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NOTE

Synthesis of Block Copolymers by Combination of Atom Transfer Radical Polymerization and Visible Light Radical Photopolymerization Methods

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ABSTRACT: A novel two-step procedure for the preparation of block copolymers by combination of atom transfer radical polymerization (ATRP) and visible light radical photopolymerization (VLRP) methods is described. In the first step of the procedure, ω-bromide functional polystyrene (PSt-Br) was synthesized by ATRP of styrene (St) in toluene at 110 °C using ethyl-2-bromopropionate and copper bromide/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine as initiator and ligand, respectively. Visible light irradiation of these polymers in the presence of dimanganese decacarbonyl [$Mn_2(CO)_{10}$] produced macroradicals at ω-chain ends capable of initiating radical polymerization of various monomers, namely methyl methacrylate (MMA), butyl acrylate (BA), and vinyl acetate (VA). In this way, depending on the termination mode of the monomer involved AB or ABA type block copolymers consisting of PSt and respective segments were readily formed. The final polymers and intermediates at various stages were characterized by ^{1}H NMR spectroscopy and gel permeation chromatography (GPC).

Introduction

Block copolymers have become increasingly important in recent years. This importance is not only due to their special chemical structures yielding unusual physical properties but also due to the availability of various synthetic methods, including recently developed controlled/living polymerizations. Polymerization of two or more monomers in a sequential manner using controlled/living polymerization methods allows preparation of block copolymer with well-defined structures and chain lengths. However, depending on specific targeted applications, it is often required to combine monomers that polymerize by different mechanisms. The transformation polymerization appears to be an elegant method to combine diverse polymerization mechanisms. This way many monomers with different chemical structures can be polymerized to yield block copolymers with novel properties. Many different modes of transformation polymerization have been reported[1] and reviewed.[2] In this laboratory, we have focused on the use of the transformation approach to demonstrate the possibility of producing block polymers by combinations of free radical polymerization with anionic insertion,[3] activated monomer,[4] cationic,[5] free radical promoted cationic,[6] and condensation[7] polymerizations. Transformations can be achieved not only between different polymerization methods but also by the same mechanism using different initiating systems.[8] For example, atom transfer radical polymerization (ATRP) can be combined with nitroxide mediated radical polymerization (NMRP), both being controlled radical polymerization methods.[9] Transformation within the same polymerization process is not limited to controlled radical polymerization. The approach was easily adapted so that conventional free radical polymerization can be combined with controlled radical polymerizations. For example, Matyjaszewski and co-workers prepared block copolymers by the combination of ATRP and conventional radical polymerization using azo or redox initiators.[10] Boutevin and co-workers successfully used the same concept by employing trichloromethyl-terminated azo initiator.[11] In our laboratory, we demonstrated that ATRP could be combined with conventional photoinitiated radical polymerization.[12] There are also numerous reports showing that a combination of two radically polymerized monomers leads to a block copolymer using conventional radical−radical transformation polymerization.[13] In these examples, mostly initiators carrying two different radical forming sites were used as transformation agents, i.e., initiators containing groups of different thermal activity,[14] thermal and photochemical activity,[15] and redox and thermal activity.[16] Photochemical synthesis of block copolymers has a number of technical and theoretical advantages over other conventional methods. Because of the applicability at low temperatures, side reactions leading to the formation of homopolymers are minimized. Further, the reactive sites can be produced at definite positions of macromolecule due to the selective absorptivity of chromophores. Various methods for the photochemical synthesis of block copolymers have been treated by two review articles.[17]

Following our continuing interest in developing photoinitiating systems and their use in various macromolecular synthesis, in this paper we report on some preliminary results about the preparation of block copolymers by combination of ATRP and visible light radical polymerization (VLRP).

Experimental Section

Materials. Styrene (St; 99%, Aldrich), butyl acrylate (BA; ≥99%, Aldrich), and methyl methacrylate (MMA; 99%, Aldrich) were passed through a basic alumina column to remove the inhibitor prior to use. Vinyl acetate (VAc; ≥99%, Acros) was distilled under reduced pressure and stored under nitrogen. *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich) used as a ligand and was distilled before use. CuBr (98%, Acros) was used as received. Dimanganese decacarbonyl, $Mn_2(CO)_{10}$ (Aldrich), was purified by sublimation and stored in a refrigerator in the dark. Toluene (99.7%, Aldrich) was dried by distillation and stored over Na. Other solvents were purified by conventional distillation procedures.

