ELSEVIER

Polymer 42 (2001) 1361–1368

polymer

www.elsevier.nl/locate/polymer

Synthesis of block copolymer by "living" radical polymerization of styrene with nitroxyl-functionalized poly(ethylene oxide)

F.J. Hua*, Y.L. Yang

The Key Laboratory of Molecular Engineering of Polymers, Fudan University, Shanghai 200433, People's Republic of China

Received 11 April 2000; received in revised form 15 May 2000; accepted 7 June 2000

Abstract

A series of well-defined block copolymers of poly(ethylene oxide-*b*-styrene)s (PEO-*b*-PS)s with narrow polydispersity were synthesized by the following two-step approach: living anionic polymerization of ethylene oxide (EO) with sodium 4-oxy-2,2,6,6-tetramethy-1-piperidinyloxy (TEMPONa) as initiator to yield PEOn with a TEMPO moiety at chain end, was followed by a stable free radical polymerization (SFRP) of styrene (St) to give a block copolymer. In the process of anionic polymerization, TEMPONa could induce living anionic opening-polymerization of EO at low temperature under which the stable niroxyl radical at the end of the PEO chain could be not destroyed at all. The TEMPO moiety in the resulting PEOn acts as a radical trapper in quantitative efficiency and St can be designed for polymerization for good control of the SFRP. Such a polymerization proceeded with a living radical mechanism. However, PEOn should be more sterically hindered and possess lower diffusion ability and thus be less efficient at trapping propagating chain radicals, resulting in enhanced polymerization rate.

Keywords: Block copolymer; Living radical polymerization; Stable free radical polymerization

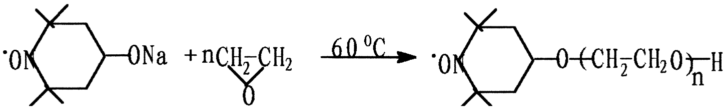
1. Introduction

Block copolymers as a unique kind of polymeric materials, can be used as compatiblizers, viscosity modifiers and so on. Design and synthesis of such a material with novel properties have attracted considerable attention on the aspect of polymer chemistry [1–3]. Several papers have been published which report the synthesis methods of block copolymers including anionic, cationic, radical polymerization and its coordinates [4–8]. However, a major drawback of ionic polymerization process is the narrow selectivity range of the monomer and the rigorous reaction conditions. Recently, a living free radical polymerization mediated by a stable nitroxyl radical such as 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and its derivatives was reported to give well-defined polymers with narrow polydispersity [9]. Nitroxide-mediated stable free radical polymerization (SFRP) was successfully used to synthesize several block, branch or star copolymers by subsequent multi-step addition of a second monomer [10–15]. A–B type block copolymer of poly(ethylene oxide) (PEO) and polystyrene (PS) in which both glassy segment and semi-crystalline segment are contained, may represent useful characteristics, e.g. high impact plastics [16,17]. Wang et al. [18] synthesized amphiphilic copolymer with uniform PEO as side chains by means of copolymerization of methacryloyl-terminated PEO macromonomer and styrene (St) in control of SFRP, but it is difficult to control the grafting site in the main bone. Yoshida et al. [19,20] found that the azo-linked polytetrahydrofuran (PTHF) with a radical initiator moiety which was obtained by living cationic polymerization of tetrahydrofuran was then decomposed in the presence of a comonomer (St) to give block copolymers. No other publications concerning PEO-*b*-PS were found in the literature. In our group, the kinetics and chain length distributions occurring in living nitroxide-mediated styrene polymerization system were simulated by using a hybrid Monte Carlo algorithm [21]. The improved polymerization rate methods for SFRP were advanced for application in experimental work successfully [22–24]. A subsequent two-step free radical polymerization approach was used to synthesize poly(methyl methyacrylate-*g*-styrene), in which low-temperature ATRP to yield PMMA or PS main backbone with dendrigraft nitroxides in the presence of polymeric nitroxyl radicals which could act as both stable radical and polymeric monomer was followed by a nitroxide-mediated SFRP process [25,26]. The copolymers containing thermally

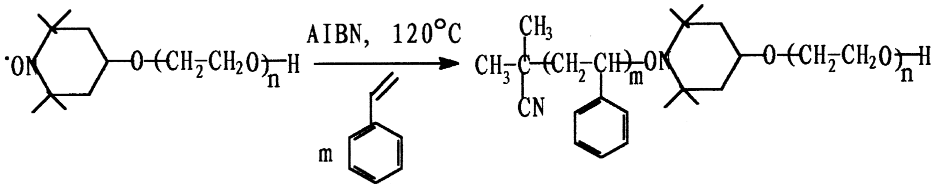
---

* Corresponding author. Tel.: +86-21-6564-2863; fax: +86-21-6564-0293.
E-mail address: fjhua@fudan.edu.cn (F.J. Hua).

