29 Photoinduced synthesis of block copolymers

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Abstract

This chapter describes synthetic pathways to prepare block copolymers via photoinduced polymerization referring to most recent studies reported in the literature. These strategies basically involve either the use of mid-chain or end-chain polymeric photoinitiators, which undergo α-cleavage upon irradiation, or telechelics carrying chromophoric moieties suitable for Type-II initiation. The resulting products are diblock or triblock copolymers depending on the mode of termination. Homopolymer formation is also likely to take place in the case of end-chain polymeric photoinitiators. However, it can be prevented as mid-chain polymeric photoinitiators are employed, as well as hydrogen abstraction type macromolecular coinitiators. Another route which exploits photochemical coupling of two different homopolymer chains in achieving block

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copolymers has also been discussed here. Photoinduced polymerizations present advantages regarding the low temperature reaction conditions. These include the minimization of homopolymer formation, and ease of polymerizing monomers with low ceiling temperatures. Furthermore, photopolymerization systems are practically applicable to curing of coatings or surfaces. It is also possible that reactive sites can be generated at definite positions in the macromolecule, due to the selective absorptivities of certain chromophores. Despite the uncontrolled nature they exhibit, photoinduced polymerizations still aid in the preparation of various macromolecular structures such as block and graft copolymers.

1. Introduction

Synthesis of novel polymeric materials has attracted increasing interest in recent years. This is a consequence of the fact that readily available materials are often insufficient to meet the requirements of the industry, especially in high-tech applications. The demanded polymers usually display combinations of two or more physical or chemical properties which can be adopted either by blending homopolymers or by chemically linking different polymer chains. The major disadvantage associated with the former approach is the incompatibility of the blended polymers and in most cases it results in microphase–separated heterogeneous mixtures. This can be avoided by the latter strategy, which involves preparation of block and graft copolymers. Thus, block and graft copolymer synthesis appears to be a versatile method in preparing polymers with improved physical and chemical properties.

Preparation of block copolymers using living polymerization techniques has been known for quite a long time. Notable example of these techniques is anionic polymerization[1], which provides end-group control and permits the synthesis of narrow polydisperse materials. However, it does not offer a full-control over the molecular weight of the synthesized macromolecules. Furthermore, the limited choice of the monomers, and the extremely demanding reaction conditions make it unsuitable for various applications.

Recently, advances in controlled polymerization techniques[2-5] such as radical, cationic, metathesis, and group transfer, have allowed for the synthesis of polymers with predetermined molecular weights and low polydispersities. Among others, controlled radical polymerization routes have been studied extensively, since they can be employed for the polymerization of numerous vinyl monomers under mild reaction conditions. These are atom transfer radical polymerization (ATRP)[6-8], nitroxide mediated polymerization (NMP)[9-11], and reversible addition-fragmentation chain transfer polymerization (RAFT)[12,13]. Synthesis of block copolymers of various macromolecular architectures can now be easily achieved by the use of controlled radical polymerization techniques.

Photoinduced polymerizations which utilize light energy to initiate chain reactions to form polymer materials, offer a number of advantages compared to thermally initiated ones. They can be conducted at room temperature, which is an outstanding advantage for both classical polymerization of monofunctional monomers and modern curing applications. By means of photopolymerization, for instance, monomers with low ceiling temperatures can easily be polymerized without depolymerization taking place. In curing of coatings or surfaces, where thermal polymerizations are not feasible, photopolymerizations can be employed with success. Moreover, reactive sites can be

generated at definite positions in the macromolecule, owing to the selective absorption of certain chromophoric groups located accordingly.

In photoinduced polymerization systems, the number of propagating radicals may be controlled by the choice of appropriate light intensities. However, since initiating species are generated continuously, growing polymer chains with large differences in chain lengths are present simultaneously in the medium. Therefore, polymers usually have a broad molecular weight distribution.

Even though, available photoinitiating systems are defficient in polymerization control, they still contribute to the field of macromolecular engineering. In particular, block and graft copolymers can be prepared by using main chain and side chain polymeric photoinitiators, respectively. By photolysis, active sites are produced at the chain ends or side chains, which serve as initiating moieties in the polymerization of a second monomer. In this manner, copolymers with almost quantitative block or graft yields can be obtained, for the fact that side reactions and, thus, homopolymer formation are minimized as a result of the low polymerization temperature.

