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Synthesis of poly(ethylene glycol-b-styrene) block copolymers by reverse atom transfer radical polymerization

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Abstract Reverse atom transfer radical polymerization (RATRP) of styrene (S) was carried out in bulk using polyazoester prepared by the reaction of polyethylene glycol with molecular weight of 3000 and 4,4′-azobis (4-cyanopentanoyl chloride) as initiator and $CuCl_2$/2,2′-bipyridine (bpy) catalyst system to yield poly(ethylene glycol-b-styrene) block copolymer. The block copolymers were characterized ^1H NMR, FT-IR spectroscopy and GPC. The ^1H NMR, and FT-IR spectra showed that formation of poly(ethylene glycol-b-styrene) block copolymer. The polydispersities of block copolymers were observed between from 1.49 and 1.98 GPC measurements.

Keywords Reverse ATRP · Styrene · PAE-3000/$CuCl_2$/bpy initiating system · Block copolymers

Introduction

Atom transfer radical polymerization (ATRP) is based on a fast, dynamic equilibrium established between the dormant species (alkyl halides) and active species (radicals), with transition metal complexes acting as reversible halogen atom transfer reagents, which keeps a very low radical concentration in the reaction system, and therefore, results in negligible radical termination and controlled polymerization [1, 2]. However ATRP has two major drawbacks: the toxicity of the halide species RX and the oxidation of the catalyst M_n^t/LX by oxygen in air. To overcome these drawbacks, Matyjaszewski and coworkers [3, 4] and Teyssie et al. [5] reported the reverse and alternative ATRP systems, respectively. Wang and Matyjaszewski [4] reported the controlled/‘living’ radical polymerization of styrene via a reverse ATRP under heterogeneous conditions employing 2,2′-azobisisobutyronitrile (AIBN)/$CuCl_2$/2,2′-bipyridine (bpy) as initiating system, but it is uncontrolled for both methyl methacrylate (MMA), and methyl acrylate (MA). Shortly thereafter, by using alkyl substituted bpy ligand such as 4-4′-di-(5-nonyl)-2,2′-bipyridine (dNbpy) as a ligand instead of bpy, Xia and Matyjaszewski [3] described the reverse ATRP under homogeneous condition, in which controlled/‘living’ polymerization of styrene (S), MMA, and MA were all successfully carried out. More recently, Teyssie et al. [5] reported that the AIBN/$FeCl_3$/PPh_3 system could be used for the synthesis of well-defined PMMA in bulk and solution polymerization of MMA at 85 °C. As mentioned above this type of ATRP approach the same type of equilibrium starting from conventional radical initiators such as peroxides or diazo compounds [6]. Recently reserve ATRP has been used for the synthesis of polymers [3, 6–26]. The efficient reverse ATRP-initiating systems for controlled/‘living’ radical polymerization have been reported, that is, AIBN/$CuCl_2$ (or $CuBr_2$)/bpy for MMA, MA, S polymerization [3, 4, 27, 28] and AIBN/$FeCl_3$/PPh_3 for MMA polymerization [29].

Reverse ATRP differs from conventional ATRP in the initiation step, in which the initiating active species or propagating active species can abstract a halogen atom from the oxidized transition-metal complex to form the dormant species and the reduced transition-metal species [7, 29, 30]. As shown in Scheme 1, in the initiation step, once generated, the initiating radicals or the propagating radicals, I. or I-P_1., can abstract the halogen atom X from the oxidized transition-metal species, XM_t^{n+1}, to form the reduced transition-metal species, M_t^n, and the dormant

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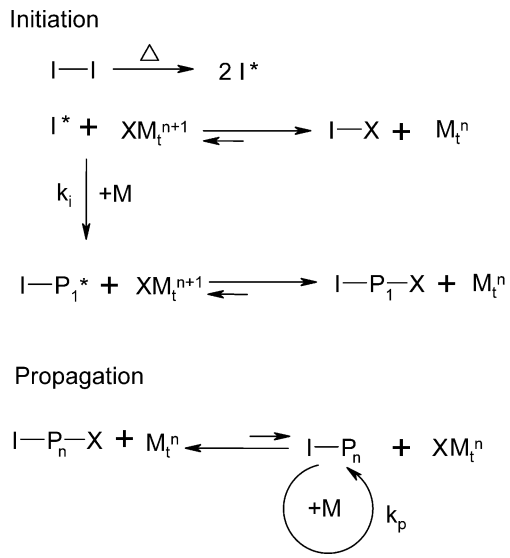


