ELSEVIER

Polymer 42 (2001) 8489–8493

polymer

www.elsevier.nl/locate/polymer

Polymer Communication

Synthesis of asymmetric difunctional initiators and their use in the preparation of block copolymers via ATRP and SFRP

U. Tunca, B. Karlıga, S. Ertekin, A.L. Ugur, O. Sirkecioglu, G. Hizal*

Department of Chemistry, Istanbul Technical University, Maslak 80626, Istanbul, Turkey

Received 8 January 2001; received in revised form 19 March 2001; accepted 22 March 2001

Abstract

Novel asymmetric difunctional initiators 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo-2-methyl propanoate and of 2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]ethyl 2-bromo propanoate were synthesized in a three-step reaction sequence and used in atom transfer radical polymerization (ATRP) of methyl methacrylate or *tert*-butyl acrylate leading to corresponding polymer with tempo moiety as chain end. These polymers were found to be efficient initiators for stable free radical polymerization (SFRP) of styrene. ^{1}H NMR and g.p.c. studies of the obtained polymers show that block copolymers are readily formed as a result of combination of ATRP and SFRP mechanisms.
© 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Asymmetric difunctional initiators; Atom transfer radical polymerization; Stable free radical polymerization

1. Introduction

During the last decade, various methods have been proposed and used for the synthesis of well defined block copolymers [1]. These methods include (a) the sequential living polymerization of monomer units (b) coupling of preformed living chain ends (c) the transformation approach, in which the first monomer is polymerized to produce a polymer with a functional group that is capable of initiating polymerization of another monomer by a different mechanism. However, the transformation route may be somewhat less convenient if any intermediate protection or further functionalisation is required.

Recently, the controlled/'living' radical polymerizations such as copper catalyst mediated atom transfer radical polymerization (ATRP) and stable free radical polymerization (SFRP) have been utilized for the synthesis of well defined, narrow polydispersity polymers [2–8]. These polymerizations involve the reversible activation and deactivation of growing radicals. During this process, a very low instantaneous concentration of propagating radicals is produced. Therefore, the low radical concentration suppresses termination reactions and leads to the formation of polymer with narrow polydispersity. One of the advantages of controlled radical polymerizations such as SFRP or ATRP is that the molecular weight and chain end functionality can be controlled. A wide range of functionality can be introduced into a polymer chain end by using an asymmetric difunctional initiator if one of the functional groups remains intact during the polymerization. This has enabled the synthesis of well defined block copolymers by a sequential two-step method or one-pot method without any transformation or protection of initiating sites. In this context, several papers have reported by using ATRP-living ring opening polymerization (ROP) [9,10], and SFRP–ROP [11–13]. In this study, emphasis is placed on the synthesis of asymmetric difunctional initiators and their use as initiators of the controlled block polymerizations of *tert*-butyl acrylate, methyl methacrylate (MMA) and styrene monomers.

2. Experimental

2.1. Materials

MMA (99% Aldrich), *tert*-butyl acrylate (tBA, 99% Aldrich), and styrene (St, 99% Aldrich) were passed through basic alumina column to remove inhibitors and then dried over CaH_2 and distilled under reduced pressure prior to use. Tetrahydrofuran (THF) (99.8%, J.T. Baker hplc grade) was dried and distilled over lithium aluminium hydride. All other reagents were purchased from Aldrich and used as received.

2-phenyl-2-[(2,2,6,6-tetramethylpiperidino)oxy]-1-ethanol (**1**) was synthesized according to the procedure of Hawker

* Corresponding author.
E-mail address: hizal@itu.edu.tr (G. Hizal).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00235-X

et al. [14] (92%). ^{1}H NMR ($CDCl_3$) δ 1.15–1.58 (m,18H), 3.72 (dd, $J = 2.5$ and 12 Hz, 1H, CH_2), 4.22 (dd, $J = 9.5$ and 12 Hz, 1H, CH_2), 5.31 (dd, $J = 2.5$ and 9.5 Hz, 1H, CH), 5.89 (br s, OH), 7.29–7.36 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 17.25, 20.66, 25.64, 32.20, 34.21, 39.99, 40.52, 61.03, 67.93, 69.18, 84.23, 126.96, 127.83, 128.31, 139.10.