In this chapter, synthetic strategies to prepare block copolymers via photoinduced polymerization will be outlined and recent studies will be presented only to clarify the-state-of-the-art.

2. Photoinduced synthesis of block copolymers
2.1. Block copolymers by α-cleavage type photoinitiation

Block copolymers can be prepared by photolyzing precursor polymers possessing photolabile groups at the chain end or at the mid chain. These groups mainly involve benzyl dimethyl ketal, benzoin ethers, hydroxy alkyl phenyl ketones, dialkoxy acetophenones, benzoyl cyclohexanol, acylphosphine oxides and alkyl amino ketones[14]. Upon irradiation, they undergo scission at carbon-carbon bonds to give free radicals, which is known as α-cleavage. These free radical species are able to initiate the polymerization and crosslinking reactions of vinyl monomers. In this process, high quantum yield of radical generation, and high photoinitiation activity are attained, owing to very short triplet lifetimes.

$$\text{R, R' : H, Alkyl, subst. Alkyl}$$

(1)
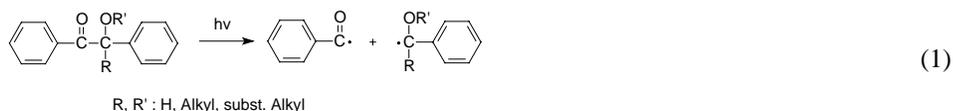
The incorporation of the photolabile groups into polymers, especially in the main chain, needs synthetic strategies to be built on the basis of chemical nature of the groups. The reader is encouraged to refer to previous review articles covering a number of such synthetic routes[15,16].

2.1.1. Block copolymers from prepolymers with end-chain photoactive moieties

Polymer chains bearing terminal photolabile groups yield diblock or triblock copolymers depending on the mode of termination. As depicted in Scheme 1, ABA type triblock copolymers are obtained when the propagating chains are terminated by combination, whereby, diblock copolymers are afforded by disproportion. On the other

hand, low molar mass radicals formed via photolysis of the chromophores can also initiate chain growth, which results in homopolymer formation. It should be noted that the combination of a propagating homopolymer with a diblock copolymer growing chain can contribute to blocking. Taking these initiation and termination aspects into consideration, it is quite likely that the final product will be inhomogeneous regarding its chemical composition.
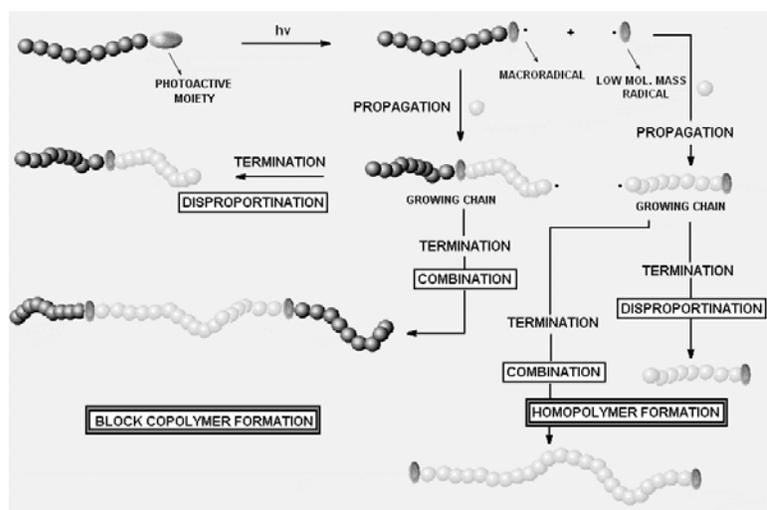

Scheme 1. Formation of various polymeric products in photoinduced synthesis of block copolymers.