Scheme 1 General reaction mechanism of reverse ATRP

species, I-X or I-P$_1$-X. In the subsequent steps, the transition-metal species, M_t^n, promotes exactly the same ATRP process as normal ATRP where $R-X/M_t^n/L_x$ are used as the initiation system. Instead of first activation of a dormant species, R-X, with M_t^n, as in the case of normal ATRP, reverse ATRP originates from the deactivation reaction between radicals, I. or I-P$_1$., and XM_t^{n+1} [3].

Block copolymers have become increasingly important in recent years [31, 32]. This importance is due to the fact that their special chemical structure yields unusual physical properties [31]. The synthesis of block copolymers, with a controlled molecular weight, a narrow molecular weight distribution, and a better-designed macromolecular structure and composition, is one of the most meaningful and challenging works in the field of polymer chemistry [33]. Block copolymers have been the subject of intense experimental and theoretical interests for more than two decades because of their practical applications as adhesives, surfactants, compatibilizers and thermoplastic elastomers [34]. The synthesis of block copolymers usually requires efficient controlled/'living' polymerization [34].

The synthesis of well-defined PS-b-P4VP by using atom transfer radical polymerization in two-step process was carried out by Chang El al. [35]. First, polystyrenes with benzyl bromide end group (PS-Br; by ATRP) were prepared as macroinitiator for the next ATRP of 4-vinyl pyridine [35].

The controlled/"living" radical polymerization of methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), and styrene by atom transfer radical polymerization (ATRP) is described by Wang et al. [36]. The effect of initiators and reaction conditions on the ATRP results was also investigated. Controlled polymerizations with predictable molecular weights were performed on MMA at 40 °C and 80 °C using a CuCl/bipyridine (bipy) catalyst system in conjunction with 1-bromoethyl benzene as the initiator [36].

In this study, polyethylene glycol azoester (PAE-3000) prepared by the reaction of 4,4′-azobis(4-cyano pentanoyl chloride) (ACPC) and poly(ethylene glycol)(PEG-3000) was used as initiator in the reverse ATRP of S to yield poly (ethylene glycol-b-styrene) block copolymers. The reverse ATRP of S was carried out in bulk using CuCl$_2$/bpy

Table 1 Reverse ATRP reaction of styrene with PAE-3000/CuCl$_2$/bpy initiating system at 110 °C

PAE-3000/CuCl$_2$/bpy (mol/mol/mol)	Code	Time (minute)	Yield of polymer (g)	Conversion (w%)	$\overline{M}_{n,th}$	$\overline{M}_{n,GPC}$	$\overline{M}_w/\overline{M}_n$	*f* (initiator efficiency) $\overline{M}_{n,th}/\overline{M}_{n,GPC}$
1.0/1.0/2.0^a	PA-3	20	0.2109	10.55	9,966	46,120	1.76	0.22
	PA-4	25	0.2707	13.54	11,521	48,166	1.63	0.24
0.5/1.0/2.0^b	PB-2	15	0.0659	3.30	7,912	25,802	1.74	0.31
	PB-3	20	0.0848	4.24	8,890	35,203	1.98	0.25
	PB-4	25	0.0891	4.50	9,160	41,015	1.82	0.22
0.7/1.0/2.0^c	PC-1	10	0.1783	8.92	11,122	49,266	1.49	0.23
	PC-4	25	0.2309	11.55	13,082	60,139	1.77	0.22
	PC-5	40	0.3010	15.05	15,693	66,076	1.75	0.24
1.0/1.0/1.6^d	PD-2	40	0.2623	13.12	11,300	50,095	1.68	0.23
	PD-4	80	0.2736	13.68	11,594	54,317	1.81	0.21
1.0/1.0/1.2^e	PE-2	40	0.2380	11.90	10,668	43,508	1.81	0.25
	PE-3	60	0.2460	12.30	10,876	44,463	1.94	0.24
	PE-4	80	0.2626	13.13	11,309	47,517	1.95	0.24
	PE-5	100	0.3155	15.76	12,683	54,088	1.86	0.23