2.2. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethyl-piperidino)oxy]ethyl 2-bromo propanoate (**2a**)

To a round bottom flask were added **1** (0.85 g, 3.06 mmol), Et_3N (0.7 ml, 5 mmol), and 20 ml of dry THF. To the reaction mixture, stirred at 0°C under nitrogen, was added dropwise 2-bromo propanoyl bromide (0.53 ml, 5 mmol) in 20 ml of dry THF over a period of 1 h. The reaction mixture was stirred at room temperature overnight. The salt was removed by filtration and after THF evaporation, the crude product was dissolved in CH_2Cl_2 and washed successively with dilute Na_2CO_3 aqueous solution and dried over anhydrous Na_2SO_4. CH_2Cl_2 was removed and the crude ester was purified by preparative TLC (8:2 hexane/ethyl acetate) to give **2a** as a pale yellow oil (0.52 g, 41%). ^{1}H NMR ($CDCl_3$) δ 0.72–1.60 (m, 18H), 1.68 (d, $J = 6.9$ Hz, 3H, CH–CH_3), 4.25 (q, $J = 6.9$ Hz, 1H, CH–CH_3), 4.41 (m, 1H, CHH), 4.64 (m, 1H, CHH), 4.95 (m, 1H, CH), 7.28–7.32 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 17.20, 20.45, 21.66, 22.14, 34.06, 39.96, 40.09, 40.55, 60.19, 67.48, 83.72, 127.75, 128.06, 128.28, 129.61, 132.76, 140.20, 169.83.

2.3. Synthesis of 2-phenyl-2-[(2,2,6,6-tetramethyl-piperidino)oxy]ethyl 2-bromo-2-methyl propanoate (**2b**).

This was prepared from **1** using the same procedure given for **2a**. The crude ester was purified by preparative TLC (9:1 hexane/ethyl acetate) to give a pale yellow oil (45%). ^{1}H NMR ($CDCl_3$) δ 0.75–1.60 (m, 18H), 1.77 (s, 6H, CH_3), 4.44 (m, 1H, CHH), 4.60 (m, 1H, CHH), 4.96 (m, 1H, CH), 7.28–7.34 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$) δ 17.22, 20.48, 22.17, 29.20, 33.98, 55.80, 59.88, 66.85, 83.40, 127.83, 127.92, 128.05, 132.80, 140.25, 170.27.

2.4. Synthesis of macroinitiators

The general procedure for ATRP was as follows: to a Schlenk tube equipped with magnetic stirring bar ligand, catalyst, the degassed monomer, solvent, and initiator were added in the order mentioned. Tube was degassed by three freeze–pump–thaw cycles, left under vacuum and placed in a thermostated oil bath at given temperature. After the polymerization, the reaction mixture was diluted with THF and then passed through a column of neutral alumina to remove metal salt. The excess of THF and unreacted monomer was evaporated under reduced pressure. Poly(methyl methacrylate) was dissolved in THF, precipitated in methanol, filtered and dried in vacuum oven at 50°C for overnight. The conversions were determined gravimetrically.

