Atom Transfer Radical Polymerization of Styrene with 2-(1-Bromoethyl)-Anthraquinone as an Initiator

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ABSTRACT: 2-(1-Bromoethyl)-anthraquinone (BEAQ) was successfully used as an initiator in the atom transfer radical polymerization of styrene with $CuBr/N,N,N',N',N''$-pentamethyldiethylenetriamine as the catalyst at $110°C$. The polymerizations were well controlled with a linear increase in the molecular weights (M_n's) of the polymers with monomer conversion and relatively low polydispersities ($1.1 <$ weight-average molecular weight $(M_w)/M_n < 1.5$) throughout the polymerizations. The resultant polystyrene thus possessed one chromophore moiety (2-ethyl-anthraquinone) at the α end and one bromine atom at the ω end, both from the initiator BEAQ. The intensity of UV absorptions of the resultant polymers decreased with increasing molecular weights of the polymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2081–2085, 2006

Key words: atom transfer radical polymerization (ATRP); polystyrene; initiators

INTRODUCTION

Atom transfer radical polymerization (ATRP) has developed rapidly since it was first proposed in 1995.[1–5] In ATRP, initiator functionality has attracted much attention due to its potential use as a functional material. A number of functional initiators were used for the ATRP of various monomers, such as styrene (St) and methyl methacrylate.[6–14] For example, Ohno et al.[9] synthesized well-defined anthracene-labeled polystyrenes (PSt's) via ATRP with 9,10-bis(1-bromoethylcarbalkoxymethyl)anthracene as the bifunctional initiator and $CuBr/4,4'$-di(n-heptyl)-2,2'-bipyridine as the catalyst with an initiation efficiency of 100%.

Anthraquinone-containing polymers have attracted researchers' interest in their photochemical and photoinitiation activities. Catalina et al.[15] synthesized novel water-soluble anthraquinone copolymers through the copolymerization of 2-acryloxy and 2-acrylamido anthraquinone monomers. The absorption, phosphorescene, photoreduction, and microsecond flash photolysis characteristics of these copolymers were examined. The photointroduced polymerization activities of these copolymers were also evaluated.[15] Meng et al.[16] prepared two polymeric dyes containing the anthraquinone structure via solution polycondensation. The polymeric dyes were applied to the mass coloration of poly(ethylene terephthalate) with good compatibility. In addition, side-chain liquid-crystalline polymers containing anthraquinone dye monomer have been reported.[17,18]

This article reports the synthesis of well-defined 2-ethylanthraquinone end-capped PSt via ATRP with 2-(1-bromoethyl)-anthraquinone (BEAQ) as an initiator and $CuBr/N,N,N',N',N''$-pentamethyldiethylenetriamine (PMDETA) as the catalyst. The aim of this study was to create a precise molecular environment for anthraquinone molecules.

EXPERIMENTAL

Materials

St (99%; Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was washed twice with an aqueous solution of sodium hydroxide (5%) and twice with deionized water, dried with anhydrous sodium sulfate overnight, and finally, distilled *in vacuo*. The distillates were stored at $-18°C$ before use. PMDETA (98%; Jiangsu Liyang Jiangdian Chemical Factory, Liyang, China) was dried with a 4-Å molecular sieve and distilled *in vacuo*. CuBr (98%; Aldrich, Milwaukee, WI,

Scheme 1

USA) was stirred with acetic acid for 12 h, washed with ethanol and diethyl ether, and then dried *in vacuo*. BEAQ was synthesized according to ref. 19. Tetrahydrofuran (THF; analytical reagent grade, Shanghai Chemical Reagent Co., Ltd.) was used without further purification. All other chemicals were used as received.