0032-3861/01/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00528-0



Scheme 1.



Scheme 2.

unstable C–ON bond in main bond have reversible combination behavior under high temperature and therefore they demonstrate special rheological behavior. In this paper, anionic living polymerization of ethylene oxide (EO) with sodium 4-oxy-2,2,6,6-tetramethyl-piperidinyloxy (TEMPONa) as initiator was first used for synthesis of PEO prepolymers (PEOns) with quantitatively functionalized terminals of TEMPO (see Scheme 1). Polymerization of St was then carried out with AIBN as initiator in the presence of such a prepolymer with nitroxyl radical as the macromolecular trapper to yield PEO-*b*-PS block copolymers with narrow polydispersity.

2. Experimental

2.1. Materials

EO, THF and St were dried by calcium hydride and then distilled before use. AIBN was purified by recrystallization with hot ethanol. 4-hydroxyl-TEMPO (HTEMPO, supplied from BASF) was purified by recrystallization with hexane as solvent. All other chemicals were purified by common methods.

2.2. Instrumentation

Molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) on a Waters Instrument equipped with two Waters Styragel columns (pore size:10^2 and 10^4 Å) in sequence (eluent, THF, 1 ml/min, 38°C, polystyrene as the standard). NETZSCH TGA 204 was used to perform measurement of conversion of St. The loss in weight gave the monomer conversion at the given time when the sample was taken out of the bottle. The infrared spectra of the prepolymer and final products were taken with a NICOLET 550 FT-IR spectrometer and ^{1}H NMR on a Bruker 300 MHz NMR spectrometer. ESR spectroscopy (Bruker ER200D-SRC) and element analysis were used for determination of the nitroxide radical.

2.3. Preparation of PEO prepolymer (PEOn)

Anionic ring-opening-polymerization of EO (see Scheme 1) was carried out in a glass ampoule with a magnetic stirrer. To 20 ml of THF in dried ampoule was added 0.2 mmol Na 4-oxy-TEMPO and 0.2 mol EO. The mixture was sealed under nitrogen atmosphere and was heated at 60°C. Polymerization reaction was ended with methanol after 10 h. The prepolymer, PEOn, was purified by precipitation with chloroform as solvent and petroleum ether as nonsolvent.

2.4. Radical polymerization

Nitroxide-mediated radical polymerization process of St in the presence of PEOn may be schematized as in Scheme 2.

The experimental process is described as follows: to a 100 ml glass bottle, 35 mmol St, 0.25 g PEOn (M_n 2500, 0.1 mmol) and 13.6 mg AIBN (0.083 mmol) were added. The mixture was stirred at room temperature for 10 min. The bottle was evacuated by three freeze–pump–thaw cycles, purged into by the purified argon for 15 min and then capped with rubber tip before placing in the heated oil-bath at 120°C. The resulting polymer was purified by precipitation with ethanol mixture (ethanol/water = 80/20, molar ratio) as nonsolvent. The block copolymer could be further purified by successive extraction using cold water and cyclohexane to remove unreacted PEOn and possible PS homopolymer.

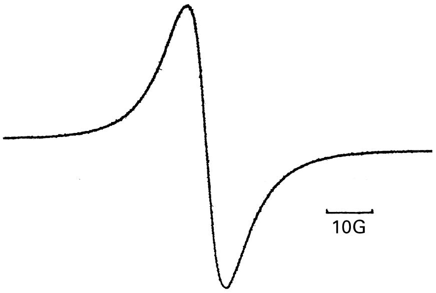


Fig. 1. ESR spectrum for solid sodium 4-oxy-TEMPO.