Quite recently, we have reported the preparation of polystyrene and poly(ε-caprolactone) macrophotoinitiators containing alkoxy phenylketone groups at the chain ends[17,18]. Regarding the preparation of polystyrene macrophotoinitiators, a monofunctional initiator was synthesized by the reaction of 2-bromopropanoyl bromide with 2-hydroxy-2-methyl-1-phenyl-propane-1-one and it was used in atom transfer radical polymerization (ATRP) of styrene to afford end-functional polystyrene (React.2&3). Poly(ε-caprolactone) macrophotoinitiators were obtained via a stannous-2-ethylhexanoate (Sn(Oct)2) catalyzed living ring-opening polymerization of ε-caprolactone using commercially available monohydroxy functional initiators (Reaction 4).

(2)

(3)

$$(4)$$
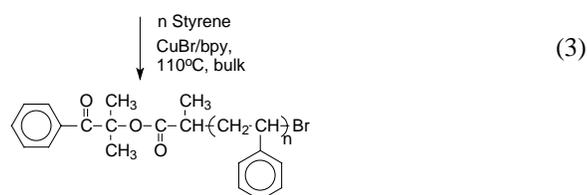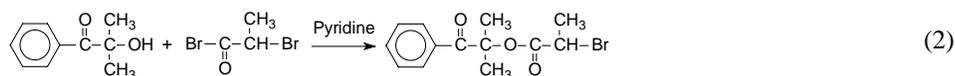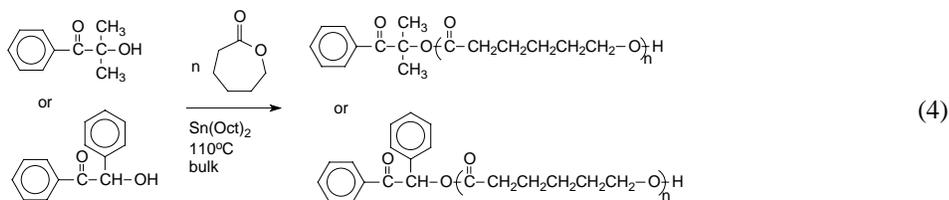
The GPC, IR, ^{1}H-NMR, UV, and fluorescence spectroscopic studies revealed that low-polydispersity polymers with desired terminal photoinitiator moieties were obtained. While potential of polystyrene macrophotoinitiator in the preparation of block copolymers was tested by control experiments, successful photoblocking was proved by GPC and ^{1}H-NMR analysis, in the case of photoinitiation with end-chain photoactive poly(ε-caprolactone). Generation of initiating species upon photolysis and subsequent polymerization of methyl methacrylate are illustrated by reactions (5) and (6) below. In the experiments, homopolymer formation occurred as expected, due to the initiation by the benzoyl radicals.

$$(5)$$

$$(6)$$
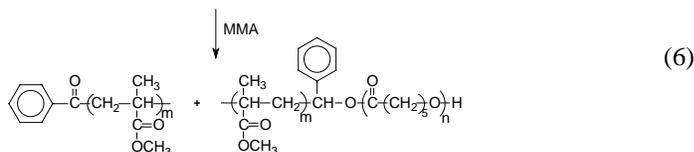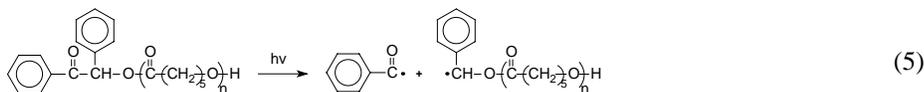
Surface morphology of the prepared block copolymer was also studied by Atomic Force Microscopy (AFM)[19]. Thin films comprising PCL-PMMA blocks as well as PMMA homopolymer displayed pitted surface morphology, which can be attributed to microphase separation between PCL and PMMA segments. The presence of PMMA homopolymer in the copolymer was found to increase the order of pits on the top surface while decreasing the distance between the pits.

2.1.2. Block copolymers from prepolymers with mid-chain photoactive moieties

When blocking is achieved with macrophotoinitiators carrying photolabile groups in the main chain, homopolymer formation resulting from low molar mass radicals can be prevented, which is a striking advantage of this strategy. Photoactive moieties can elegantly be incorporated into the main chain starting from a bifunctional low molar mass initiator. In this way, polymerization proceeds in two directions and, hence, macrophotoinitiators with mid-chain photoactive groups are obtained (Scheme 2).