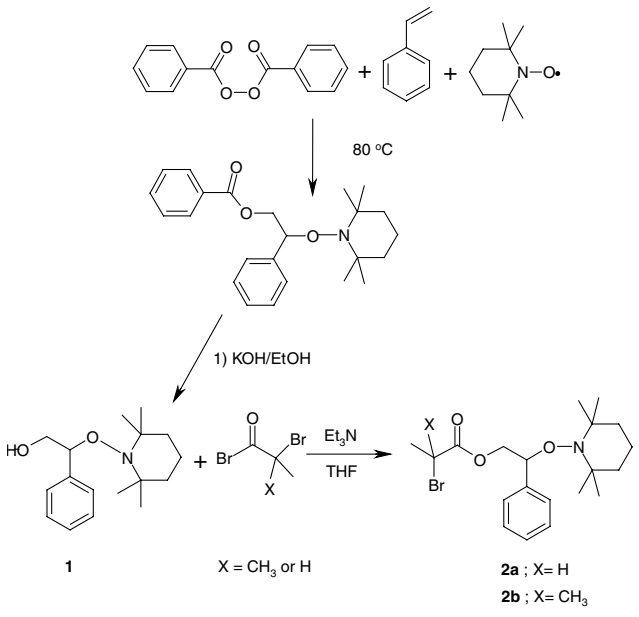
PMMA macroinitiator was prepared in 50 vol.% diphenyl ether (DPE) solution at 90°C using CuCl/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst and **2b** as the initiator, respectively. Poly(*tert*-butyl acrylate) (PtBA) macroinitiator was prepared in bulk at 90°C using CuBr/PMDETA as the catalyst and **2a** as the initiator, respectively.

2.5. Synthesis of block copolymers

The block copolymers were prepared by the SFRP polymerization of styrene using the above obtained polymers as macroinitiators. The reaction mixture containing styrene and macroinitiator was degassed and polymerized at 125°C for given times.

2.6. Characterization

Size exclusion analyses (g.p.c.) were performed with a set-up consisting of a Knauer pump and RI detector (model M 64) and three Waters Styragel columns (HR 4, HR 4E, and HR 3). THF was used as eluent at a flow rate of 0.3 ml/min at 30°C. The molecular weight of the polymers was calculated with the aid of polystyrene and poly(methyl methacrylate) standards. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 250 spectrometer (250 MHz for proton and 62.90 MHz for carbon) in $CDCl_3$. The glass transition temperatures (T_g) were recorded on a Perkin–Elmer DSC 6 instrument at a heating rate of 10°C/min under nitrogen.



Scheme 1.