Table 1
A series of PEOns with different molecular weights

Types of PEOn	$M_{n,GPC}$[a]	$M_{n,spin}$[b]	$M_{n,NMR}$[c]	Polydispersity	Functionalities
PEOn-2500	2650	2520	2480	1.05	0.94
PEOn-3500	3460	3420	3350	1.10	0.97
PEOn-4500	4430	4560	4400	1.11	0.99

[a] Measured by GPC, calibrated by standard polystyrene.
[b] Estimated by measuring spin number on ESR instrument, e.g. $M_{n,spin} = M_s/N$, where M_s is the spin number/g and N is the molar constant.
[c] Calculated by ^{1}H NMR measurements.

3. Results and discussion

3.1. Synthesis of PEOn with a TEMPO moiety

The initiator, sodium 4-oxy-TEMPO was first prepared by the reaction of 4-hydroxyl-TEMPO (HTEMPO) with Na in dried THF at low temperature of 40°C. The value calculated for $C_9H_{17}NNaO_2$ was consistent with that obtained by element analysis data (Na, 12.2%; C, 55.71%; H, 8.79%; N, 7.22%). A typical ESR spectrum for solid sodium 4-oxy-TEMPO shows a sharp signal and *g* value of 2.0066 which is identical to that for HTEMPO with high concentration state (as shown in Fig. 1). The calculated spin number by integral intensity was applied to estimate the molecular weight which was found to be consistent with the element analysis result mentioned above. It indicates that the stable nitroxyl radical on sodium 4-oxyl-TEMPO molecule was not destroyed during the process of HTEMPO reduction by Na at low temperature. PEOn was prepared by an anionic ring-opening polymerization of EO with TEMPONa as initiator (see Scheme 1). A series of PEOns with different molecular weights were similarly prepared by adjusting the molar ratio of sodium 4-oxy-TEMPO to EO (as listed in Table 1). All the resulting polymers showed a unimodal GPC trace which gave a narrow polydispersity value of less than 1.2. ESR spectra in Fig. 2(a) and (b) shows sharp spin signal for solid PEOn (M_n, 2500) and three fine signal for such a PEOn in benzene (concentration 20 mg/ml), which are assigned to typical nitroxyl radical. The molecular weight estimated by spin number was found to be close to that by GPC, calibrated by standard polystyrene (see Table 1). Ascorbic acid can easily reduce TEMPO to the corresponding hydroxylamine by the reaction shown in Scheme 3 [27]. ^{1}H NMR spectrum for reduced product of PEOn is shown in Fig. 3, in which the single signal at 1.2–1.3 ppm originates from the methyl protons in hydrazine moiety and the sharp signal at 3.64 ppm was assigned to the methylene protons in the $-CH_2CH_2O$ unit of the PEO

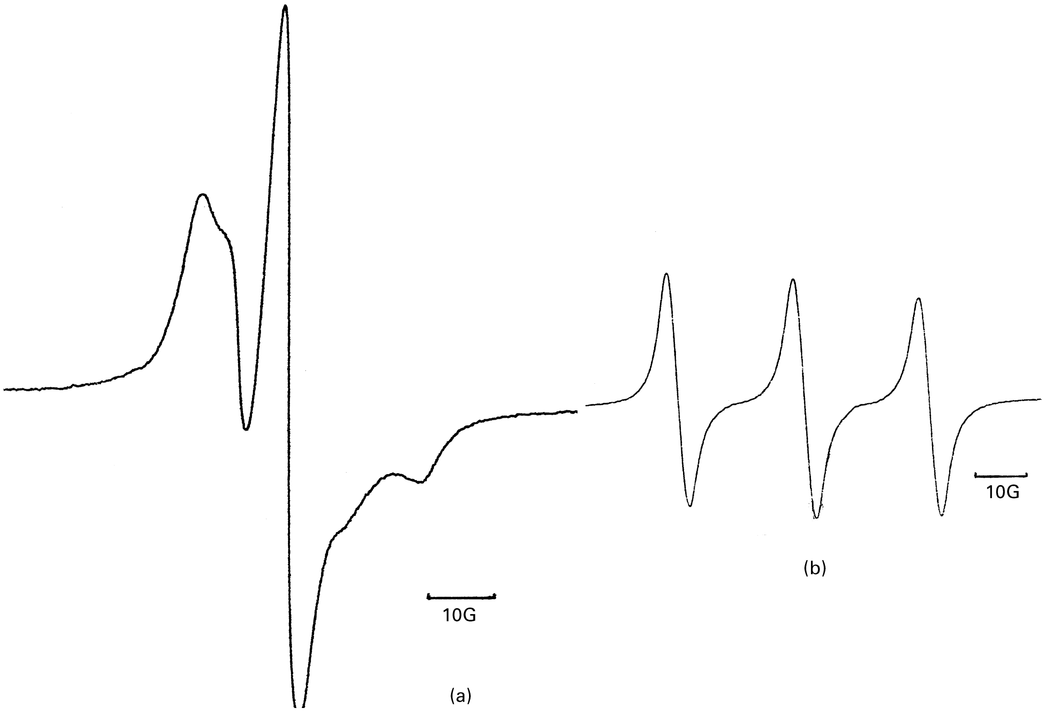
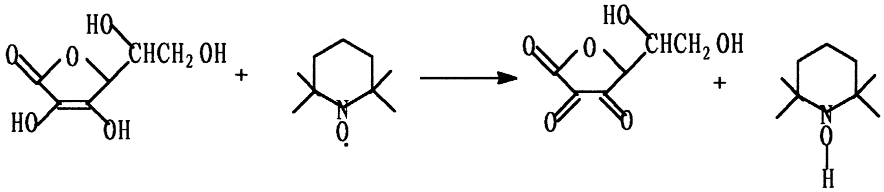