We employed this methodology in the preparation of a polystyrene macrophoto-initiator possessing a mid-chain photoactive alkoxy phenylketone moiety and proposed to use it in photoblocking applications[18]. A low molar mass bifunctional ATRP initiator was synthesized by reacting 2-hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl propan-1-one with 2-bromopropanoyl bromide, and subsequently utilized in ATRP of styrene in conjunction with CuBr/bipyridine complex to give the desired product as shown below.

Scheme 2. Synthesis of block copolymers by the photolysis of precursor polymers carrying mid-chain photoactive moieties.

It is expected that this macrophotoinitiator can be useful in photoblocking reactions, producing initiating macroradicals upon chain scission through the in-chain alkoxy phenylketone groups when photolyzed.

2.2. Block copolymers by H-abstraction type photoinitiation

Block copolymers can alternatively be prepared with the aid of photoinitiating systems consisting of sensitizers, such as benzophenones, and a coinitiator such as alcohols, and amines[20]. Radicals are generated by a bimolecular process wherein photoexcited aromatic ketone is reduced by hydrogen abstraction from the coinitiator as illustrated in reaction 7. Notably, the radicals formed on the coinitiator are considered as the initiating radicals while ketyl radicals are unable to initiate a polymerization due to steric hindrance. Consequently, a homopolymer formation is prevented. When a polymeric coinitiator, that is a polymer possessing a terminal amine or alcohol functionality, is used to polymerize a different monomer, the resulting polymer will be a block copolymer.

(7)

In a recent study[21], we reported the use of *N,N*-dimethylaniline end-functional polystyrenes in the preparation of block copolymers via photoinduced radical polymerization of methyl methacrylate (MMA) to yield poly(St-*block*-MMA). 4-(Dimethylamino)benzyl 4-(bromomethyl) benzoate was synthesized by the esterification of 4-(bromomethyl)-benzoyl chloride and [4-(dimethylamino)phenyl]methanol in diethyl ether and was further used to initiate the ATRP of styrene in the presence of

CuBr/bipyridine complex to afford the dimethylamino-terminated polymeric co-initiator for photoinduced polymerization (8). The results are summarized in Table 1.

As expected, polymers with increasing chain lengths were obtained upon decreasing the initial concentration of the initiator and increasing the polymerization time.

(8)

(9)

(10)

(11)
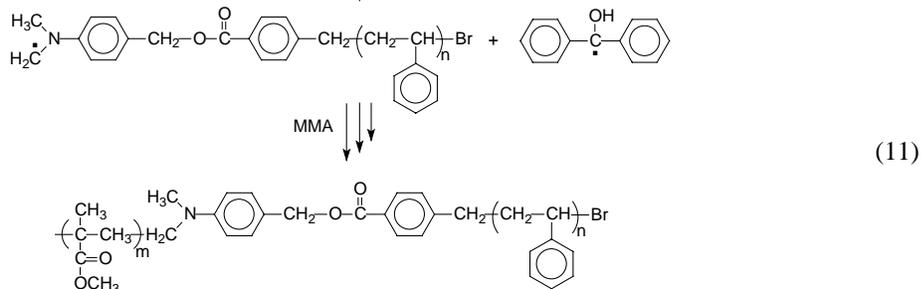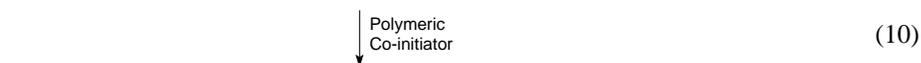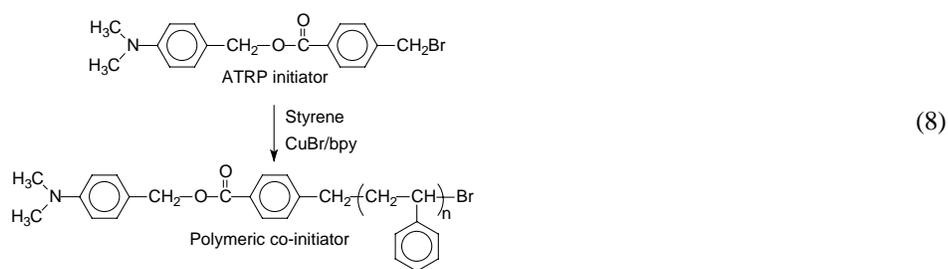
The molecular weights determined by GPC and ^{1}H-NMR agreed well with the theoretical values calculated according to the equation given below:

$$\overline{M}_{n,\text{th}} = \frac{[M_0]}{[I_0]} \times 104 \times (\text{conversion}) + \overline{M}_{n,\text{initiator}}$$

where M_0 and I_0 are the initial molar concentrations of the monomer and initiator, respectively.

