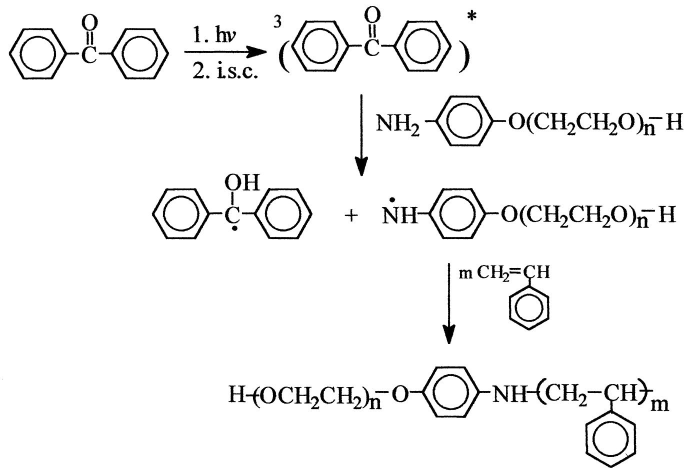
The ethylene oxide prepolymer with Schiff base end group was deprotected by acidolysis with acetic acid. Then the recovered amino group, in conjuction with benzophenone, formed a charge transfer complex under UV irradiation to initiate radical polymerization of styrene.



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Neat block copolymers of ethylene oxide and styrene were thus formed since only macroradicals with aniline end groups are capable of initiating the polymerization.

Photoblocking by Electron Transfer

According to Bamford et al. [36], terminal carbon-centred macroradicals are formed upon irradiation of polymers having CX_3, CHX_2, CH_2X end groups (X is halogen) in the presence of carbonyl compounds of transition metals, preferably $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. These compounds absorb light at rather long wavelengths. The principal radical-generating reaction is an electron transfer process from transition metal to halide, the former assuming a low oxidation stage (presumably zero).

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2\ Mn(CO)_5 \qquad (31)$$

$$R{-}CCl_3 + Mn(CO)_5 \longrightarrow R{-}\dot{C}Cl_2 + Mn(CO_5)Cl \qquad (32)$$

We have reported [37] another bifunctional initiator, *N,N'*-bis(trichloroacetyl)-4,4'-azodi(4-cyanopentanamide), $CCl_3CONHCO(CH_2)_2C(CH_3)(CN)N{=}NC(CH_3)(CN)CONHCOCCl_3$, to obtain polymers containing CCl_3 groups. Using this polymer, block copolymers can be obtained by applying the method proposed by Bamford: the polymer is irradiated with UV light in the presence of manganese decacarbonyl and an appropriate monomer.

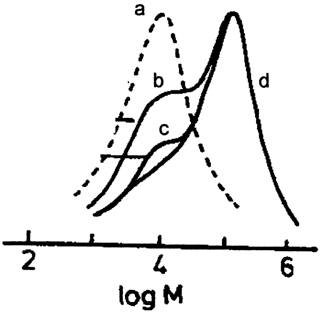
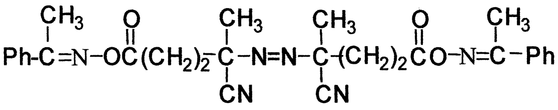


Figure 2. Size exclusion chromatograms recorded with products formed by irradiation of Cl_3C-PSt-CCl_3 in the presence of MMA and $Mn_2(CO)_{10}$ after different times: (a) polystyrene precursor, (b) 45 min, (c) 90 min, (d) 180 min

On irradiation, the carbonyl decomposes into $Mn(CO)_5$. The latter reacts with terminal CCl_3 groups yielding macroradicals which can start the polymerization of a monomer contained in the system. The formation of a block copolymer was clearly shown by SEC analysis as can be seen in Figure 2, where chromatograms recorded for the prepolymer and for the prepolymeric products obtained after different irradiation times are presented. The development of the new peak, ascribed to the block copolymer, correlates with the decrease of the prepolymer peak with increasing irradiation time.