Fig. 2. ESR spectrum for PEOn (M_n 2500) which was prepared under the following the conditions: TEMPONa:EO = 1:60 (molar ratio) in 20 ml THF at 60°C. (a) In solid state; (b) in benzene solution (20 mg/l).



Scheme 3.

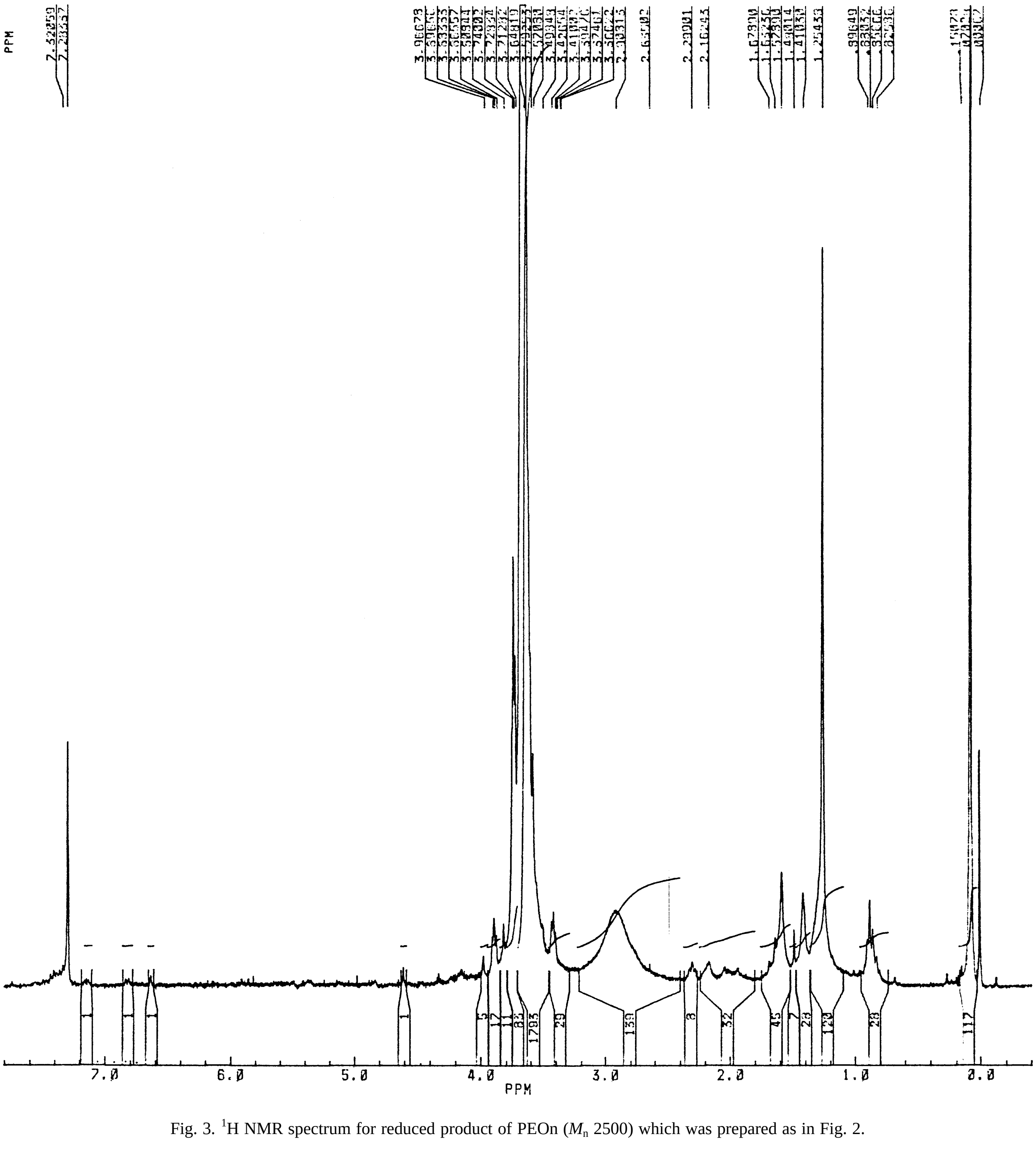


Fig. 3. ^{1}H NMR spectrum for reduced product of PEOn (M_n 2500) which was prepared as in Fig. 2.

Table 2
A series of PEO-*b*-PSs corresponding to PEOns with different molecular weights

Types of PEO-*b*-PS	$M_{n,GPC}$[a]	$M_{n,NMR}$[b]	Polydispersity
PEO-*b*-PS-2500	12,300	12,050	1.38
PEO-*b*-PS-3500	17,180	16,900	1.38
PEO-*b*-PS-4500	16,500	16,200	1.40

[a] Measured by GPC, calibrated by standard polystyrene.
[b] Calculated by ^{1}H NMR measurement.

chain. The probable molecular weight calculated by using integral intensive ratio of methylene in PEO chain at 3.64 ppm and methyl in hydrazine moiety at 1.2–1.3 ppm was found to be 2480, close to that obtained by GPC (see Table 1). The functionalities ($f = M_{n,NMR}/M_{n,GPC}$) for these PEOns are in the range of 0.9–1.0.

3.2. Polymerization of St in the presence of PEOn with a TEMPO moiety

St polymerization can take place with AIBN as initiator in the presence of PEOn carrying a TEMPO moiety at 120°C. The results are listed in Table 2. The copolymers originating from PEOns with different molecular weights gave a very narrow molecular weight distribution of under 1.4.

Fig. 4 illustrates the GPC traces at different given times in the process of polymerization of St and PEOn (M_n 2500). In initial period, another peak apart from the initial peak assigned to PEOn emerged gradually to form a broad peak while molecular