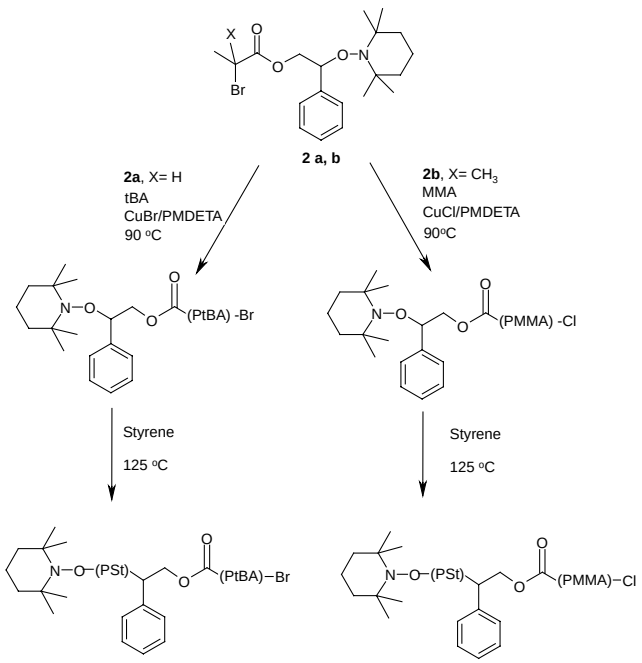
3. Results and discussion

3.1. Syntheses of initiators

The synthetic approach for the preparation of asymmetric difunctional initiators is depicted in Scheme 1. 1-(Benzyloxy)-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1-piperidinyloxy)-ethane was synthesized according to the procedure reported by Hawker et al. [14]. It was then hydrolyzed with aqueous potassium hydroxide to give **1** in quantitative yield. Asymmetric difunctional initiators (**2a** and **b**) were prepared from **1** and the corresponding acid bromides in ca. 45% yield after purification. The obtained **2a** and **b** were characterized by ^{1}H and ^{13}C NMR. ^{1}H NMR spectra of both initiators showed no signal corresponding to OH protons of the starting material 1, indicating quantitative esterification (Fig. 1). Moreover, the ^{1}H NMR spectrum of **2b** displayed a quartet (at 4.25 ppm, $J = 6.9$ Hz) and a doublet (at 1.67 ppm, $J = 6.94$ Hz) peak for the CH and CH_3 protons of the 2-bromopropionyl group, respectively. A sharp singlet appearing at 1.77 ppm in the ^{1}H NMR spectrum of **2b** was assigned to $(CH_3)_2CBr$ protons.

3.2. Homo and block copolymerizations

Syntheses of macroinitiators and block copolymers were prepared as illustrated in Scheme 2. The nitroxy-functional ATRP initiator **2b** was used to perform controlled polymerization of MMA in conjunction with CuCl complexed by PMDETA as catalyst at 90°C in 50 vol.% diphenyl ether. This led to formation of PMMA macroinitiator with TEMPO moiety at the chain end. As shown in Table 1 (expt 1), the molecular weight of the resulting



Scheme 2.

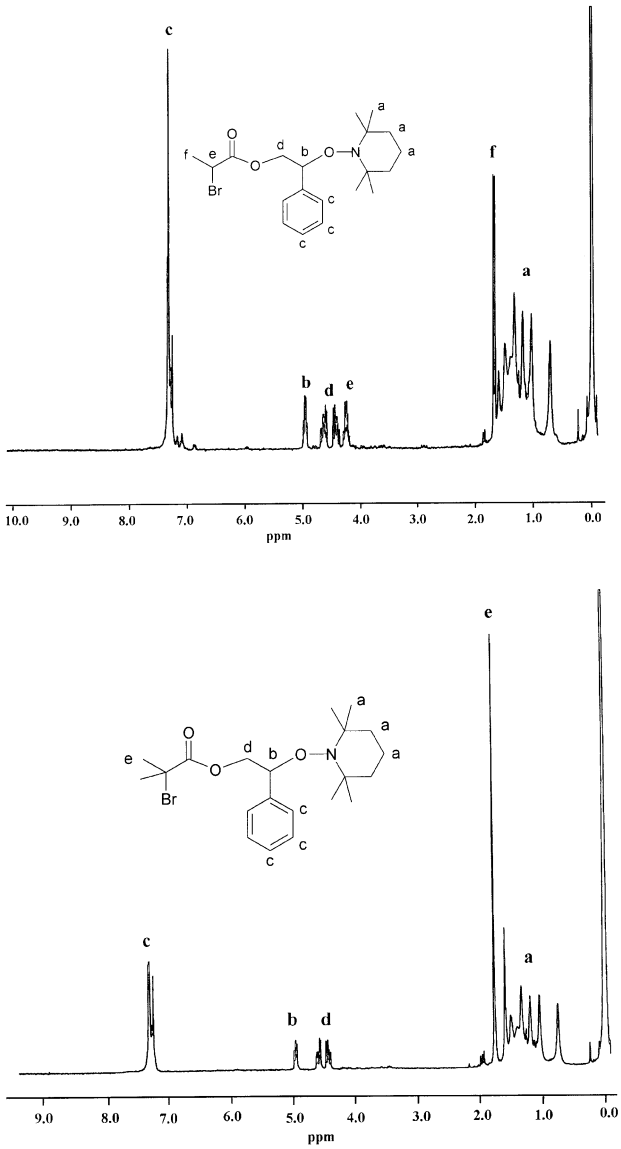


Fig. 1. ^{1}H NMR spectra of **2a** and **b** in $CDCl_3$.

