

Synthesis of a well-defined anthracene-labelled polystyrene by atom-transfer radical polymerization

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Abstract

The atom-transfer radical polymerization of styrene was carried out in bulk at 110°C with a newly synthesized bromine-containing anthracene derivative, 9,10-bis(1-bromoethylcarbalkoxymethyl)anthracene (ANTDBr), as a bifunctional initiator and a cuprous bromide complex Cu(I)Br/2dHbipy (dHbipy = 4,4'-di-*n*-heptyl-2,2'-bipyridine). g.p.c. and n.m.r. studies revealed that the initiation efficiency of ANTDBr is 100% and the polymerization proceeds in a controlled fashion, providing low-polydispersity polystyrenes with one anthracene chromophore in the middle of the main chain. This success opens up a new route to well-defined anthracene-labelled polymers including random and/or block copolymers, which will be useful as probe polymers to study, e.g., local chain dynamics by the fluorescence depolarization technique. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Anthracene-labelled polystyrene; Atom-transfer radical polymerization; Bifunctional initiator

1. Introduction

Because of its high sensitivity the fluorescence depolarization technique has frequently been used for qualitative and quantitative studies of molecular motion and segmental orientation in polymer systems. For this purpose, a fluorescent probe must be introduced into a polymer chain without perturbing the mobility of the polymer chain. Valeur et al. [1] and Sasaki et al. [2] independently synthesized narrow-polydispersity polymers labelled with an anthracene chromophore in the middle of the main chain by living anionic polymerization and studied local chain motions of the polymers. This kind of anthracene-labelled polymer has unique advantages—anthracene is relatively small in size so that the steric hindrance might be small. Another advantage is its definite (uniaxial) transition moment along the main chain when the anthracene molecule is bonded at its 9- and 10-positions. This is very important for sensitive measurements of local chain motions and segmental orientations. Living anionic polymerization, however, requires involved procedures, and not many kinds of polymer have been synthesized by this method for the present purpose.

We here have adopted an alternative approach of controlled/‘living’ radical polymerization to simply incorporate an anthracene chromophore in the middle of a well-defined

polymer chain. This novel polymerization method has attracted much attention as a new and robust synthetic route to well-defined, low-polydispersity polymers including random and/or block copolymers with controlled architecture [3–7]. The atom-transfer radical polymerization (ATRP) technique reported by Matyjaszewski et al. is one of the most powerful methods in this polymerization category. It is applicable to various monomers such as styrenics, (meth)acrylates and acrylonitrile [8,9]. Cho recently carried out the ATRP of methyl methacrylate using 9,10-bis(chloromethyl or bromomethyl)anthracene as a bifunctional initiator with limited success [10]; the benzyl radical resulting from this initiator may be unstable, which probably explains the observed low efficiency of initiation (about 15–20%). In this work, we have designed a novel anthracene-containing bifunctional initiator with high initiation efficiency and succeeded in synthesizing well-defined polystyrenes with an anthracene chromophore in the middle of the main chain.

2. Experimental

2.1. Materials

Commercially obtained styrene (Wako Pure Chemicals,

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Japan) was purified by vacuum distillation over CaH_2 . Cu(I)Br (99.999%, Aldrich Chem. Co.) was used as received. 4,4'-Di-*n*-heptyl-bipyridine (dHbipy) was prepared by the dilithiation of 4,4'-dimethyl-2,2'-bipyridine followed by coupling with *n*-hexyl bromide as described elsewhere [8,9]. 2-Bromopropionyl bromide was obtained from Nacalai Tesque, Japan. 9,10-Bis(hydroxymethyl)anthracene was prepared by the procedure of Nakaya et al. [11]. Unless otherwise specified, other reagents were purchased from commercial sources and used as received.

