Photoinduced Synthesis of Block Copolymers by Combining Atom Transfer Radical Polymerization and Photoinduced Radical Oxidation/Addition/Deactivation

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Abstract: A new polymerization mechanistic transformation strategy, combining two different techniques of controlled polymerization modes, namely atom transfer radical polymerization (ATRP) and photoinduced radical oxidation/addition/deactivation (PROAD), is effectively used for the block copolymers' formation. Thus, mono- or bi- bromide functional polystyrenes (PS-Br or Br-PS-Br) synthesized by light-induced ATRP were used as a macroinitiator on isobutyl vinyl ether in the living cationic polymerization via PROAD process to give the corresponding block copolymers. Thus, depending upon the macroinitiator's surface, AB/ABA type block copolymers (PS-*b*-PIBVE or PIBVE-*b*-PS-*b*-PIBVE) were formed. The final polymers and precursor polymers were characterized by spectral and chromatographic analyses.

INTRODUCTION

There are limitations for the synthesis of segmented copolymers by one polymerization mode owing to the structure and comparative reactivity of the monomeric species and the others involved. Although there are various synthetic approaches to obtain such copolymers, mechanistic transformation methodology that combines different polymerization techniques appears as one of the most commonly applied techniques due to the immediacy and operational simplicity (1). In recent years, many block and graft copolymers were synthesized via different transformation approaches involving different polymerization techniques (2-5). With the recent notable evolution in controlled/living polymerizations, the concept is further extended to ionic, controlled free radical, metathesis, Ziegler–Natta, activated monomer, and group transfer reactions (6-11). In some other studies, it was also proved that transformations could be achieved in the same polymerization mode using different initiating systems. For instance, two differing controlled radical polymerization methods, namely nitroxide-mediated radical polymerization (NMRP) and atom transfer radical polymerization (ATRP), were used in combination for this purpose (2, 12). In another study, Yagci and co-workers represented successful block copolymerization by the combination ATRP and light induced free radical polymerization (13).

Photoinduced polymerizations involving cationic and free radical modes are also often used in such mechanistic transformations (14, 15). Numerous photoinitiators with different absorption features have been employed for the both modes (16-18). Such light-induced systems represent several advantages over conventional thermal techniques regarding the level of control since they can be accurately moderated in terms of wavelength, polarization direction, and intensity, allowing spatial and temporal control of the reactions. With the recent significant progress made in controlled polymerization techniques, the use of light has been implanted to such systems (19). Thus, common controlled polymerization methods were triggered by light as adapted from thermal counterparts including reversible addition–fragmentation chain transfer polymerization, also known as RAFT (20), NMRP mentioned above (21), ATRP (22-25), and some cationic polymerization techniques (26). Very recently, we have reported a new light-induced system of initiation (27) for isobutyl vinyl ether's living/controlled cationic polymerization by dimanganese decacarbonyl [$Mn_2(CO)_{10}$] (28). Scheme 1 shows the process of visible light irradiation of $Mn_2(CO)_{10}$, which then decomposes into $\cdot Mn(CO)_5$ radicals to abstract the halide from the alkyl bromide compound which results with the formation of radicals at carbon center. Then, diphenyliodonium ions oxidize these radicals to the related cations. The formed carbocations add IBVE, and bromide anions rapidly deactivate them to form a-halide functional end group. In a controlled manner, poly(vinyl ether) chains were then grown through successive photoinduced radical oxidation/addition/deactivation (PROAD) scheme.
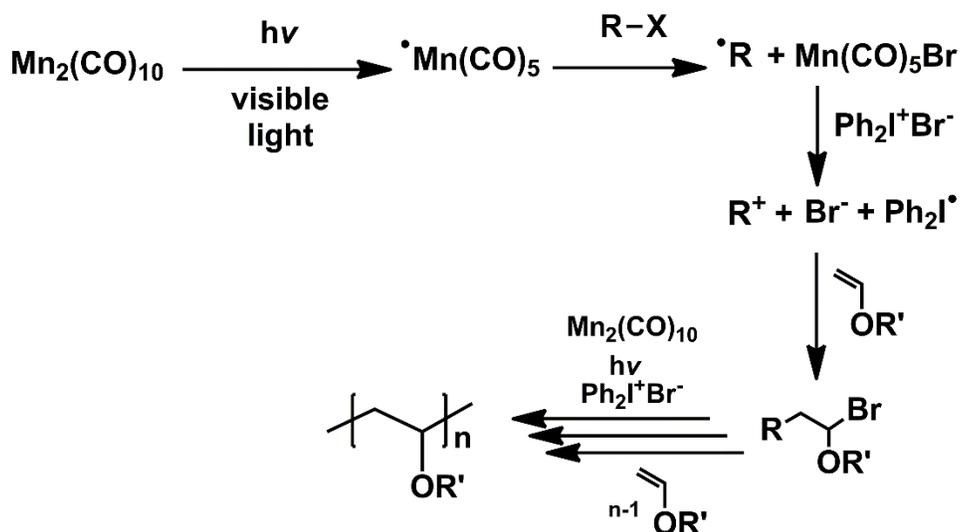
Scheme 1: Photoinduced living cationic polymerization of vinyl ethers by PROAD.