Polymerization

A typical ATRP procedure was carried out as follows: a dry tube was quantitatively filled with CuBr, PMDETA, BEAQ, and St in sequence. After the reaction mixture was bubbled with nitrogen, the tube was sealed under nitrogen and then immersed in a thermostated oil bath
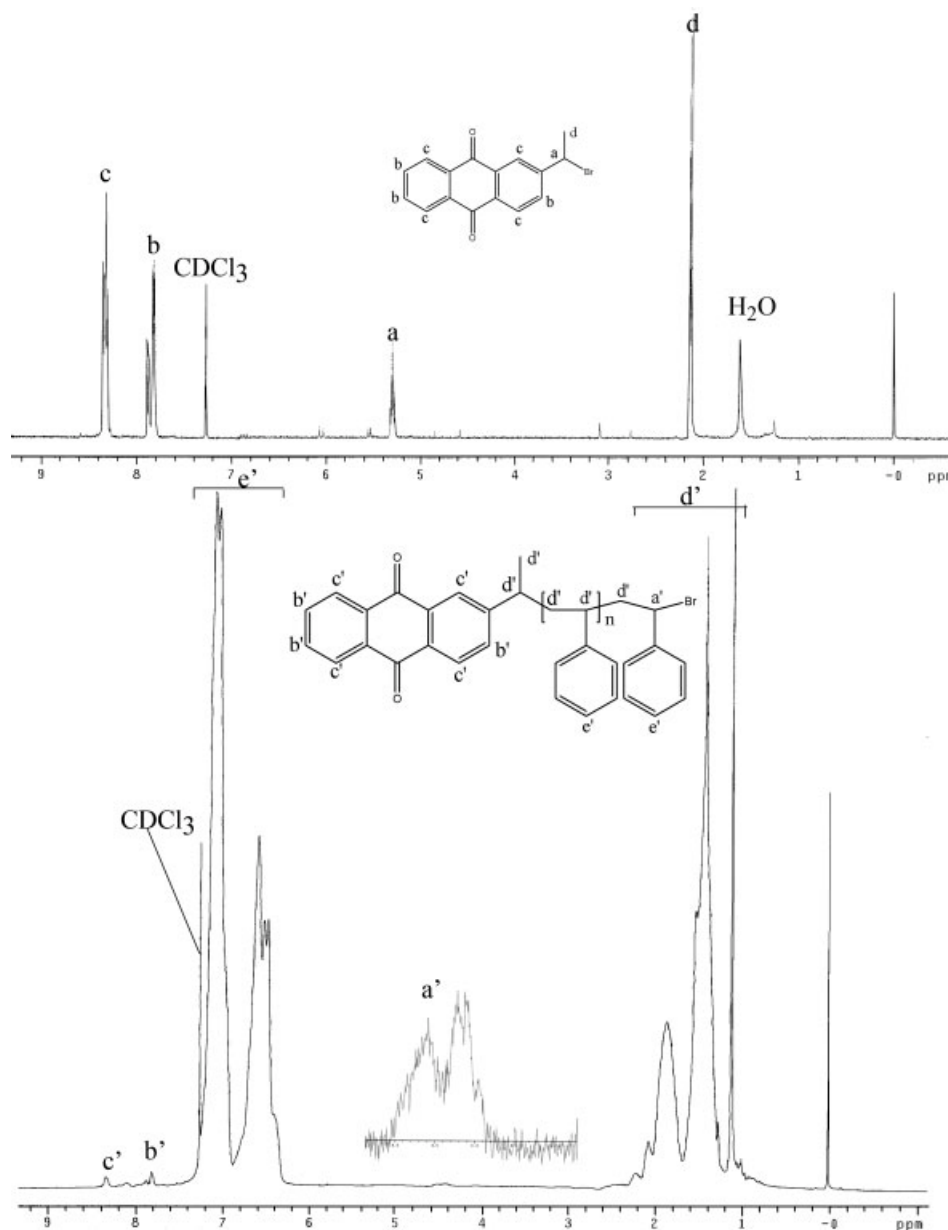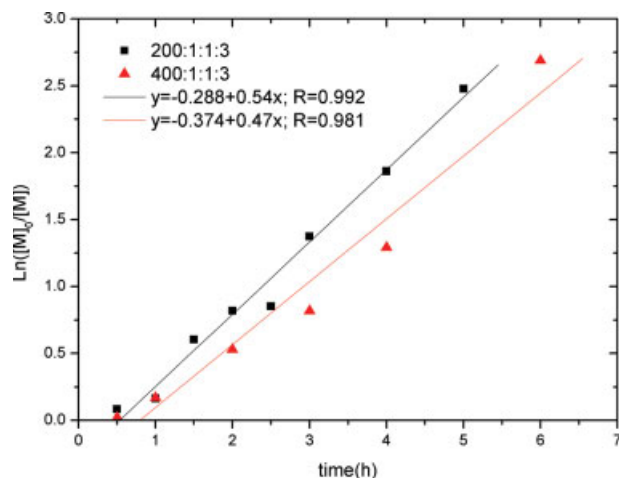