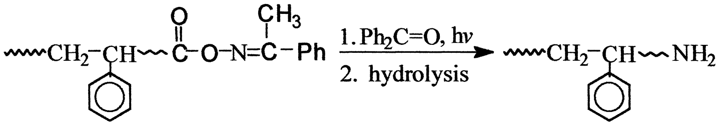
POLYMER FUNCTIONALIZATION VIA PHOTOINDUCED RADICAL PROCESS

The synthesis of prepolymers with deliberately introduced reactive end groups (telechelics) is an attractive field of polymer science because of their utilization as crosslinkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents. An alternative way to living polymerization, and a very often used pathway to introduce functional groups to polymers, is the use of bifunctional initiators in radical polymerization. A variety of bifunctional initiators have been used for the purpose. The functional initiator approach to synthesize amino telechelics causes some complications since amino compounds participate in chain transfer reactions. On the other hand, the use of the photochemistry of acyloxyimino grous allows the preparation of side- and main-chain amino telechelics. Song et al. reported [38] that pendant amino groups can be introduced effectively when polymers bearing acyloxyimino groups are irradiated in the presence of benzophenone and subsequently hydrolyzed. Following this strategy, we reported [39] a convenient and simple synthetic method for the preparation of amino telechelics by radical polymerization using acyloxyimino azo initiator (AOAI) and subsequent photolysis and hydrolysis.



$$Ph\text{-}\overset{CH_3}{C}{=}N\text{-}O\overset{O}{\overset{\|}{C}}(CH_2)_2\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2)_2\overset{O}{\overset{\|}{C}}O\text{-}N{=}\overset{CH_3}{C}\text{-}Ph$$

AOAI

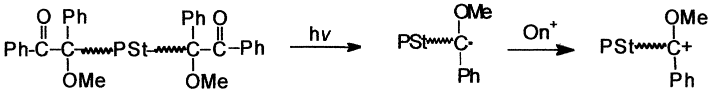


(33)

The obtained amino-terminated telechelics were subjected to chain extension with adipoyl chloride and gave positive evidence for the ability of amino chain ends to participate in polyamidation.

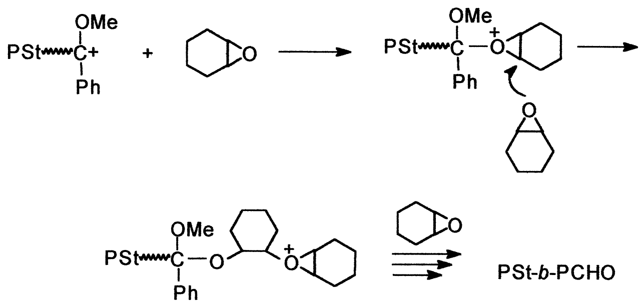
BLOCK COPOLYMERS VIA PHOTOINITIATED CATIONIC POLYMERIZATION

The use of photoactive polymers in blocking reactions are not limited to radical processes. Electron-donating polymeric radicals can conveniently be oxidized to polymeric carbocations to promote cationic polymerization of cyclic ethers and alkyl vinyl ethers. We have demonstrated [40] that irradiation of benzoin-terminated polymers in conjunction with pyridinium salts as oxidants in the presence of cyclohexene oxide makes it possible to synthesize block copolymers of different chemical nature.



$$Ph\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{OMe}{\overset{Ph}{C}}\sim PSt\sim\underset{OMe}{\overset{Ph}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}Ph \xrightarrow{h\nu} PSt\sim\underset{Ph}{\overset{OMe}{C}}\cdot \xrightarrow{On^+} PSt\sim\underset{Ph}{\overset{OMe}{C}}+ \;+\; On^{\cdot}$$

(34)