In the current study, we present a novel protocol to prepare block copolymers through a mechanistic transformation which combines ATRP and PROAD. Depending on the macroinitiator used, AB or ABA type block copolymers were formed. Additionally, the segment lengths could be adjusted by varying polymerization conditions. Block copolymers formed by the described chemistry had low molecular weight distribution due to the controlled nature of both modes.

EXPERIMENTAL SECTION

Materials

Styrene (St; 99%, Aldrich) was passed through a basic alumina column to remove the inhibitor prior to use. Isobutyl vinyl ether (IBVE, 99%, Aldrich) was distilled from CaH_2 in vacuum. Dimanganese decacarbonyl ($Mn_2(CO)_{10}$, 99%, Aldrich) was purified by sublimation and stored in a refrigerator in the dark. N,N,N',N'',N''-Pentamethyldiethylenetriamine (PMDETA; 99%, Aldrich) was distilled prior to use. Copper(II) bromide ($Cu^{II}Br_2$, 99%; Acros), Copper(I) bromide (CuBr, 98%, Aldrich), ethyl-2-bromopropionate (>99%, Aldrich), diphenyliodonium bromide ($Ph_2I^+Br^-$, 97%, Aldrich), dimethylformamide (DMF, 99.8%, Aldrich), tetrahydrofuran (THF, ≥99%, Merck) and methanol (99.9%, Aldrich) were used as received.

Characterization

^{1}H NMR spectra were recorded on an Agilent VNMRS 500 (500 MHz). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer FTIR Spectrum One spectrometer. Gel-permeation chromatography (GPC) measurements were obtained from a ViscotekGPC max Autosampler system consisting of a pump module (GPCmax, Viscotek Corp., Houston, TX, U.S.A.), a combined light

scattering (Model 270 Dual Detector, Viscotek Corp.), and a refractive index (RI) detector (VE 3580, Viscotek Corp.). The light scattering detector (λ_0 = 670 nm) included two scattering angles: 7° and 90°. The RI-detector was calibrated vs polystyrene standards having narrow molecular weight distribution, and so, the quoted molecular weights of the polymers are expressed in terms of polystyrene equivalents. Two columns, that is, a 7,8 × 300 mm LT5000L, Mixed, Medium Org and a 7,8 × 300 mm LT3000L, Mixed, Ultra-Low Org column equipped with a guard column 4.6 × 10 mm (Viscotek, TGuard), were used for the chloroform eluent at 35 °C (flow rate: 1 mL min−1). Data were analyzed using ViscotekOmniSEC Omni-01 software.

Synthesis of PS-Br

First, PS-Br was synthesized as described previously.(23) In a typical reaction, St (4 mL, 34.8 mmol), PMDETA (8 mL, 3.5 x 10^{-2} mmol), $Cu^{II}Br_2$ (8.4 mg, 3.5 x 10^{-2} mmol), EtBP (24.4 mL, 18.8 x 10^{-2} mmol), $Mn_2(CO)_{10}$ (3.9 mg, 9.4 x 10^{-3} mmol) and methanol (0.2 mL, 5 mmol) were charged into a Schlenk tube (i.d = 10 mm) equipped with a magnetic stirring bar and the reaction mixture was degassed by three freeze–pump–thaw cycles and left in a vacuum. The mixture was irradiated by a Ker-Vis blue photoreactor equipped with six lamps (Philips TL-D 18 W) emitting light nominally at 400–500 nm at room temperature. The light intensity was 45 mW cm^{-2} as measured by a Delta Ohm model HD-9021 radiometer. After the given time, the mixture was diluted with THF and precipitated in a tenfold excess of methanol. The polymer was dried under vacuum at room temperature.