a: PAE-3000=1.92×10^{-5} mol, CuCl$_2$=1.92×10^{-5} mol, bpy=3.84×10^{-5} mol, styrene=1.92×10^{-2} mol
b: PAE-3000=0.96×10^{-5} mol, CuCl$_2$=1.92×10^{-5} mol, bpy=3.84×10^{-5} mol, styrene=1.92×10^{-2} mol
c: PAE-3000=1.34×10^{-5} mol, CuCl$_2$=1.92×10^{-5} mol, bpy=3.84×10^{-5} mol, styrene=1.92×10^{-2} mol
d: PAE-3000=1.92×10^{-5} mol, CuCl$_2$=1.92×10^{-5} mol, bpy=3.07×10^{-5} mol, styrene=1.92×10^{-2} mol
e: PAE-3000=1.34×10^{-5} mol, CuCl$_2$=1.92×10^{-5} mol, bpy=2.30×10^{-5} mol, styrene=1.92×10^{-2} mol

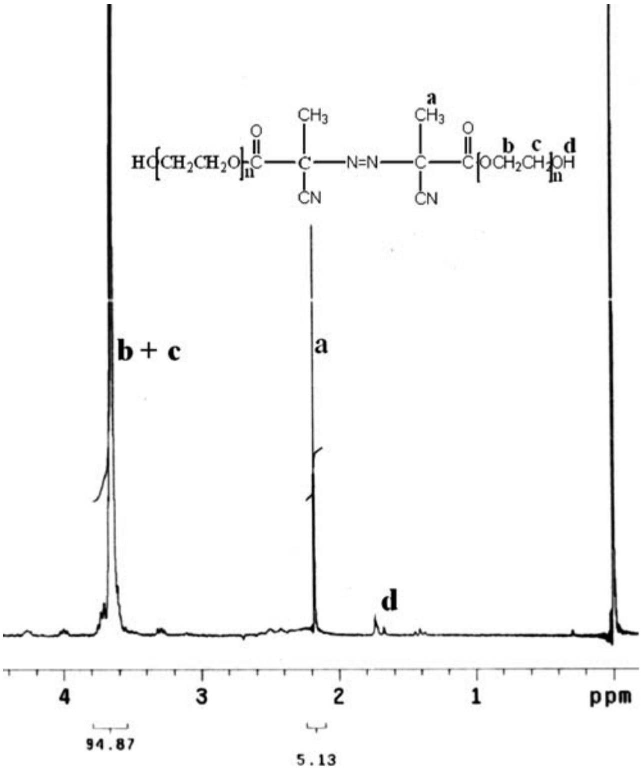


Fig. 1 ^{1}H NMR spectrum of the polyethylene glycol azoester (PAE-3000)

complex as catalyst. A well-defined poly(ethylene glycol-b-styrene) block copolymers with a high molecular weight and narrow polydispersities was obtained through the polymerization of S by this process.

Experimental section

Materials

$CuCl_2$, PCl_5, benzene, polyethylene glycol (M_n=3000), triethylamine, and bpy were supplied from Merck and used as received. 4,4′-azobis(4-cyano pentanoic acid) was supplied from Fluka and used as received. Styrene (S) was supplied from Merck and washed with a %10 aqueous NaOH, water dried over $CaCl_2$ respectively, and was then distilled on CaH_2 under reduced pressure before use. All other chemicals were reagent grade and used without further purification.

Synthesis of 4,4′-azobis(4-cyano pentanoyl chloride) and polyethylene glycol azoester

4,4′-azobis(4-cyano pentanoyl chloride) (ACPC) was obtained by the reaction of 4,4′-azobis(4-cyano pentanoic acid) (ACPA) with PCl_5 and recrystallized from chloroform solution [37]. Polyethylene glycol azoester (PAE-3000) was synthesized by the reaction of ACPC and polyethylene glycol (M_n=3000) PEG-3000 in the presence of triethylamine in benzene at room temperature as follows: Into a flask equipped with magnetic stirrer and addition funnel were placed 300 ml of benzene, 6,44 g (18,4 mmol) ACPC, 3,72 g (36,8 mmol) triethyl amin and 110,4 g (36,8 mmol) PEG-3000. The mixture was stood overnight at ambient temperature. The evaporation of the solvent, flask content was precipitated into cold diethyl ether. The yield was found as 64.6 g.