PMMA determined by g.p.c. is in reasonable agreement with those obtained from the theoretical and NMR calculation using the aromatic signals of the initiator as an end group and its molecular weight distribution is narrow. The low initiator efficiency (i.e. 0.8) for the MMA polymerization can be attributed to the some side reaction that occurs at initiation step. Subsequently, the bulk polymerization of styrene using the PMMA macroinitiator obtained previously was carried out at 125°C in Table 1 (expt 3). In order to confirm block copolymer formation, successive extractions with cyclohexane and acetonitrile were performed. However, both the weight and g.p.c. trace did not change after extraction. Fig. 2 represents the g.p.c. chromatogram of the precursor PMMA and poly(methyl methacrylate-*b*-styrene) copolymer. The block copolymer structure was also elucidated by ^{1}H NMR. The ^{1}H NMR spectrum displays signals at 3.6 ($-OCH_3$ of PMMA) and 6.3–7.2 ppm (ArH

Table 1
Synthesis and characterization of macroinitiators and block copolymers

Run	Monomer	$[M]_0$ mol l^{-1}	Initiator	Time (h)	Temperature (°C)	Conversion (%)	$M_{n,\ theo}$	$M_{n,\ gpc}$	$M_{n,\ nmr}$	M_w/M_n
1[a]	MMA	4.67	**2b**	2	90	60	6000	7500[b]	7400	1.13
2[c]	tBA	6.83	**2a**	4	90	85	10 900	13 900[d]	–	1.32
3	St	8.73	PMMA[e]	19	125	74	14 900	18 000[d]	15 500	1.30
4	St	8.73	PtBA[f]	16	125	60	29 300	30 700[d]	28 000	1.52

[a] CuX = CuCl, Ligand = PMDETA, $[M]_0/[I]_0/[CuX]/[L] = 100:1:1:1$.
[b] Molecular weight was calculated on the basis of the poly(methyl methacrylate) standards.
[c] CuX = CuBr, Ligand = PMDETA, $[M]_0/[I]_0/[CuX]/[L] = 100:1:1:1$.
[d] Molecular weight was calculated on the basis of the poly styrene standards.
[e] Initiator = PMMA (expt 1), $[M]_0/[I]_0 = 100$.
[f] Initiator = PtBA (expt 2), $[M]_0/[I]_0 = 200$.

of PSt). Based upon a comparison of the aromatic protons to $-OCH_3$ protons of PMMA, the molecular weight of the block copolymer was calculated. As can be seen from Table 1 (expt 3), there is reasonable agreement between the molecular weights determined by g.p.c. and the calculated NMR values. Furthermore, MWDs remained narrow for both polymerizations. These observations suggest that the TEMPO moiety of the asymmetric difunctional initiator **2b** remains intact during the ATRP of MMA; therefore, the SFRP of styrene proceeds cleanly, resulting in an AB type block copolymer.

The same approach was applied to obtain poly(*tert*-butyl acrylate-*b*-styrene) copolymer. First, PtBA macroinitiator containing TEMPO functionality chain ends was prepared using **2a** as the initiator and CuBr complexed by PMDETA as the catalyst in bulk at 90°C for 4 h in Table 1 (expt 2). Second, PtBA was used as a macroinitiator for the SFRP of styrene in bulk at 125°C in Table 1 (expt 4). The observed molecular weights of homopolymer and block copolymer are higher than the theoretical ones. This result may be attributed to different hydrodynamic volume of PtBA and polystyrene calibration standards. The g.p.c. traces of macroinitiator and block copolymer are shown in Fig. 3. The new peak at higher molecular weight is ascribed to the block copolymer. Furthermore, the absence of the PtBA macroinitiator peak on the g.p.c. trace of the block copolymer indicates the complete conversion of the macroinitiator to the block copolymer. The ^{1}H NMR spectrum of poly(*tert*-butyl acrylate-*b*-styrene) exhibits the major peaks, which are characteristic of the styrene and *tert*-butyl acrylate comonomers. Integration of the signals at 1.43 ($C(CH_3)_3$ of PtBA) to 6.3–7.2 ppm (ArH of PSt), allows the overall molecular weight to be calculated ($M_n = 28\ 000$). This value is in reasonable agreement with the theoretical molecular weight calculated from $M_{n,theo} = ([M]_0/[I]_0 \times \text{conv.} \times 104) + 13\,900$, where 104 and 13 900 are the molecular weight of styrene and PtBA macroinitiator, respectively.