weight increased gradually. The copolymer shows a unimodal GPC trace and no peak due to the prepolymer was observed after 2 h. These results indicate that the TEMPO moiety at the end of PEOn chain was engaged in copolymerization to yield the block copolymer (PEO-*b*-PS). Furthermore, the linear dependence of molecular weight deviated from the “living” peak on conversion and the linear relationship of $\ln(M_0/M)$ versus reaction time (as shown in Figs. 5 and 6, respectively) demonstrates that polymerization of St can be controlled in the presence of PEOn with TEMPO moiety in a way similar to SFRP with HTEMPO [9] and thus copolymers with narrow polydispersity were obtained (MD $<$ 1.5 as shown in Table 2). In fact, PEOn acted as macromolecular trapper of the stable nitroxyl radical of HTEMPO in the process of polymerization. However, PEOn should be more sterically hindered and possess lower diffusibility than HTEMPO, so that it could be less efficient at trapping the initiating radicals. As a result, double peaks during the initial polymerization are unavoidable as shown in Fig. 4. The polymerization rate of St in the presence of PEOn is faster than that with the same quantitative amount of HTEMPO (see Fig. 6), which demonstrates that TEMPO moiety connected at the end of PEOn is less efficient at trapping the propagating chain radicals because of the high steric hindrance of PEOn with long EO chain. Furthermore, the polymerization rate for St system in the presence of PEOn with smaller molecular weight increases slightly. This is probably related to the high viscosity or low diffusion ability of PEOn with longer EO chains.