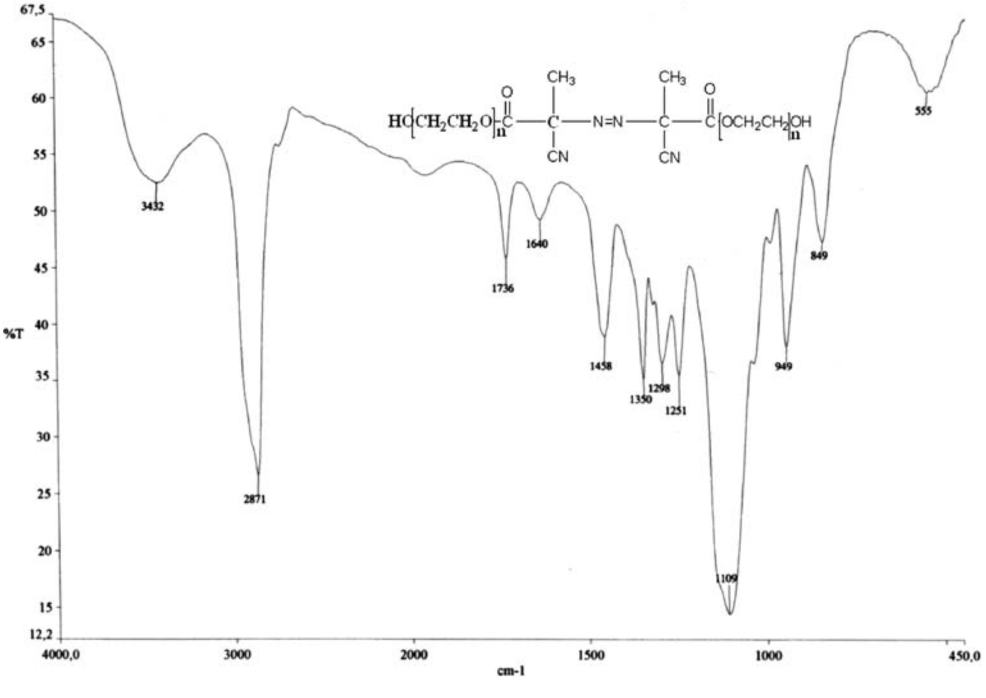
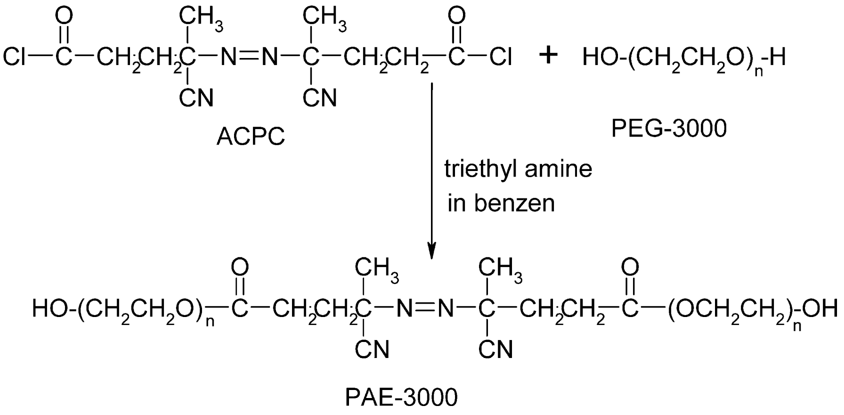


Fig. 2 FT-IR spectrum of the polyethylene glycol azoester (PAE-3000)