2.2. Preparation of 9,10-bis(1-bromoethylcarbalkoxymethyl)anthracene (ANTDBr)

To a cold suspension of 9,10-bis(hydroxymethyl)anthracene (400 mg, 1.68 mmol) in dry *N,N*-dimethylformamide (30 mL) with triethylamine (510 mg, 5.04 mmol), 2-bromopropionyl bromide (1.09 g, 5.04 mmol) was added dropwise at 0°C. The mixture was magnetically stirred for 1 h at 0°C and then for another 2 h at room temperature. The clear solution obtained was mixed with cold water (20 mL) and extracted with chloroform (3×30 mL). The combined extracts were dried over anhydrous sodium sulfate. After the solvent was evacuated off, the crude product was purified by flash silica gel chromatography with chloroform as eluent to yield a slightly yellow solid. Yield: 75% (640 mg). ^1H n.m.r. (CDCl_3 , δ , ppm): 1.80 (d, 6H, 2CBrCH_3), 4.37 (q, 2H, 2CHBr), 6.25 (q, 4H, $2\text{CH}_2\text{OOC}$), 7.63 (m, 4H, aromatic H), 8.39 (m, 4H, aromatic H).

$\text{C}_{22}\text{H}_{20}\text{O}_4\text{Br}_2$ (508.22)	Calc.:	C 51.99	H 3.97
	Found:	C 52.01	H 3.87

The structure of ANTDBr is given in Fig. 1a.

2.3. General procedure for the ATRP of styrene using ANTDBr

A glass tube was charged with a predetermined amount of a mixture of Cu(I)Br and dHbipy, to which styrene containing a prescribed concentration of ANTDBr was quickly added. The mixture was immediately degassed by three freeze–thaw cycles, sealed under vacuum, and finally placed in an oil bath thermostatted at 110°C. After a prescribed time the tube was quenched to room temperature and opened. Part of the sample solution was studied by gel permeation chromatography (g.p.c.) after appropriate dilution with tetrahydrofuran (THF). The monomer conversion was estimated by comparing the g.p.c. peak area of the produced polymer with that of a standard polystyrene dissolved in THF at a known concentration.

The remaining sample solution was diluted with chloroform and poured into methanol. The precipitate was purified by reprecipitation with a chloroform (solvent)–methanol (non-solvent) system and dried in vacuo to yield a polymer as a white powder.

2.4. Measurements

g.p.c. analysis was performed on a Tosoh GPC-8020 high-speed liquid chromatograph equipped with a Tosoh differential refractometer RI-8020. The column system, which consisted of Tosoh gel columns G2500H, G3000H, and G4000H, was calibrated with standard polystyrenes. THF was used as an eluent and temperature was maintained at 40°C. Proton-nuclear magnetic resonance (^1H n.m.r.) spectra were obtained on a JEOL JNM/AL400 400 MHz spectrometer. Absorption and fluorescence emission spectra were obtained on a Shimadzu UV2200A u.v.–visible

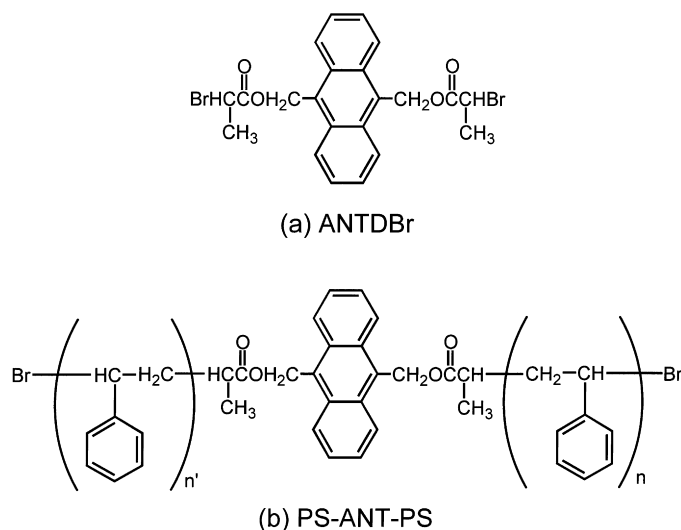


Fig. 1. Chemical structures of (a) ANTDBr and (b) PS-ANT-PS.

spectrophotometer and a Perkin–Elmer LS50B fluorescence spectrophotometer, respectively.