Synthesis of Br-PS-Br

Bifunctional polystyrenes were prepared essentially as described elsewhere.(29)
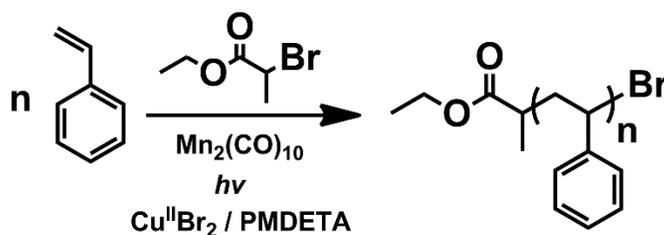
Synthesis of PS-*b*-PIBVE

A representative block copolymerization process was as follows; obtained PS-Br (80 mg, 3 × 10^{-5} mol), IBVE (1 mL, 7.7×10^{-3} mol), propylene carbonate (2 mL), $Ph_2I^+Br^-$ (7 mg, 2 × 10^{-5} mol) and $Mn_2(CO)_{10}$ (7.5 mg, 2 × 10^{-5} mol) were added to the Pyrex tube which was previously heated with a heat gun under vacuum and flushed with dry nitrogen. The solution was also flushed with nitrogen for 4−5 min and sealed. The formulation was stirred and exposed to light continuously at ambient temperature. At the end of the irradiation, the resultant polymer was precipitated in excess methanol and dried under reduced pressure.

RESULTS AND DISCUSSION

It is possible to create any cation from radicals generated by various techniques via electron transfer reactions. In various studies, not only low-molar-mass free radicals, but also polymeric radicals

could be oxidized to the corresponding cations (30). Although corresponding block or graft copolymers are formed by described methods, cationic polymerization steps of the approaches were suffering from the uncontrolled polymerization mechanism. The possibility of using a recently developed photoredox catalytic system for living cationic polymerization let us employ the same redox process for the block copolymerization.

In the described approach, block copolymers were obtained in two distinct steps. The overall process for the example of monofunctional macroinitiator is as follows. In the first step, a bromide functional PS was synthesized by ATRP of St under visible light irradiation using ethyl-2-bromopropionate, $Mn_2(CO)_{10}$ and $Cu^{II}Br_2$/PMDETA initiator, photosensitive compound, catalyst and ligand, respectively (Scheme 2).

Scheme 2: Synthesis of PS-Br via ATRP.

In the second step, the photolysis of $Mn_2(CO)_{10}$ in the presence of the obtained macro co-initiators initiated the PROAD of IBVE initiated resulting in the formation of the block copolymers, PS-*b*-PIBVE (Scheme 3-A). Since only $Mn_2(CO)_{10}$ absorbs the light in the irradiation region, upon irradiation, $Mn(CO)_5$ radicals were formed from the decomposition of the of $Mn_2(CO)_{10}$ and they abstracted bromine atom from the macroinitiator. Then the generated polymeric radicals were oxidized by diphenyliodonium ions to the related initiating cations. Due to the living/controlled nature of the both steps, block copolymers with narrow molecular weight distributions were obtained.