^{1}H NMR spectrum of the final copolymer, shown in Fig. 7, exhibits signals at 6.7–7.3 ppm which can be attributed to styrene. The number-average degree of polymerization of St in the copolymer, estimated from the intensity ratio of methlyne protons at 3.64 ppm in OCH_2CH_2 to phenyl ones at 6.7–7.3 ppm, was found to be close to the theoretical value according to the following equation (see Table 2):

$$M_n = M_{n,PEOn} + [M_{St}] \times \text{conv\%} \times M_{w,St}/[\text{PEOn}]$$

These results indicate that polymerization of St in the

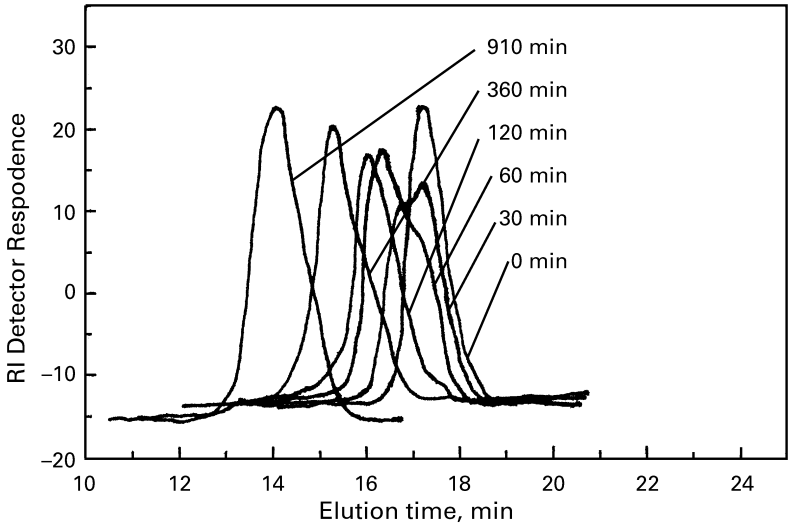


Fig. 4. GPC traces for intermediates taken at different times during the process of polymerization (120°C), SFRP polymerization conditions: PEOn:AIBN:St = 1.2:1:300 (molar ratio) at 120°C.

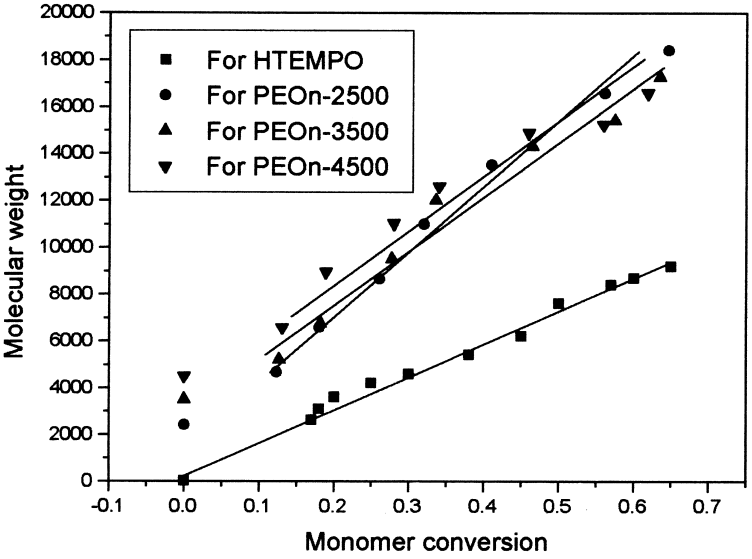


Fig. 5. Dependence of molecular weight on monomer conversion in SFRP of St in the presence of PEOn and HTEMPO. Reaction conditions are identical to those in Fig. 4.

presence of PEOn proceeded via a living radical mechanism and that the well-defined PEO-*b*-PS with narrow polydispersity was prepared as schematized in Scheme 2.

In conclusion, PEO-*b*-PSs with narrow polydispersity were prepared by combining living anionic polymerization and SFRP. Ring-opening polymerization of EO with sodium 4-oxy-TEMPO as initiator gives PEOn with a TEMPO moiety. St, with PEOn as macromolecular trapper, then polymerizes (which can be controlled) by SFRP. Sterically hindered PEOn with high molecular weight is less efficient at trapping propagating chain radicals, and so can enhance the polymerization rate. However, PEO-*b*-PS copolymers undergo reversible decomposition–combination reaction at high temperature (in general, >95°C) because of the unstable C–ON bond between the PS and PEO segments. The semi-crystalline PEO segment can demonstrate self-organizing behavior. A study of the rheological behaviors of these copolymers are in progress and the reports will be submitted soon.