3. Results and discussion

The ATRP of styrene was carried out using ANTDBr as a bifunctional initiator. Fig. 2 shows g.p.c. curves of the polymers obtained. It can be seen that the molecular weight increases with increasing polymerization time, keeping with M_w/M_n ratio remarkably small. Fig. 3 shows the plot of $\ln([M]_0/[M])$ against polymerization time t , where $[M]$ represents the monomer concentration and the subscript zero denotes the initial state ($t = 0$). A linear relationship was obtained, indicating that the radical concentration stays constant throughout the course of the polymerization. Fig. 4 shows the number-average molecular weight M_n and polydispersity index M_w/M_n of the produced polymers as a function of conversion. The M_n linearly increases with conversion, and more importantly, the values of M_n agree well with those calculated from the conversion/ $[\text{ANTDBr}]_0$ ratio (solid line in the figure). Fig. 4 also shows that the M_w/M_n ratio stays around 1.1 at all conversions. Together with the straight kinetic plot in Fig. 3, these results confirm that the polymerization proceeds in a ‘living’ fashion with negligible contribution from transfer and termination reactions.

The good agreement between the measured and calculated M_n values shown in Fig. 4 means that each initiator added to the solution generates at least one growing end but not necessarily two. To evaluate the initiation efficiency, the

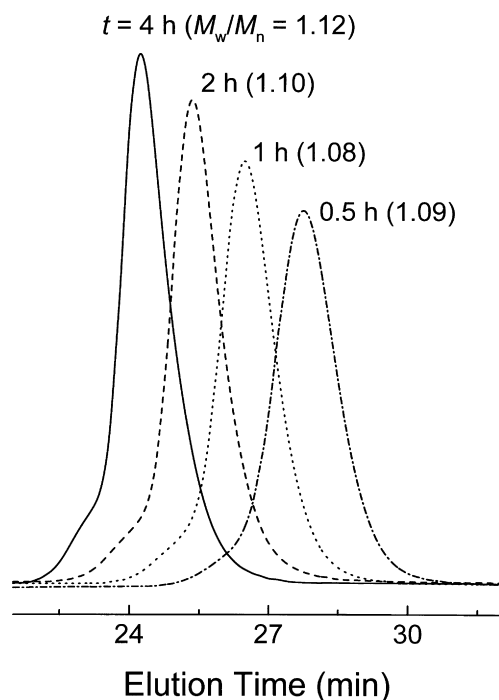


Fig. 2. g.p.c. curves of the polymers obtained by the ANTDBr-initiated polymerization of styrene in bulk at 110°C: $[\text{styrene}]_0 = 8.0 \text{ M}$; $[\text{ANTDBr}]_0 = 0.04 \text{ M}$; $[\text{Cu(I)Br}]_0 = [\text{dHbipy}]_0/2 = 0.08 \text{ M}$.

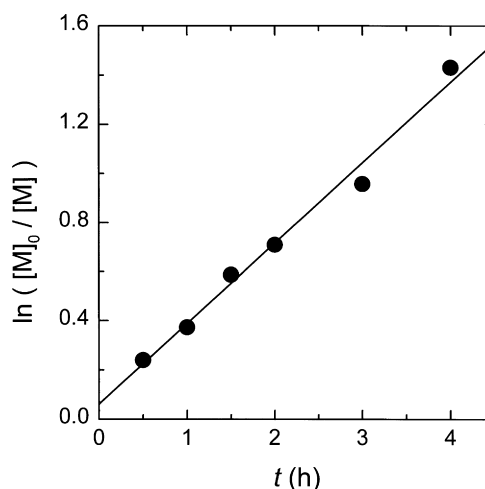


Fig. 3. Time–conversion plot for the polymerization of styrene in bulk at 110°C: $[\text{styrene}]_0 = 8.0 \text{ M}$; $[\text{ANTDBr}]_0 = 0.04 \text{ M}$; $[\text{Cu(I)Br}]_0 = [\text{dHbipy}]_0/2 = 0.08 \text{ M}$.