Scheme 2 The reaction pathway of PAE-3000



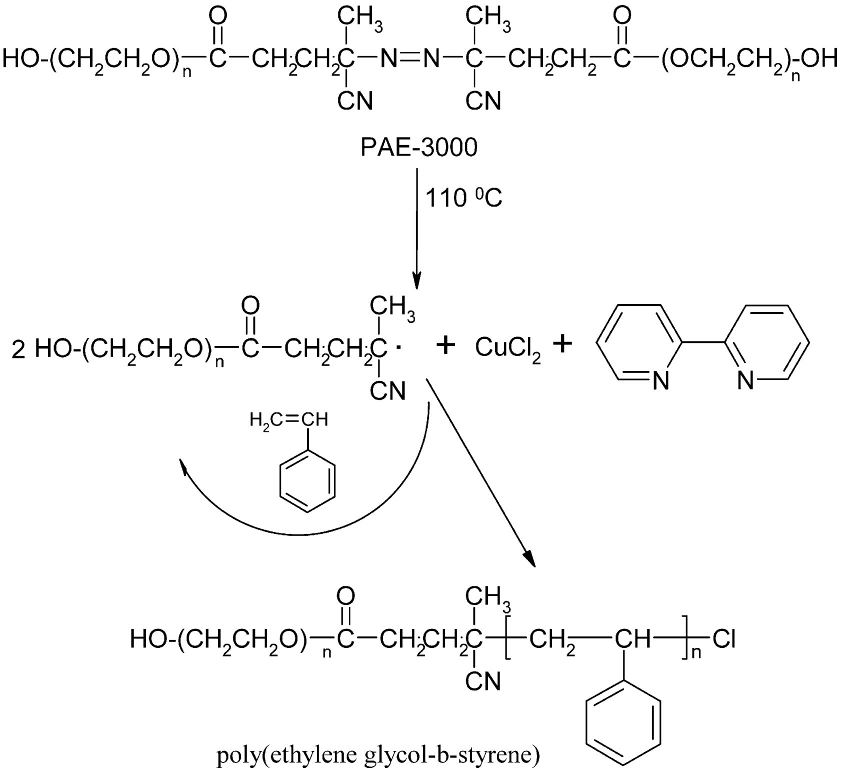
Reverse ATRP of S with PAE-3000

The dry schlenck tubes containing the reaction mixture of monomer, PAE-3000, $CuCl_2$, and bpy were degassed by vacuum and nitrogen and sealed under vacuum. Then the tubes were immersed in a silicone oil bath thermostat at 110 °C. At a certain interval, schlenck tube was cooled to quench the polymerization. The schlenck tube content was diluted with ethyl acetate. The solution was filtered and precipitated with methanol to yield the polymer product. The dried poly (ethylene glycol-b-styrene) was dissolved in THF and passed through a small neutral alumina column to remove the remaining copper catalyst. The purified block copolymer was dried at 30 °C under vacuum for three day. The polymerization conditions and the results are listed in Table 1.

Characterization of the products

GPC chromatograms were obtained using a Waters 510 instrument with THF as the solvent at a flow rate of 1 mL/min. A calibration curve was generated with six polystyrene standards: 2500, 2950, 5050, 20000, 52000, and 96400 Da, of low dispersity purchased from Polyscience. FT-IR spectra were recorded of the polymer films cast from $CHCl_3$ solutions, using a Perkin Elmer 1600 Series FT-IR Spectrometer. ^{1}H-NMR of the products