Acknowledgements

This project was supported by the Open Fund from the Key Laboratory of Molecular Engineering of Polymers in China.

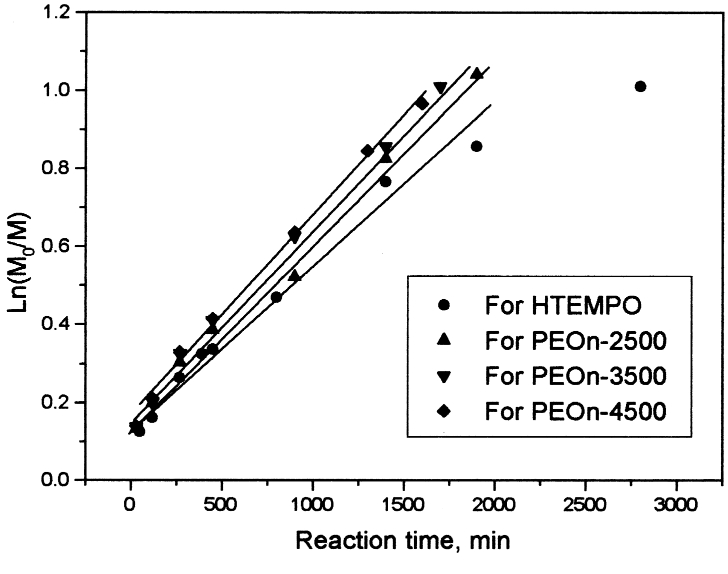


Fig. 6. Dependence of ln(M_0/M) on reaction time in SFRP of St in the presence of PEOn and HTEMPO. Reaction conditions are identical to those in Fig. 4.