Additionally, to represent the high adaptability of the described process, ABA block copolymers were also formed by similar strategy. Thus, by using bifunctional PS as macroinitiator PIBVE-*b*-PS-*b*-PIBVE block copolymers were also obtained (Scheme 3-B).
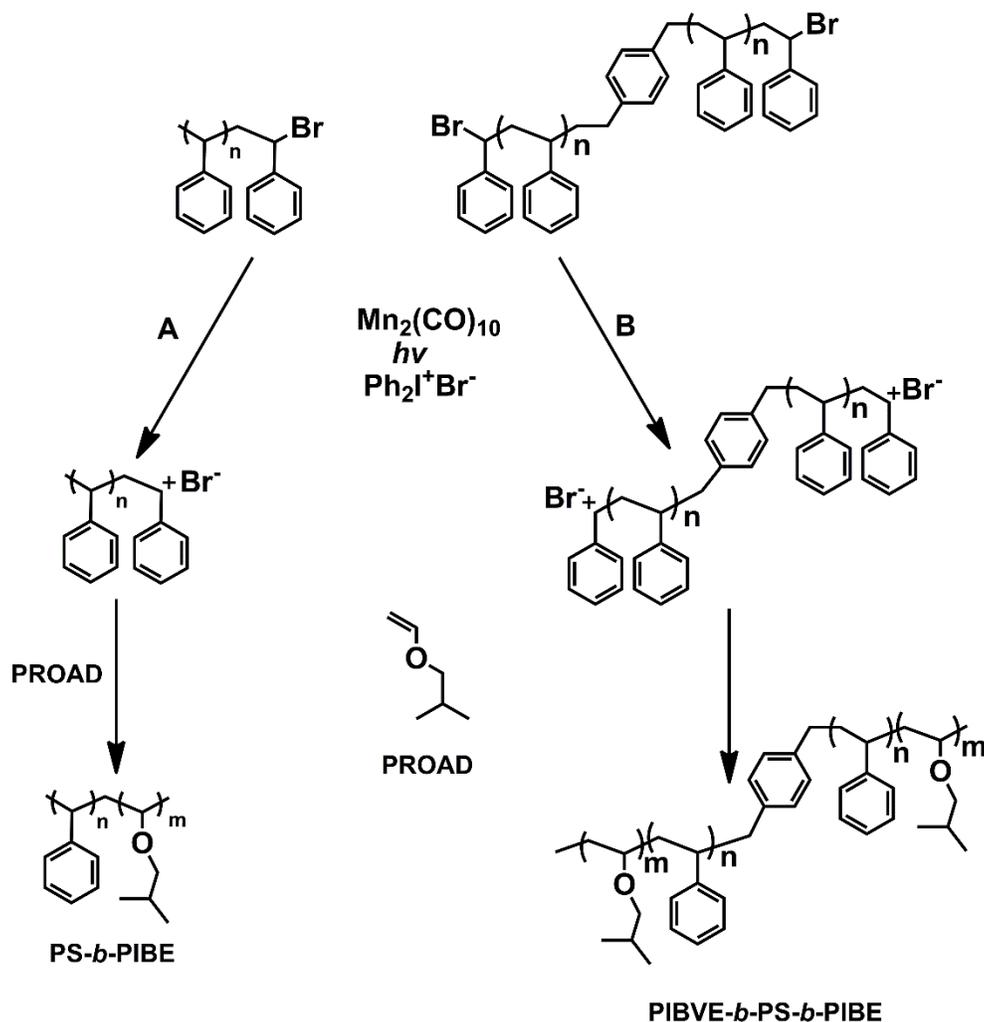
Scheme 3: Synthesis of block copolymers by sequential ATRP and PROAD.

As can be seen from results are collected in Table 1, depending on the polymerization conditions polymers with different segment length were readily formed. Prolonged irradiation time of the PROAD process results into higher PIBVE chain length Table 1.

Table 1: Block copolymerization of IBVE by PROAD.

Polymer	Macroinitiator	Time (min.)	$M_{n,GPC}$ (g.mol^{-1})	PDI
PS-*b*-PIBVE-1	PS-Br[a]	45	3950	1.20
PS-*b*-PIBVE-2	PS-Br[a]	90	4680	1.24
PS-*b*-PIBVE-3	PS-Br[a]	135	5200	1.28
PIBVE-*b*-PS-*b*-PIBVE	Br-PS-Br[b]	90	6400	1.29

[a] M_n = 2300 g mol^{-1}, PDI = 1.20, [b] M_n = 2800 g mol^{-1}, PDI = 1.21.

The successful block copolymerization was confirmed by ^{1}H NMR analysis of the precursor polymer and the resulting block copolymers. As can be seen from Figure 2, the appearance of new signals

between 3–3.7 ppm corresponding to the -OCH_2 protons of isobutyl vinyl ether clearly indicates the presence of PIBVE segments.
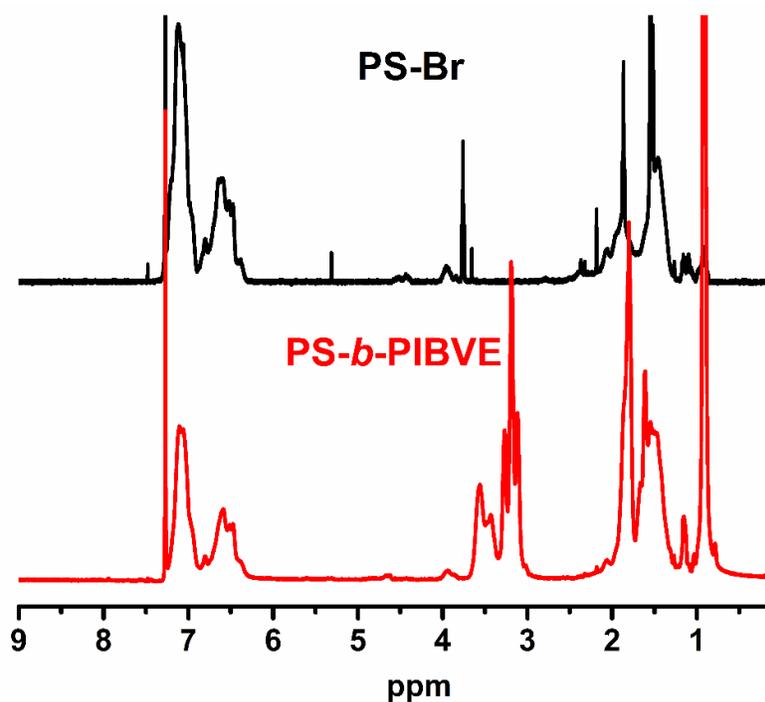
Figure 1: ^{1}H NMR spectra of PS and PS-*b*-PIBVE.