Scheme 3 Reverse ATRP of styrene with PAE-3000/$CuCl_2$/bpy initiating system



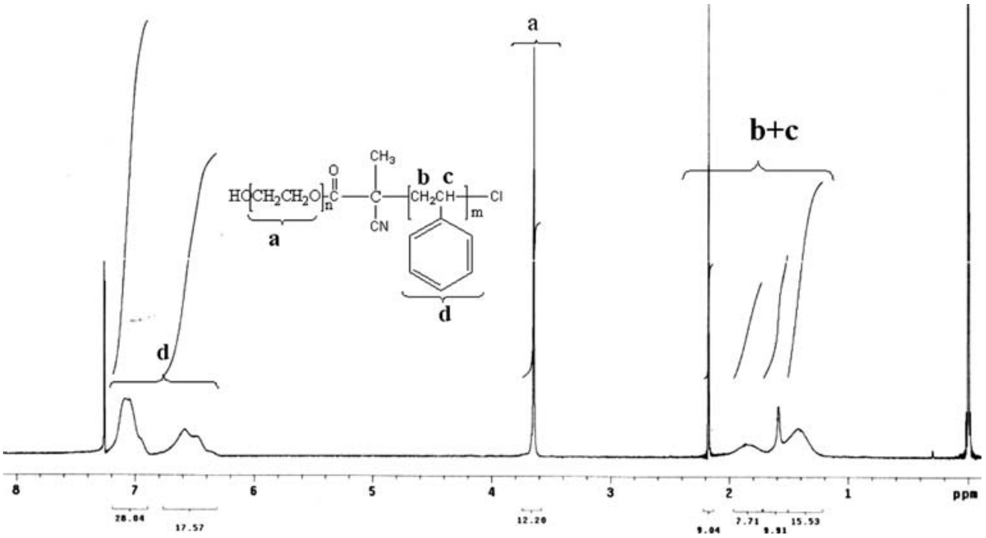


Fig. 3 ^{1}H NMR spectrum of the poly (ethylene glycol-b-styrene) block copolymer

was recorded using a Varian/Mercury-200 NMR Spectrometer, in $CDCl_3$ solvent and tetra methyl silane as the internal standard.

Results and discussion

Synthesis of polyethylene glycol azoester (PAE-3000)

The ^{1}H NMR and FT-IR spectrum of PAE-3000 was shown Figs. 1 and 2, respectively. The polydispersity of the PAE-3000 was observed 1.52. The M_n of the PAE-3000 was 4,480. There was an increase in the molecular weights of the PAE-3000 of the original PEG (M_n is approximately 3000). It may be supposed that chain extension occurred during the end capping reaction since the observed molecular weights of PAE-3000 were greater than the PEG. The reaction pathways may be represented as shown in Scheme 2.

Synthesis of poly(ethylene glycol-b-styrene) block copolymers

Polyazoester prepared by the reaction of ACPC and PEG was used as macroinitiator in the reverse ATRP of S to yield poly(styrene-b-ethylene glycol) block copolymer. The reverse ATRP of S was carried out in bulk using $CuCl_2$/bpy