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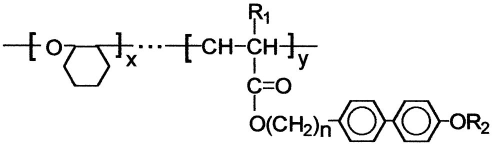
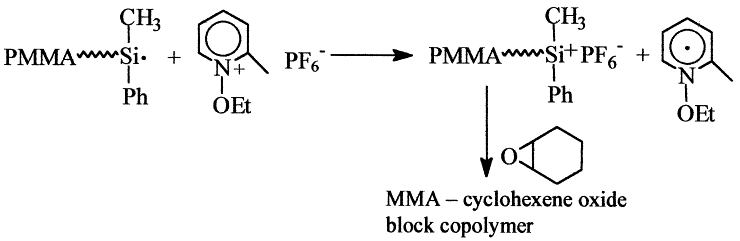
For the practical value of this process, we have prepared [41] block copolymers of crystalline and liquid-crystalline segments of the following structure by using the same synthetic strategy.



Poly(epichlorohydrin) functionalized with benzoin groups by activated monomer polymerization was also used in such promoted cationic polymerization to yield epichlorohydrin and cyclohexene oxide block copolymers.

We have shown previously [42,43] that the cationic polymerization of cyclohexene oxide is initiated by UV irradiation of solutions containing an alkoxypyridinium salt and polysilane. A plausible explanation of the mechanism involves oxidation of silyl radicals with pyridinium ions, addition of the cation formed to cyclohexene oxide and initiation of chain propagation by the resulting oxonium ion. The same reaction principle was applied to the polymerization of cyclohexene oxide using remaining polysilane units in PMMA, obtained by partial photodegradation of polysilane, and pyridinium ions [32].

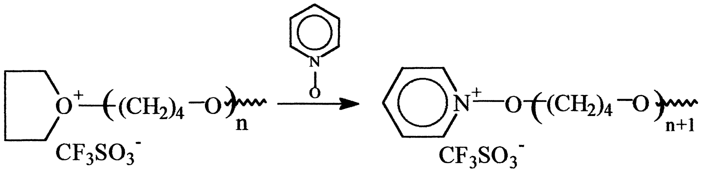


(36)

(37)

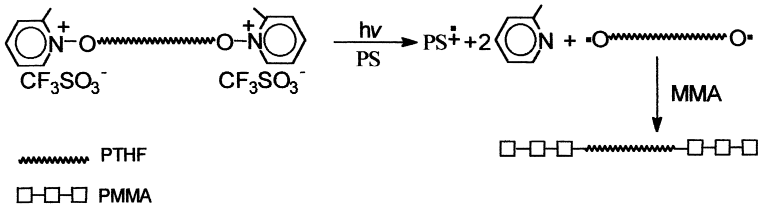
Although block copolymers are the main product, a considerable amount of homopolymers was also formed, which may be due to extensive degradation of polysilane units during irradiation. Moreover, the character of the initiation mechanism, which needs further investigation, may contribute to the formation of non-blocked component.

Living ends of cationic polymerization of tetrahydrofuran (THF) initiated with trifluoromethanesulfonic anhydride can be terminated with pyridinium *N*-oxide derivatives as shown below.



(38)

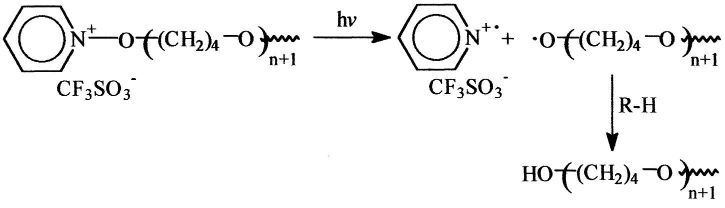
Poly(tetrahydrofuran) with terminal *N*-alkoxypyridinium ions can participate in photoinduced electron transfer to yield photosensitizer radical cation and macroradical [44]. The latter readily initiates polymerization of methyl methacrylate resulting in the formation of MMA and THF block copolymers in quantitative yields. Although the photodecomposition is cationic in nature, photoblocking reaction is induced by radical species.