Figure 1 ^{1}H-NMR spectra of (a) BEAQ and (b) PSt in CDCl$_3$.

Figure 2 First-order kinetic plots for the bulk polymerization of St at 110°C. $[St]_0/[BEAQ]_0/[CuBr]_0/[PMDETA]_0$ = (■) 200 : 1 : 1 : 3 and (▲) 400 : 1 : 1 : 3. ($[St]_0$, $[BEAQ]_0$, $[CuBr]_0$ and $[PMDETA]_0$ represent, respectively, initial molar concentrations of St, BEAQ, CuBr and PMDETA.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
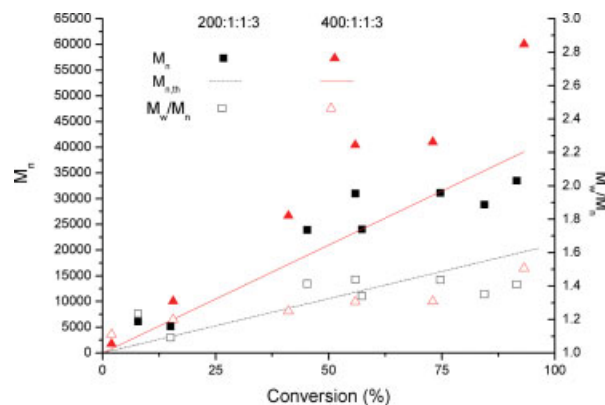
at 110°C. We stopped the polymerizations at a desired time by cooling the tubes with cold water. Afterwards, the tube was opened, and the contents were diluted with THF. Then the solution was poured into a large amount of methanol/HCl (volume ratio = 100 : 5) mixture. The polymers were filtered and dried *in vacuo*.

Characterizations

The conversion of the monomer was determined by gravimetry. The molecular weights and molecular weight distributions of the polymers were determined on a Waters (Palo Alto, CA, USA) 1515 gel permeation chromatograph equipped with a refractive-index detector and HR 1, HR 3, and HR 4 columns with a molecular weight range of 100–500,000 calibrated with PSt standard samples. THF was used as the eluent at a flow rate of 1.0 mL/min at 30°C. ^{1}H-NMR spectra were recorded on an INOVA (Milford, MA, USA) 400-MHz spectrometer at ambient temperature with CDCl$_3$ as the solvent and tetramethylsilane as the internal standard. Ultraviolet–visible (UV–vis) absorption spectra of the polymers and initiator in chloroform solutions were performed on a Shimadzu (Kyoto, Japan) UV-240 UV–vis recording spectrophotometer at ambient temperature.

RESULTS AND DISCUSSION

The new 2-ethylanthraquinone-containing initiator, BEAQ (Scheme 1), was used in the bulk polymerization of St. The polymerization was carried out at 110°C via ATRP with CuBr/PMDETA as the catalyst (Scheme 1). According to the mechanism of ATRP,
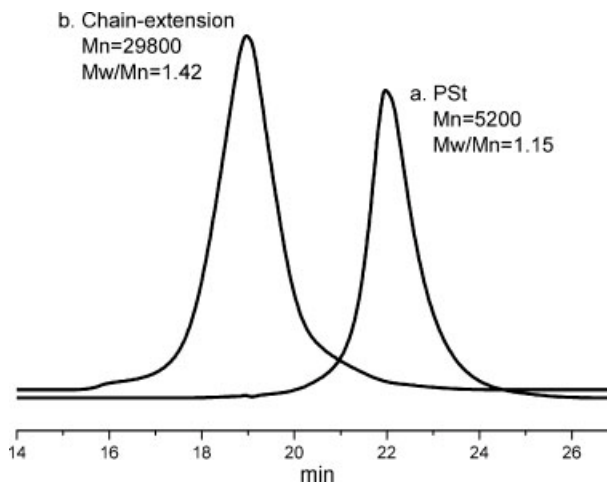
the resultant polymers (PSt's) should have been covalently attached the chromophore (2-ethylanthraquinone) at the α end of the polymer chains.