Figure 2 shows GPC traces of the precursor polymer and the final block copolymers. The clear shift of the GPC trace to higher elution volumes indicates an increase in the molecular weight after the block copolymerization process. Furthermore, any residuals from the remaining unreacted precursor polymer or from free PIBVE were not observed. The higher molecular weights were observed when Br-PS-Br was used as initiator under the identical experimental conditions that of PS-Br.
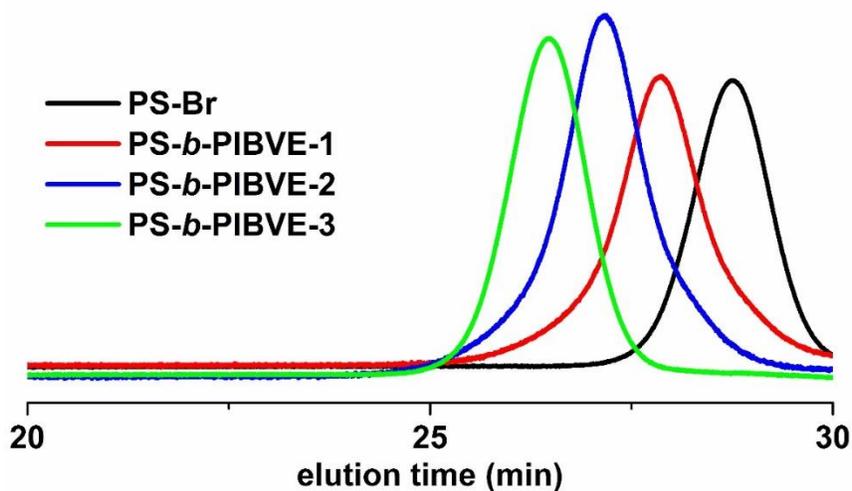
Figure 2: GPC traces for PS-Br and PS-*b*-PIBVE at different time intervals.

The IR spectra of the block copolymers demonstrate the characteristic bands for both the PS and PIBVE chains (Figure 3). Thus, in addition to the typical aromatic bands, the spectrum shows the characteristic etheric bands of the IBVE around 1100 cm^{-1}.
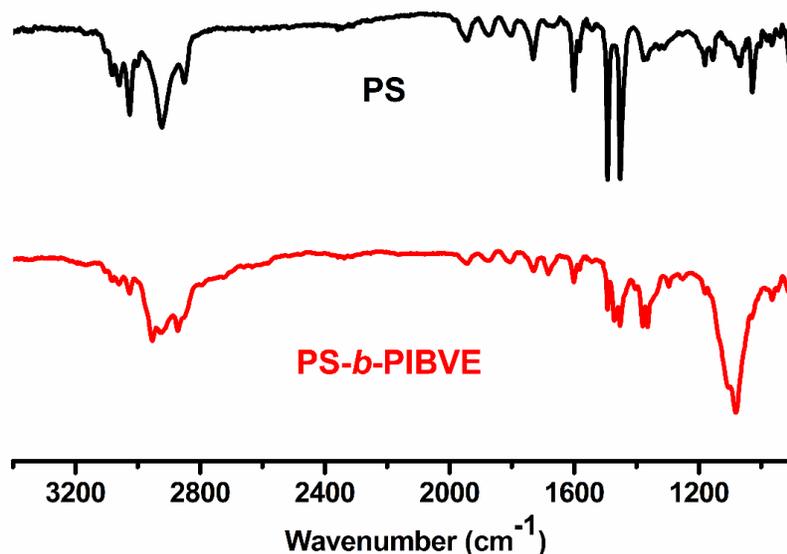
Figure 3: FT-IR spectra of PS and PS-*b*-PIBVE.

In conclusion, a simple transformation approach for the synthesis of block copolymers in a controlled manner by combination of ATRP and PROAD processes has been shown. The method lets us directly use of halide functional polymers gained by atom transfer radical polymerization, in the subsequent visible light-induced living/controlled cationic polymerization of a second monomer to give block copolymers. Both steps, ATRP and PROAD, require relatively mild conditions compared to conventional thermal systems as they are triggered by light. Moreover, the growth of the segments can be adjusted by varying experimental conditions.

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