^1H n.m.r. spectrum of the purified polymer with a relatively low molecular weight was recorded. Fig. 5 represents the 400 MHz ^1H n.m.r. spectrum of the polymer ($M_n \cong 2700$) compared with that of ANTDBr in part. The possible assignments of peaks are shown in the figure. The peaks assignable to the methylene, methyne, and methyl protons (k, l, and m, respectively) of ANTDBr are shifted when the bromine atom is replaced with a polystyrene chain. In the spectrum of the polymer sample, no signal was observed at around 6.2 ppm which corresponds to the methylene proton of ANTDBr, and the integral areas of the isolated peaks d, e, and j relative to those of the anthracene ring protons a and b were found to be very close to the values calculated for the

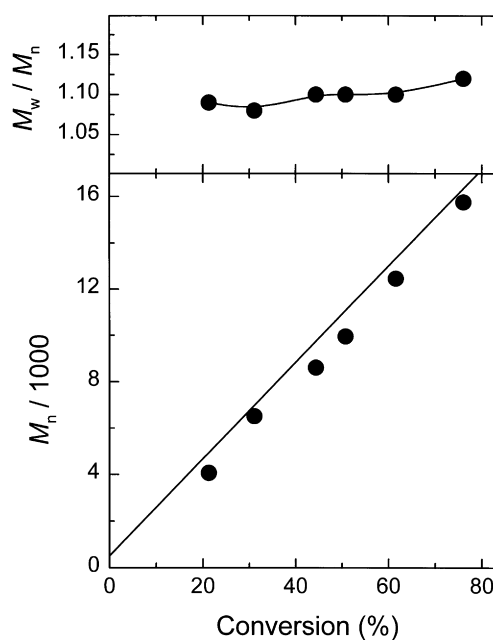


Fig. 4. Values of M_n and M_w/M_n as a function of monomer conversion; bulk polymerization at 110°C: $[\text{styrene}]_0 = 8.0 \text{ M}$; $[\text{ANTDBr}]_0 = 0.04 \text{ M}$; $[\text{Cu(I)Br}]_0 = [\text{dHbipy}]_0/2 = 0.08 \text{ M}$.