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Table 1. Visible Light-Induced Block Copolymerization of Various Monomers (0.5 mL) Using PSt-Br (M_n = 2090 g·mol^{-1}, M_w/M_n = 1.12, 16 mg, 7.7 × 10^{-6} mol) and $Mn_2(CO)_{10}$ (9.2 mg, 2.3 × 10^{-5} mol) in Toluene (0.25 mL) at λ = ca. 430 nm

polymer[a]	monomer (mol·L^{-1})	k_p[b] (L·mol^{-1}·s^{-1})	convn (%)	M_n (g·mol^{-1})[c]	PDI[c]	block copolymer composition (mol % PSt)
PSt	St[d] (5.83)	187	6.0	4850	1.15	100
PSt-*b*-PMMA	MMA (6.03)	450	5.8	5530	1.64	61
PSt-*b*-PVAc	VAc (7.24)	117	6.7	2990	1.13	57
PSt-*b*-PBA	BA (4.68)	679	7.7	22 500	3.36	14

[a] Polymer acronyms: PSt, polystyrene; PMMA, poly(methyl methacrylate); PVAc, poly(vinyl acetate); PBA, poly(butyl acrylate). [b] From ref 26. [c] Number-average molecular weights ($M_{n,}$) and polydispersities (PDIs) were determined using gel permeation chromatography. [d] Chain extension.

General Procedure for Atom Transfer Radical Polymerization (ATRP). Monomer (St, 87.3 mmol), ligand (PMDETA, 0.87 mmol), catalyst (CuBr, 0.87 mmol), initiator (ethyl-2-bromopropionate, 0.87 mmol), and deoxygenated solvent (toluene) were added, consecutively, to a Schlenk tube equipped with a magnetic stirring bar. The tube was degassed by three freeze−pump−thaw cycles, left under vacuum, and placed in a thermostated oil bath (110 °C) for 25 min. After the polymerization, the reaction mixture was diluted with tetrahydrofuran (THF) and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer were evaporated under reduced pressure. The resulted polymer, bromo ω-end-functionalized polystyrene (PSt-Br), was dissolved in a small amount of THF, and precipitated in 10-fold excess methanol. The polymer was dried under vacuum at room temperature (yield % = 17.0; $M_{n,GPC}$ = 2090 g·mol^{-1}; M_w/M_n = 1.12).

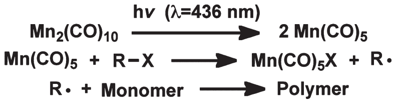
General Procedure for Visible Light Radical Polymerization (VLRP). A typical photopolymerization procedure is as follows. $Mn_2(CO)_{10}$ (9.2 mg, 2.3 × 10^{-5} mol) and 0.5 mL of MMA (4.7 × 10^{-5} mol) were added to a solution of PSt-Br (16 mg, 7.7 × 10^{-6} mol) in 0.25 mL of deoxygenated toluene in a Pyrex tube. The solution was flushed with nitrogen for 4−5 min. The reaction tube was sealed off and irradiated with a dental LED lamp (Bluephase) supplied by Ivoclar Vivadent Company. The wavelength range is 430−490 nm and maximum light performance is 1110 mW cm^{-2} ± 10%. At the end of 1 h irradiation, the polymerization solution was poured into cold methanol. The precipitated polymer was filtered off and dried in vacuo (Yield % = 5.8; $M_{n,GPC}$ = 5530 g·mol^{-1}; M_w/M_n = 1.64). Similarly, VLRP of BA, VAc, and St were also carried out using $Mn_2(CO)_{10}$ and PSt-Br under the same conditions (see Table 1 for details).

Analysis. Molecular weights and polydispersities of the polymers were determined by gel permeation chromatography (GPC) using a Viscotek GPCmax Autosampler system consisting of a pump, three ViscoGEL GPC columns (G2000H_{HR}, G3000H_{HR}, and G4000H_{HR}) (7.8 mm internal diameter, 300 mm length), a Viscotek UV detector, and a Viscotek differential refractive index (RI) detector with THF as eluent at a flow rate of 1.0 mL·min^{-1} at 30 °C. The effective molecular weight separations of the columns are ranging from 456 to 42 800 g·mol^{-1} for G2000H_{HR}; from 1050 to 107 000 g·mol^{-1} for G3000H_{HR}; and from 10 200 to 2 890 000 g·mol^{-1} for G4000H_H. Both detectors were calibrated with polystyrene standards having narrow molecular weight distribution and so the quoted molecular weights of the polymers therefore are expressed in terms of polystyrene equivalents. Data were analyzed using Viscotek OmniSEC Omni-01 software. ^{1}H NMR spectra of the polymers were recorded with $Si(CH_3)_4$ as an internal standard using a Bruker AC250 (250.133-MHz).

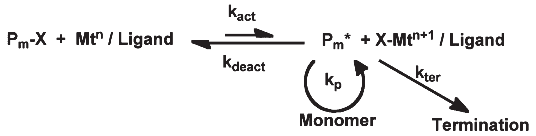
Results and Discussion

About 4 decades ago, Bamford demonstrated that carbon-centered radicals were formed upon irradiation (λ = ca. 436 nm) of organic halides in the presence of dimanganese decacarbonyl, $Mn_2(CO)_{10}$.[18] Upon absorption of light, $Mn_2(CO)_{10}$ decomposes to $Mn(CO)_5$ (Scheme 1). The latter reacts with the terminal halide group, yielding initiating alkyl radicals. Both bromine and chlorine compounds are found to be effective, and there is no initiation when no halide is present.