The molecular weight distributions were narrowed, which is the characteristic of a mediated polymerization. However, a slight increase in the polydispersities was observed for longer polymerization times indicating the presence of some side reactions, such as that the second methyl groups of dimethyl amino functions might be involved in the radical generation and, hence, further polymerization, leading to chain extension.

Subsequently, several experiments were carried out using this precursor polymer to explore the photopolymerization of MMA via radical polymerization route. Polymerization in neat MMA gave a polymer which gave rise to a bimodal GPC trace which is typical for these conditions as MMA is known to autopolymerize and part of

Table 1.   ATRP of St in bulk using bromine terminal initiator.

Run	Initial conc. $(mol \cdot L^{-1})$	Polym. Time (min)	Polymer	Conv. (%)	Mn_{th}	Mn_{H-NMR}	Mn_{GPC}	M_w/M_n
1	0.15	47	a	26.4	1950	2000	1850	1.24
2	0.08	120	b	18	2400	2500	2600	1.34
3	0.08	380	c	45	5500	4800	4950	1.37
4	0.02	1620	d	43	20000	20200	19500	1.5

Bulk, $[I]_0/[CuBr]/[bpy] = 1/1/3$ molar, temperature: 110^oC
Mn_{H-NMR} was calculated from the ratio of integrals corresponding to aromatic protons and dimethylamino ones.

the initial PSt was not involved in the formation of block polymer. However, after extraction with various solvents pure block copolymers with ca. 50 % blocking yield were obtained. As a control experiment this procedure was repeated with a low-molar mass initiator. Much higher conversion was observed. Thus, terminal amino groups participate effectively in the radical generation process. Furthermore, repetition of the polymerization in solution generated materials with almost ideal blocking. The effect of the reaction time on the polymerization was also examined. Notably, the conversion increased from 2.8 to 41.2 by increasing irradiation time. The molecular weights were also increased as reflected by the shift of the iniatial GPC peak to higher elution volumes (Figure 1).
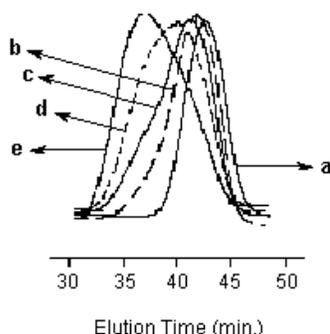

Figure 1. GPC traces of PSt (**a**) and block copolymers (PSt-b-PMMA) at different conversions; 2.8 (**b**), 10.2 (**c**), 21.2 (**d**), and 41.2 (**e**).

In a similar analogy, graft[22] and branched[23,24] copolymers were prepared from *N,N*-dimethyl amino side-chain functional precursor polymers, as well. Another study based on the use of anionically prepared amino functional poly(ethylene oxide) as a hydrogen donor in the preparation of poly(ethylene oxide-*block*-styrene) was reported by Huang[25].

2.3. Block copolymers by photoinduced coupling of chemically different homopolymer chains

Block copolymers can also be accessed via photoinduced coupling of chemically different homopolymer chains. These chains might carry either identical or different