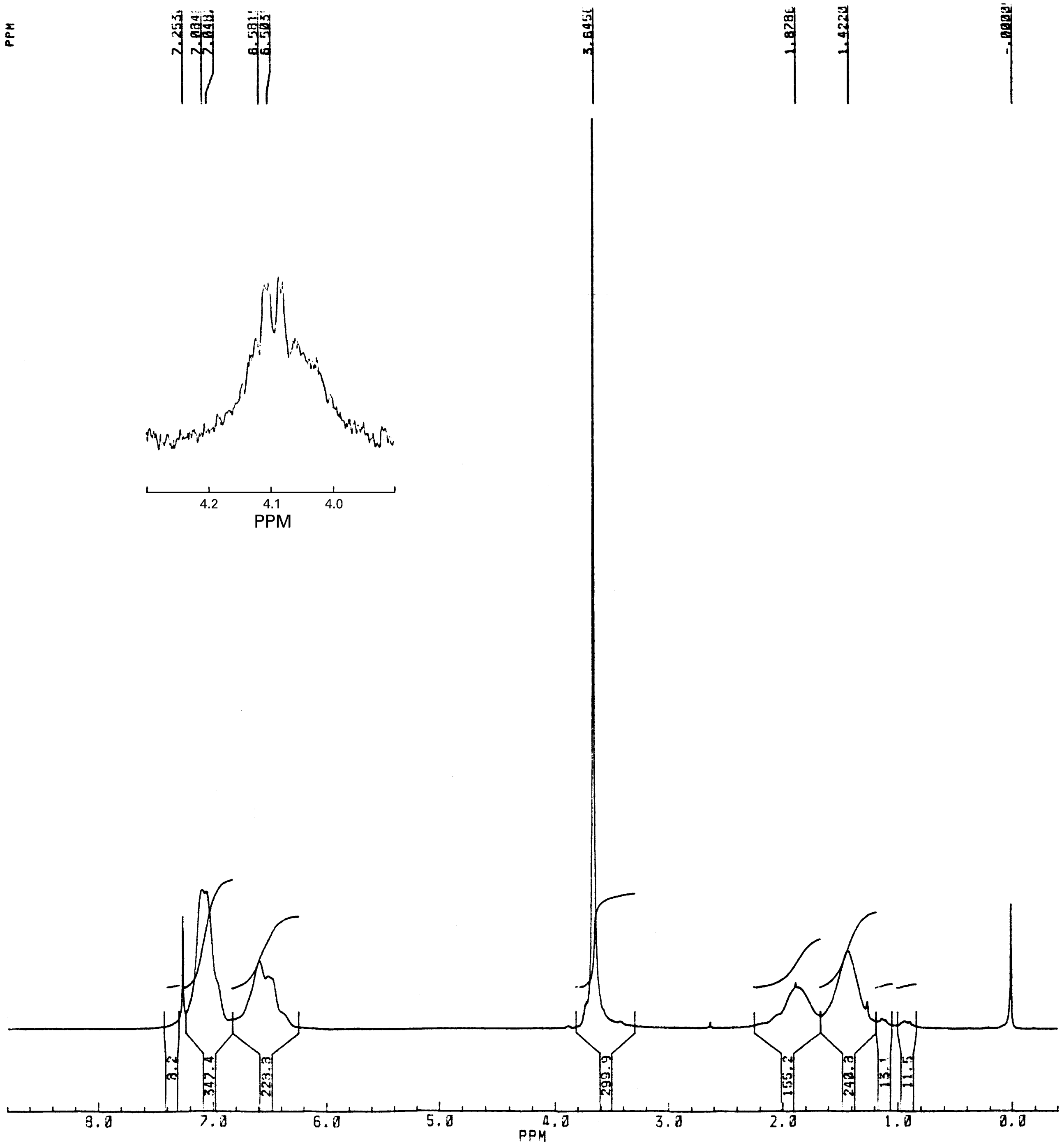


Fig. 7. ^{1}H NMR spectrum for diblock PEO-*b*-PS prepared with PEOn (M_n 2500) under the conditions given in Fig. 4.

References

[1] Suzuki T, Murakami Y, Takegami Y. Polym J 1980;12:183.

[2] Capek I, Riza M, Akashi M. Makromol Chem 1992;193:2843.

[3] Kawaguchi S, Winnik MA, Ito K. Macromolecules 1995;28:1159.

[4] Ishizu K, Kakura T. J Polym Sci: Polym Lett Ed 1983;21:405.

[5] Suzuki T, Murakami Y, Tsuji Y. J Polym Sci: Polym Lett Ed 1976;14:675.

[6] Baines FL, Billingham NC, Armes SP. Macromolecules 1996;29:3416.

[7] Georges MK, Veregin RPN, Hamer PK. Polym Prepr 1994;35(2):582.

[8] Georges MK, Hamer GK, Listigovers NA. Macromolecules 1998;31:9087.

[9] Georges MK, Veregin RPN, Kazmaier PM, et al. Macromolecules 1993;26:2987.

[10] Grubbs RB, Hawker CJ, Dao J. Angew Chem Int Ed Engl 1997;36:270.

[11] Webster OW. Science 1991;251:887.

[12] Hawker CJ, Frechet JM. J Am Chem Soc 1990;112:7638.

[13] Hawker CJ, Frechet JM. J Am Chem Soc 1991;113:4583.

[14] Turner SR, Walter F, Voit BI. Macromolecules 1994;27:1611.

[15] Gauthier M, Moller M. Macromolecules 1991;24:4548.

[16] Minoura Y, Kasuya T, Kawamura S, et al. J Polym Sci A-1 1967;5:43.

[17] Galin J, Galin M, Calme P. Makromol Chem 1970;134:273.
[18] Wang YB, Huang JL. Macromolecules 1998;31:4057.
[19] Yoshida E, Takata T, Endo T. Macromolecules 1992;25:7282.
[20] Yoshida E, Sugita A. Macromolecules 1996;29:6422.
[21] He J, Zhang H, Chen J, et al. Macromolecules 1997;30:8010.
[22] He JP, Li CM, Hua FJ, et al. Polym J 1999;31:585.
[23] Li CM, He JP, Li L, et al. Macromolecules 1999;32:7012.
[24] He JP. Doctoral dissertation. 1999, China.
[25] Liu B, Hu CP, Hua FJ, et al. China Synth Rubber Ind 1999;22(6):373.
[26] Hua FJ, Yang YL, Liu B, et al. China Synth Rubber Ind 2000;23(1):49.
[27] Paleos CM, Dais P. J Chem Soc Chem Commun 1977:345.