The thermal analysis of block copolymers showed a single T_g at 108 and 91°C for poly(methyl methacrylate-*b*-styrene) and poly(*tert*-butyl acrylate-*b*-styrene), respectively.

Fig. 2. g.p.c. traces of PMMA macroinitiator (a) and poly(methyl methacrylate-*b*-styrene) copolymer (b).

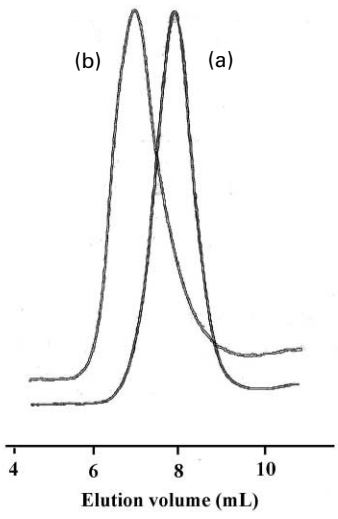


Fig. 3. g.p.c. traces of PtBA macroinitiator (a) and poly(*tert*-butyl acrylate-*b*-styrene) copolymer (b).

In conclusion, novel asymmetric difunctional initiators **2a** and **b** were synthesized and successfully used in the preparation of block copolymers via combination of ATRP and SFRP routes. We have demonstrated a versatile synthetic approach leading to (meth)acrylate–styrene block copolymers. Further studies concerning block copolymer synthesis using SFRP–ATRP sequence are in progress.

References

[1] Yagci Y, Mishra MK. In: Mishra MK, editor. Macromolecular design: concept and practice, New York: Polymer Frontiers International, 1994. Chapter 10.
[2] Wang J-S, Matyjaszewski K. Macromolecules 1995;28:7901.
[3] Wang J-S, Matyjaszewski K. J Am Chem Soc 1995;117:5614.
[4] Sawamoto M, Kato M, Kamigaito M, Higashimura T. Macromolecules 1995;28:1721.
[5] Percec V, Barboiu B, Newmann A, Ronda JC, Zhao H. Macromolecules 1996;29:3081.
[6] Percec V, Barboiu B, Kim H-J. J Am Chem Soc 1998;120:305.
[7] Rizzardo E. Chem Aust 1987;54:32.
[8] Georges MK, Veregin RPN, Kazmaier PM. Macromolecules 1993;26:2987.
[9] Hedrick JL, Trollsas M, Hawker CJ, Atthoff B, Claesson H, Heise A, Miller RD. Macromolecules 1998;31:8691.
[10] Xu Y, Pan C, Tao L. J Polym Sci Polym Chem Ed 2000;38:436.
[11] Hawker CJ, Hedrick JL, Malmström EE, Trollsas M, Mecerreyes D, Moineau G, Dubois Ph, Jérome R. Macromolecules 1998;13:213.
[12] Mecerreyes D, Moineau G, Dubois Ph, Jérome R, Hedrick JL, Hawker CJ, Malmström EE, Trollsas M. Angew Chem Int Ed 1998;37:1274.
[13] Weimer WM, Scherman OA, Sogah YD. Macromolecules 1998;31:8425.
[14] Hawker CJ, Barclay GG, Orellana A, Dao J, Devonport W. Macromolecules 1996;29:5245.