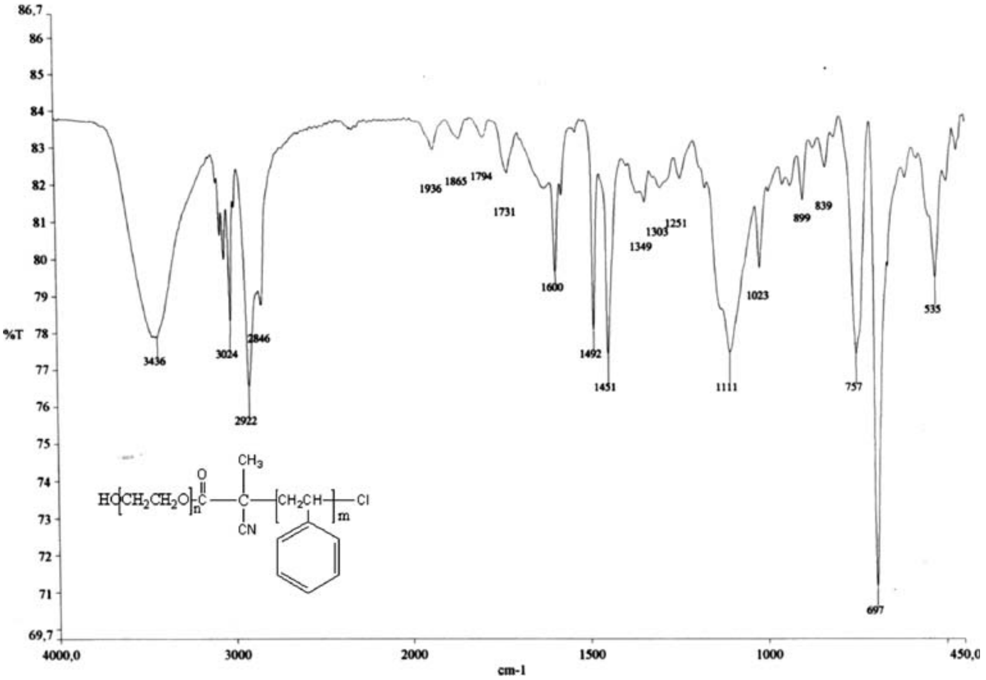


Fig. 4 FT-IR spectrum of the poly (ethylene glycol-b-styrene) block copolymer

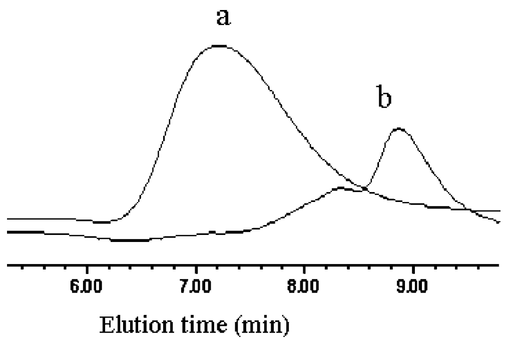


Fig. 5 GPC curves of (**a**) poly (ethylene glycol-b-styrene) block copolymer (code PA-1 in Table 1), M_n=50,398 g/mol and (**b**) polyethylene glycol azoester (PAE-3000), M_n=4480 g/mol

complex as catalyst. The reaction pathways may be represented as shown in Scheme 3.

The polydispersity(PDI) values of the block copolymers lie between 1.49 and 1.98, as shown in Table 1. The PDI ratio of PAE-3000 used as macroinitiator was 1.54. This value also affected the PDIs of the block copolymers. Considering the initial PDI of PAE (M_w/M_n=1.54) block copolymers with reasonably low PDIs may be prepared depending on polymerization conditions. Because it is known that a radical polymerization with termination by coupling makes a polymer with PDI ~ 1.5, and with termination by disproportionation makes a polymer with MWD ~ 2.0, the observed PDI in this polymerization is very normal for a conventional radical polymerization. The molecular weight obtained GPC of block copolymers was higher than the theoretical value. The initiator efficiency of block copolymers was between 0.12 and 0.41, as shown in Table 1. Yan and coworkers [38] reported the reverse ATRP of MMA initiated by AIBN/$FeCl_3$/isophthalic acid, the polymerization was controlled up to a molecular weight of 50,000, and the polydispersity index is 1.4, the observed molecular weight was higher than the theoretical value, which indicates the relatively low initiator efficiency.

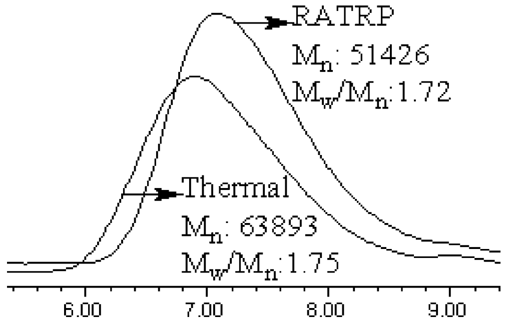


Fig. 6 GPC curves of poly (ethylene glycol-b-styrene) block copolymers prepared via thermal radical polymerization (PAE-3000=9.6× x10^{-5} mol, styrene=1.92×10^{-2} mol) and reverse ATRP(PAE-3000= 9.6×10^{-5} mol, $CuCl_2$=9.6×10^{-5} mol, bpy=1.92×10^{-4} mol, styrene= 1.92×10^{-2} mol) of styrene at 110 °C for 1 h

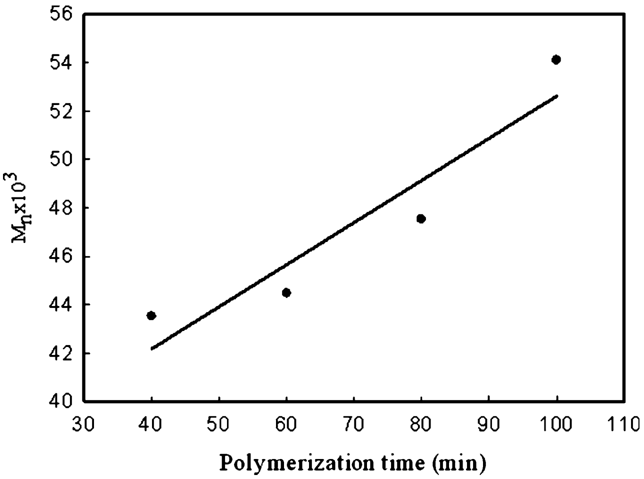


Fig. 7 Dependence of molecular weights of the block copolymers on polymerization time