Figure 1 shows the ^{1}H-NMR spectra of BEAQ [Fig. 1(a)] and resultant polymer [Fig. 1(b)] in CDCl$_3$. The typical proton signals (7.8–8.4 ppm)[20] of the BEAQ are shown in Figure 1(a). These signals were also seen in the resultant polymers [Fig. 1(b)], which indicates that the 2-ethylanthraquinone moiety in BEAQ was successfully attached to the polymer. Furthermore, the signals at 4.4–4.6 ppm were assigned to the protons of —CH— groups in PSt adjacent to bromine in the chain end. These results confirm that the PSt chains were functionalized by the 2-ethylanthraquinone chromophore and bromine at the polymer chain end.

The kinetic plots of the polymerization of St with BEAQ as the initiator and CuBr/PMDETA as the cata-

Figure 3 Dependence of M_n and M_w/M_n on the conversion for the ATRP of St at 110°C. $[St]_0/[BEAQ]_0/[CuBr]_0/[PMDETA]_0$ = (■) 200 : 1 : 1 : 3 and (▲) 400 : 1 : 1 : 3. ($[St]_0$, $[BEAQ]_0$, $[CuBr]_0$ and $[PMDETA]_0$ represent, respectively, initial molar concentrations of St, BEAQ, CuBr and PMDETA.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]


Figure 4 GPC curves of PSt (a) before chain extension and (b) after chain extension. $[St]_0 : [Macroinitiator]_0 : [CuBr]_0 : [PMDETA]_0 = 400 : 1 : 1 : 3$; temperature = 110°C.
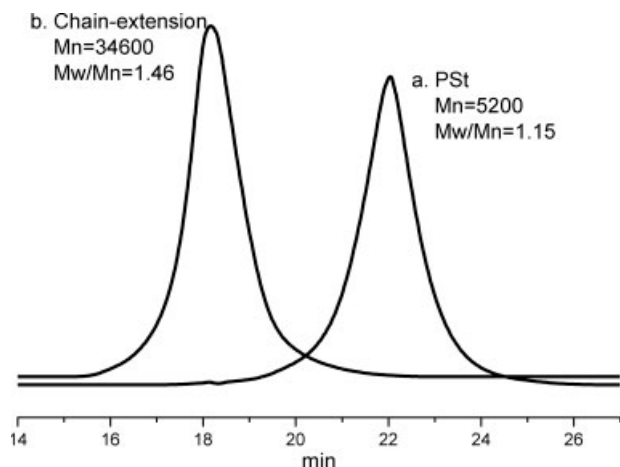
Figure 5 GPC curves of (a) PSt before chain extension and (b) PSt-*b*-PMMA after chain extension. [MMA]$_0$: [Macroinitiator]$_0$: [CuBr]$_0$: [PMDETA]$_0$ = 400 : 1 : 1 : 3. ([MMA]$_0$, [Macroinitiator]$_0$, [CuBr]$_0$ and [PMDETA]$_0$ represent, respectively, initial molar concentrations of MMA, PSt macroinitiator, CuBr and PMDETA.) temperature = 110°C.

lyst with two different monomer-to-initiator molar ratios at 110°C are shown in Figure 2. The linearity of the semilogarithmic plot of ln([M]$_0$/[M]) versus time for the both ratios indicated that the polymerizations were first-order kinetics with respect to the monomer, and the concentration of the growing radicals remained constant throughout the polymerizations. However, induction periods were observed at both monomer-to-initiator molar ratios. This may be explained by the slow establishment of the equilibrium between active and dormant species. This also may have resulted from impurities in the reaction systems.