Scheme 1. Free Radical Photopolymerization Initiated by Photolysis of $Mn_2(CO)_{10}$ under Visible Light Irradiation



Scheme 2. General Mechanism of Atom Transfer Radical Polymerization



Such visible light initiation was successfully employed in the synthesis of various graft and block[19] copolymers even in heterogeneous conditions[20] by using prepolymers possessing suitable side- and end-chain halide functionality. Recently, this system in conjunction with certain additives has been used as an initiating system for controlled/living radical polymerizations.[21] Because of the possibility of generation of electron donor radicals, this system was also used for visible light free radical promoted cationic polymerization of structurally different monomers such as vinyl ethers and epoxides.[22]

Among various controlled radical polymerization methods, ATRP seems to be the most versatile method because of its simplicity and applicability to a wide range of monomers.[23] Moreover, it provides many possibilities in structural and architectural design and allows the development of new products with monomers currently available. ATRP involves reversible homolytic cleavage of a carbon−halogen bond by a redox reaction between an organic halide (R−X) and a transition metal, such as copper(I) salts (Scheme 2).[24]

Polymers obtained by ATRP contain terminal halide groups, which can be activated by the $Mn_2(CO)_{10}$. Thus, ATRP of styrene initiated by ethyl-2-bromopropionate, using CuBr/PMDETA catalytic system was performed. As the bromide functional polystyrene (PSt-Br) was intended to be used in the subsequent photoinitiation process, the conditions of ATRP (high concentration of initiator, 0.09 mol·L^{-1}, and short reaction time, 25 min) were deliberately selected so as to obtain a low molecular weight polymer, combined with a satisfactory conversion and polydispersity. The low molecular weight polymer would also provide better spectral characterization, particularly for the halide end group that is crucial for the photoinitiating system described. Accordingly, in this reaction stage the macroinitiator (PSt-Br, M_n = 2090 g·mol^{-1}, M_w/M_n = 1.12) possessing one reactive bromide group at the chain end was obtained. Subsequently, this macroinitiator was used to initiate the free radical polymerization of vinyl monomers through visible light irradiation at room temperature. Since PSt-Br does not absorb at the irradiation wavelength, λ = 436 nm, all the light is absorbed by $Mn_2(CO)_{10}$. $Mn(CO)_5$ formed from the photodecomposition of the excited state of $Mn_2(CO)_{10}$ abstracts bromine atom from the macroinitiator, PSt-Br, to generate polymeric radicals capable of initiating the polymerization of the second monomer. The overall process is represented in Scheme 3 on the example of the preparation of styrene-methyl methacrylate block copolymer.

All of the monomers were polymerized effectively, yielding the corresponding block copolymers (Table 1). As seen in Figure 1, unimodal GPC traces with a small shoulder are observed. Shifts to higher molar mass for all polymers are also found. The conversions, molecular weights and distributions are strongly related to the structure and reactivity of polystyryl radical to the monomers employed in the photoinitiated polymerization step. Similar dependency was also observed by Kamigaito and co-workers.[21c] Generally, molecular weight distributions were higher than those obtained by controlled radical polymerization methods. However, due to the room temperature conditions, except butyl acrylate (BA) polymerization, these values are still low compare to that obtained by conventional thermally induced free radical polymerization. Under certain conditions,[25] $Mn_2(CO)_{10}$ based initiating systems yield polymers with relatively low molecular weight distributions. Much higher molecular weight and its distribution observed in the case of BA may be attributed the high propagation rate constant of this particular monomer.[26] In order to confirm the efficiency of the photoinitiating system we also used St monomer in the second stage. After the photolysis, the molecular weight of polystyrene doubled as a result of successful chain extension via VLRP.

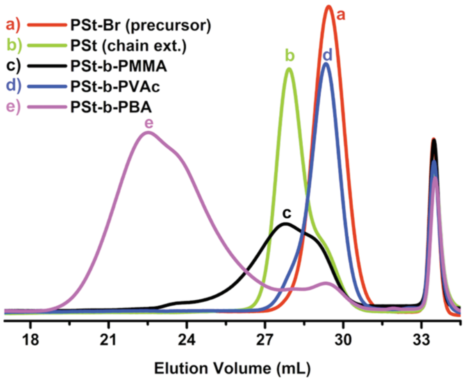
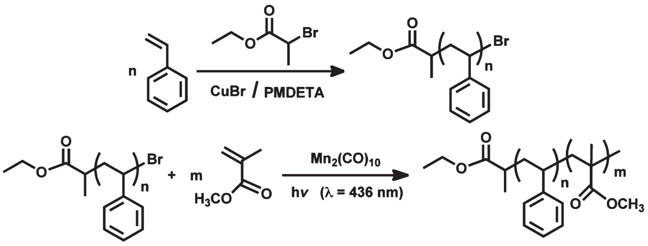