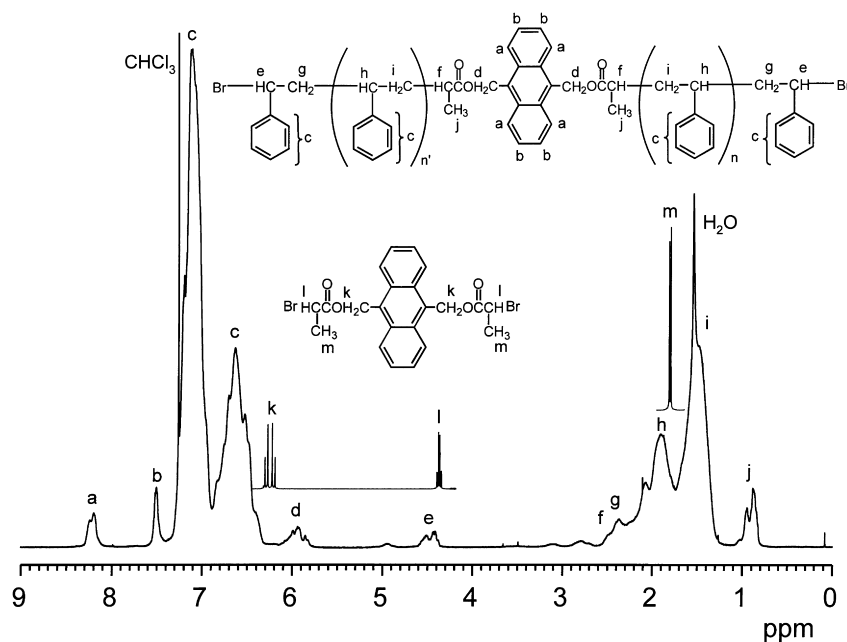


Fig. 5. Typical ^1H NMR spectrum of PS-ANT-PS. The solvent was CDCl_3 .

desired structure shown in the figure. This means that no detectable fraction of the 1-bromoethyl carbalkoxymethyl group remains unreacted and virtually all the polymer chains have a bromine atom at both ends. These results lead to the conclusion that ANTDBr generates two growing ends per chain ($\sim 100\%$ initiation efficiency), giving a narrow-polydispersity polystyrene with the anthracene chromophore (PS-ANT-PS, see Fig. 1b). The high initiation efficiency and the high degree of chain-end functionality confirm that the anthracene chromophore is located in the middle of the chain.

Fig. 6 shows the absorption and fluorescence emission spectra of PS-ANT-PS dissolved in THF at room temperature. Both spectra show the vibrational structures

characteristic of the anthracene chromophore. These spectra were independent of the molecular weight. These suggest that the decomposition of the anthracene chromophores did not occur to any detectable degree under the present polymerization conditions.

4. Conclusion

The ATRP of styrene in bulk at 110°C using ANTDBr as a bifunctional initiator proceeds in a 'living' fashion, giving low-polydispersity polystyrenes with one anthracene chromophore in the middle of the polymer chain. The ANTDBr is clearly superior to other anthracene-containing

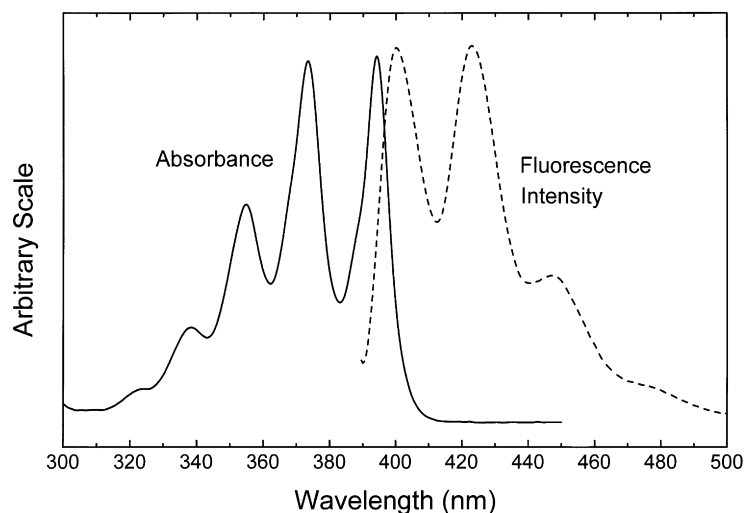


Fig. 6. Absorption and fluorescence emission spectra of PS-ANT-PS dissolved in THF at room temperature. The excitation wavelength was 395 nm.

bifunctional initiator such as 9,10-bis(chloromethyl or bromomethyl)anthracene in that the initiation efficiency of the ANTDBr is virtually 100%. Thus this work has broadened the practical synthetic route to well-defined polymers with the anthracene chromophore. Moreover, this system can be extended to the polymerization of other vinyl monomers to which ATRP is applicable, and more interestingly to the synthesis of chromophore-labelled block and random copolymers. These polymers will be particularly useful in the study of, e.g., local chain dynamics and polymer orientation and miscibility, which will be the topics of forthcoming publications [12].

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