Figure 3 shows that the number-average molecular weights (M_n's) of the polymers increased linearly with monomer conversion; however, they were higher than the corresponding number-average molecular weight theoretical values ($M_{n,\text{th}}$ = Conversion × M_{St} × [St]$_0$/
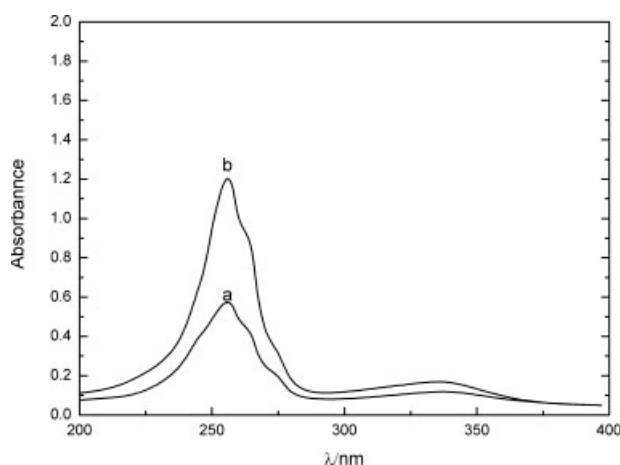
Figure 6 UV–vis spectra of (a) BEAQ and (b) 2-ethylanthraquinone end-capped PSt in chloroform.

TABLE I
UV Absorption of Anthraquinone End-Capped PSt

Polymer	M_n (GPC)	Concentration (mg/mL)	Absorbance ($\lambda = 327$ nm)
I	5,200	0.80	0.990
II	23,000	0.80	0.412
III	33,500	0.80	0.366

[Initiator]$_0$ + MW$_{\text{initiator}}$, where [St]$_0$, [Initiator]$_0$, M_{St}, and MW$_{\text{initiator}}$ are the initial concentrations of St and initiator and the molecular weights of St and initiator, respectively), which may indicate inefficient initiation of BEAQ. The narrow molecular weight distribution [1.1 < weight-average molecular weight (M_w)/M_n < 1.5] of the polymers is also shown in Figure 3.

According to the mechanism of ATRP, if the end of the polymer chain has a halogen atom, it can be used as a macroinitiator to initiate the polymerization of a fresh feed of monomer in the presence of an ATRP catalyst, such as CuBr/PMDETA. Figure 4 shows the gel permeation chromatography (GPC) curves of the polymers before chain extension [Fig. 4(a)] and after chain extension [Fig. 4(b)]. M_n of PSt increased to 29,800 from 5200 after the chain extension reaction. However, the molecular weight distribution of the final polymer (M_w/M_n = 1.42) was broader than that of the PSt macroinitiator (M_w/M_n = 1.15), which may have been due to both the side reaction in the period of chain propagation and the dead polymer chains existing in the macroinitiator. Furthermore, the macroinitiator (PSt) was also used to initiate the polymerization of a fresh feed of methyl methacrylate under the same conditions. The GPC curves of the PSt macroinitiator and the final polymer, polystyrene-block-poly(methyl methacrylate) (PSt-*b*-PMMA), obtained after the chain extension reaction are shown in Figure 5. These results thus demonstrate the presence of a bromine atom at the ω end of the PSt chain. All of these results indicate that ATRP of St initiated by BEAQ was a well-controlled or living polymerization.

The UV–vis spectra of BEAQ and the obtained polymer are shown in Figure 6. The UV–vis spectrum of the 2-ethylanthraquinone end-capped PSt was identical to that of BEAQ in shape. The UV absorptions of 2-ethylanthraquinone end-capped PSt's with different M_n values in chloroform are shown in Table I. The intensity of the UV absorptions of the resultant polymers decreased with increasing M_n values of the polymers. These results further confirm that 2-ethylanthraquinone units were definitely covalently attached to the polymers.

CONCLUSIONS

BEAQ was used as an initiator for ATRP of St, and well-defined 2-ethylanthraquinone end-capped poly-

mers were obtained. The polymerizations were well controlled with a linear increase in the molecular weights of polymers with monomer conversions and relatively low polydispersities ($1.1 < M_w/M_n < 1.5$) throughout the polymerizations.

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