Figure 1. Gel permeation chromatography traces of block copolymers synthesized by visible light induced block copolymerization of various monomers (0.5 mL) using ω-bromo-functionalized polystyrene (PSt-Br, M_n = 2090 g·mol^{-1}, M_w/M_n = 1.12, 16 mg, 7.7×10^{-6} mol) and $Mn_2(CO)_{10}$ (9.2 mg, 2.3×10^{-5} mol) in toluene (0.25 mL) at λ = ca. 430 nm: PSt-Br (a); polystyrene by chain extension (PSt) (b); polystyrene-*b*-poly(methyl methacrylate) (PSt-*b*-PMMA) (c); polystyrene-*b*-poly(vinyl acetate) (PSt-*b*-PVAc) (d); polystyrene-*b*-poly(butyl acrylate) (PSt-*b*-PBA) (e).

Conventional free-radical polymerization of methacrylate monomers terminates mainly by a disproportionation process,[17a] which in the present polymerization system results in the formation of AB block copolymers, PSt-*b*-PMMA.[27] However, any preference for a combination termination mechanism would eventually yield ABA block structure. The structure of the block copolymers was confirmed by ^{1}H NMR analysis. As shown in Figure 2, the ^{1}H NMR spectra of the block copolymers exhibit characteristic resonances of both PSt and the block segments.

In conclusion, although these results are preliminary in nature, they clearly indicate that block copolymers can successfully be synthesized by combination of ATRP and VLRP processes. The synthetic approach described here was quite facile, since at least in principle, any polymer obtained by ATRP could be used as macroinitiator for the VLRP of a second monomer to yield corresponding block copolymers. The synthetic conditions of VLRP were mild compared to those of the conventional thermal methods. The facile synthetic method is expected to extend to the synthesis of other block copolymers via combination of ATRP with free radical promoted cationic polymerization.[22] It is well established that the radicals stemming from the photolysis of

Scheme 3. Synthesis of Block Copolymers of Styrene and Methyl Methacrylate by Sequential ATRP and Visible-Light-Radical Polymerization (VLRP)



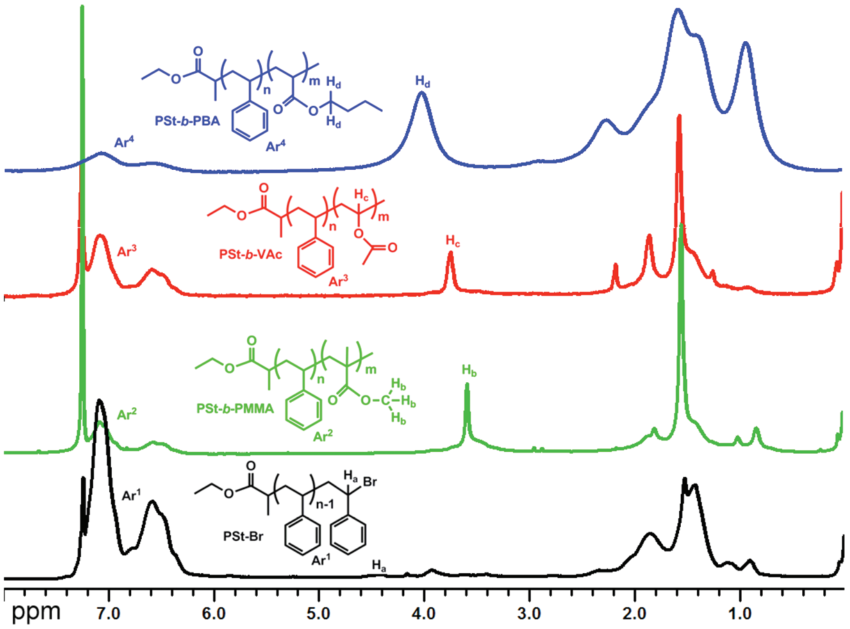


Figure 2. ^{1}H NMR spectra of block copolymers of methyl methacrylate (b), vinyl acetate (c) and butyl acrylate (d) and their precursor polystyrene (a) in $CDCl_3$ (see Figure 1 for the block copolymerization conditions).

organic halides in the presence of $Mn_2(CO)_{10}$ can readily be oxidized to the corresponding cations by suitable oxidants. The described method can also be used for the VLRP of bifunctional monomers using polymers obtained by ATRP leading to the formation of networks with dangling chains. Further studies in these lines are now in progress.

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