chromophores in the chain ends, which undergo coupling reaction with each other upon absorbing radiation. In this case, as well, homopolymer formation is quite probable as a result of reaction between the two identical chains. The mechanism is depicted in Scheme 3.
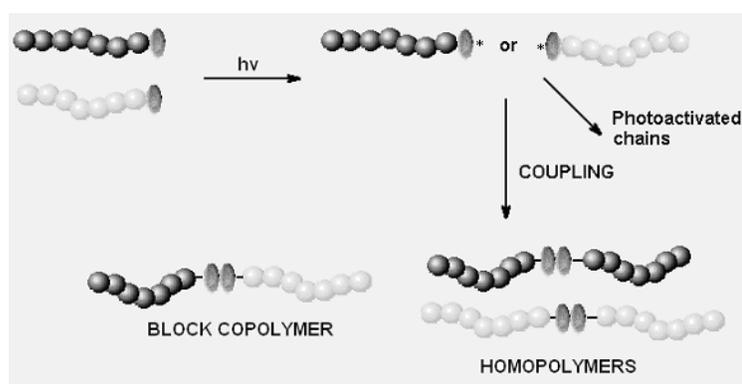

Scheme 3. Synthesis of block copolymers by photoinduced coupling of chemically different homopolymer chains carrying different reactive groups at the chain ends.

In a recent work reported by Goldbach *et al.*[26,27], poly(styrene-*block*-methyl methacrylate) containing an anthracene dimer photocleavable junction point was prepared via UV-photocoupling of high molecular weight telechelic polystyrene and poly(methyl methacrylate) bearing anthracene end groups. These groups were introduced into the polymers either by end-capping or acting as initiators in the anionic polymerization of styrene and methyl methacrylate. Upon exposure to UV irradiation at wavelengths greater than 300 nm., anthracene groups went through end-coupling reaction in THF solution to form [4 + 4] anthracene photodimers (Scheme 4).

After 150 h of irradiation, a mixture of products involving the coupled polystyrene homopolymer, P(S-AA-S), coupled PMMA homopolymer, P(MMA-AA-MMA), and the desired diblock copolymer, P(S-AA-MMA) was obtained as evidenced by GPC. Homopolymer by-products were removed with selective solvents. The bisanthracene junction point was shown to be sensitive to temperatures at /or above 135 °C, resulting in the cleavage of the diblock copolymer into homopolymers.

Bartz *et al.*[28] and Coursan *et al.*[29] independently showed that low molecular weight anthracene end-functionalized polystyrene and poly(methyl methacrylate) (Mn<10.0K) can be photodimerized under UV irradiation at 366 nm and quantitatively decoupled by irradiation at 280 nm with no cross-linking or degradation of the polymers.

In this contribution, basic strategies dealing with block copolymer synthesis through light induced polymerization have been reported with particular reference to recent works conducted in the area. It is still a challenge to prepare macromolecular materials with tailor-made properties employing photopolymerization techniques. We wish that advances in photopolymerization systems will bring about new discoveries endowing these systems with controlled//living nature. Such a breakthrough will definitely open new pathways to achieve macromolecular architectures by using photoinduced polymerization routes.
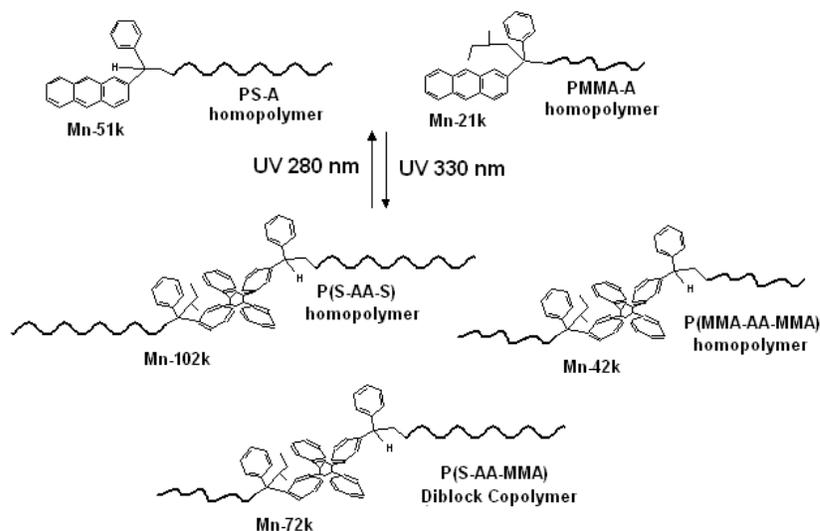
Scheme 4. UV coupling of anthracene end-functionalized PS and PMMA.

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