Based on the assumption that one molecule of PAE-3000 initiator generated two polymer chains, the theoretical molecular weight ($M_{n,cal}$) for reverse ATRP was calculated according to Eq. 1, where $[M]_o$ and $[PAE\text{-}3000]_o$ represent the initial concentrations of monomer (S) and PAE-3000 initiator, $(MW)_o$ is the molecular weight of the monomer, and 4480 is the molecular weight of PAE-3000 initiator.

$$M_{n,cal} = 4480 + \left\{ \left([M]_o / \left(2[PAE - 3000]_o \right) \right) \right\} \times (MW)_o \times \text{conversion} \tag{1}$$

The results of polymerizations conducted in the presence and absence of $CuCl_2$/ligand were also compared as shown in Fig. 6. In the absence of $CuCl_2$/ligand, we obtained a PEG-b-PS block copolymer having M_n=63893 g/mol and M_w/M_n= 1,75 at 110 °C for 1 h. Under the same polymerization conditions, but with $CuCl_2$/ligand present, we observed a slower polymerization rate (M_n=51426 g/mol) and a narrower molecular weight distribution (M_w/M_n=1.72).

A plot of the molecular weight of the block copolymers against the polymerization time is shown in Fig. 7. As can be seen, M_n of the block copolymers increased linearly with the polymerization time, which indicates that this polymerization proceeds via living radical mechanism.

Characterization of the polymers

The characterization of the block copolymer films, which are mostly transparent, can be summarized as follows. There was an increase in the molecular weights of the block copolymers of the original macroinitiator (PAE-3000). Increases in the molecular weights of the products when compared with the macroinitiators confirm block copolymer formation.

The ^{1}H NMR spectrum of PAE-3000 macroinitiator in Fig. 1 showed the characteristic signals at 3.7 ppm for –OCH_2 and –CH_2 protons, at 1.7 ppm for CH_3 protons and 2.2 ppm –OH protons. The IR spectrum of PAE-3000 in Fig. 2 showed characteristic absorptions at 1736 cm^{-1} for the ester carbonyl group, at 1251 cm^{-1} for the C–O stretch, 1900 cm^{-1} for CN groups, 2871 cm^{-1} for –CH_2 bend, 3432 cm^{-1} for –OH groups. The formation of poly(ethylene glycol-b-styrene) block copolymer was also supported by ^{1}H NMR. The ^{1}H NMR spectrum of the block copolymer in Fig. 3 showed 1.4-2.2 ppm region for –CH_2 and –CH protons of styrene, 3.6 ppm for –CH_2 protons attached PEG unit, 6.5–7.1 ppm region for aromatic proton of styrene. The IR spectrum of poly(ethylene glycol-b-styrene) block copolymer in Fig. 4 showed characteristic absorptions at 1731 cm^{-1} due to the ester carbonyl group of the macroinitiator, at 1251 cm^{-1} for the C–O stretch of the PEG chain, 3436 cm^{-1} for –OH groups of the PEG chain, 1936 cm^{-1} for –CN groups of the macroinitiator, 2922 cm^{-1} for –CH_2 groups of PEG and styrene chains, 3024 cm^{-1} for aromatic –CH groups of styrene chains. Block copolymer formation was also demonstrated by gel permeation chromatography (GPC). The chromatograms recorded with initial PAE-3000 and block copolymer as shown in Figs. 5 and 6. The chromatograms indicate a unimodal molecular weight distribution in both cases and an increase in the molecular weight as a result of block copolymerization (Fig. 7).

Conclusions

A reverse ATRP was performed with a new initiating system, PAE-3000/Cu(II)/bpy, for the living/controlled radical polymerization of S at 110 °C to yield well-defined PEG-b-PS with a high molecular weight and a narrow polydispersity. The M_n values of the polymers increased with increasing monomer conversion, and the polydispersity decreased with conversion in agreement with the ATRP process. Although these results are preliminary depends on chosen ligand, they clearly demonstrate how a bifunctional polymeric free radical initiator can be used to produce PEG-b-PS block copolymers of styrene which is susceptible to reverse ATRP.

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