(39)

(40)

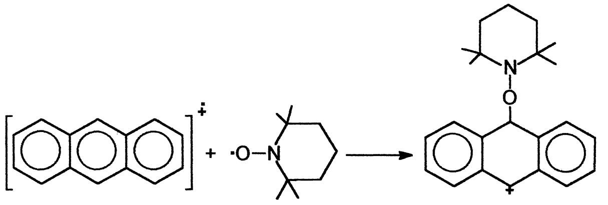
A useful approach [45] to polymer functionalization also involves direct or sensitized photodecomposition of pyridinium ions at the poly(tetrahydrofuran) chain ends. This is accomplished by hydrogen abstraction of the polymeric alkoxy radicals formed. The hydroxy functionality was evidenced by end-capping and polycondensation reactions.



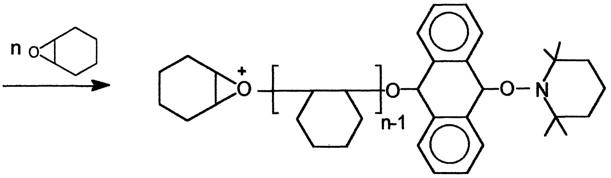
(41)

(42)

Anthracene-photosensitized cationic polymerization of cyclohexene oxide at $\lambda = 350$ nm in conjunction with onium salts, namely *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) or diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$), in the presence of a stable radical, 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO), yielded polymers with alkoxyamine terminal groups. Electron transfer between anthracene and onium salt yields anthracene radical cations which are quickly trapped by the nitroxide radicals to give, consequently, alkoxyamine functional dihydroanthryl cations capable of initiating cationic polymerization of cyclohexene oxide.

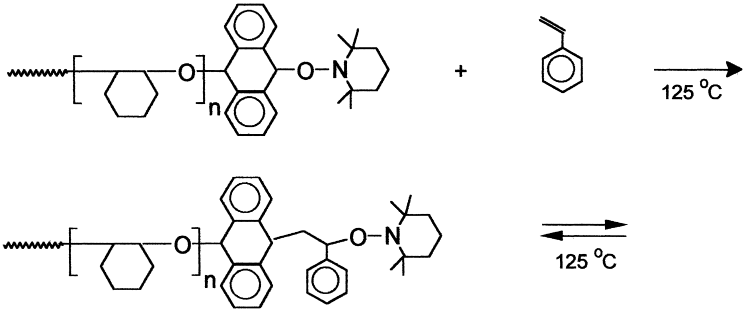


(43)

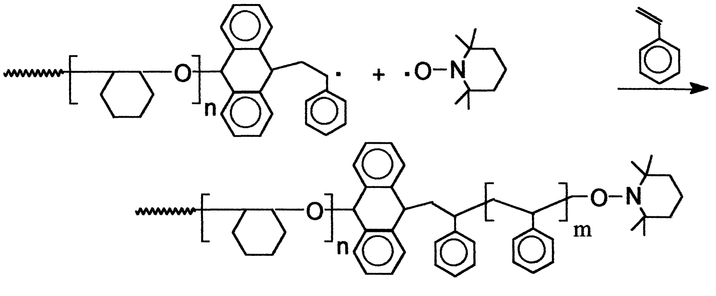


(44)

These polymers were found to be efficient initiators for stable-radical polymerization (SFRP) of styrene [46]. IR, ^{1}H NMR spectral analysis and GPC studies of the obtained polymers show that block copolymers are readily formed as a result of combination of photosensitized cationic and stable-radical polymerization mechanisms.



(45)



(46)

In conclusion, it is clear that design and synthesis of various types of block copolymers can be realized by photoinduced radical and cationic polymerizations. All the aforementioned procedures are promising for synthetic utilization but are still far from the controlled/living conditions. Further improvements can be expected, so that it may become possible to synthesize polymers with well defined structures by using photoinitiating systems.

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