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Short communication

Synthesis of polytetrahydrofuran with alkoxyamine end-groups and its use in block copolymerization with styrene

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Abstract—Alkoxyamine-terminated polytetrahydrofurans were prepared by terminating the mono- and bi-functional living polymerization of tetrahydrofuran with sodium alkoxyamine. The resulting polymers could initiate the radical polymerization of styrene in accordance with a controlled mechanism to afford block copolymers. The transformation from living cationic to controlled free radical polymerization has been achieved.

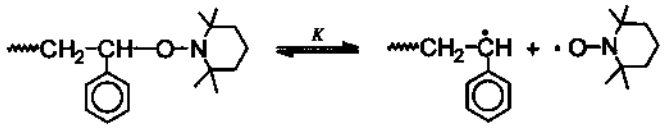
Keywords: Living cationic polymerization; controlled free radical polymerization; transformation reaction; block copolymers.

1. INTRODUCTION

Precise control of the molecular weight and structure is undoubtedly the most important prerequisite for the synthesis of advanced polymeric materials. Living polymerizations are, so far, the best processes to prepare macromolecules with a complex and controlled architecture. A variety of well-defined polymers with specific functionalities can be synthesized by living anionic and cationic polymerization techniques [1–5]. It has long been difficult to achieve living conditions for free radical polymerizations, because of the propensity of propagating radicals to undergo facile radical–radical reactions. Early approaches to achieve living radical polymerization were based on the iniferter concept. Despite the fact that sequential addition of monomers leads to the formation of block copolymers, polymers obtained by using the iniferter concept do not show narrow polydispersities. Thus, control of the macromolecular architecture cannot be achieved by iniferter systems.

Following the pioneering work of Rizzardo and co-workers, special attention has recently focused on the use of nitroxyl stable radicals such as TEMPO in order to achieve living conditions in free radical polymerization [7, 8]. In principle, these stable radical-mediated polymerizations involve reversible termination of the polymer

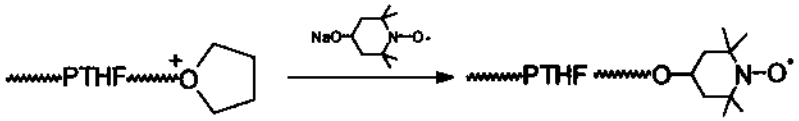
radical with TEMPO and chain growth during the lifetime of the polymeric radical as shown below [9–12]:



(1)

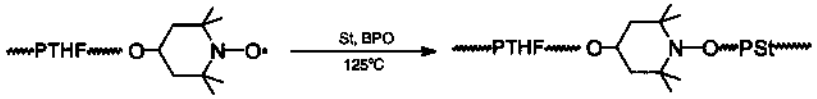
Although transfer and bimolecular termination reactions can be minimized, and so that the polymerization can be considered controlled, stable radical-mediated polymerization is limited to styrene and derivatives. Therefore, block copolymers consisting of monomers with different structures cannot be prepared by this method. However, nitroxide-mediated radical polymerization can certainly be applied to monomers other than styrene under living conditions. The phenomenon is now well established and that is why atom transfer polymerization has been developed for broader monomer selectivity.

Recently, Yoshida and Sugita described the synthesis of polytetrahydrofuran (PTHF) possessing a nitroxyl radical, by terminating the polymerization of living PTHF with sodium 4-oxy TEMPO [13].



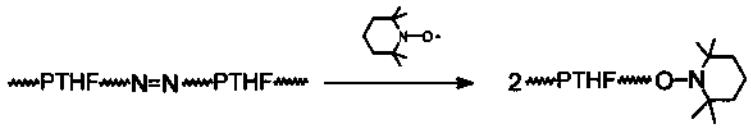
(2)

The polymer obtained in this way acted as a counter radical in the polymerization of styrene in the presence of a free radical initiator to yield polystyrene-*b*-polytetrahydrofuran.



(3)

Quite recently, we have extended stable radical-mediated polymerization to polymeric initiators obtained by cationic polymerization [14]. In this case, ω-alkoxyamine PTHF was obtained and upon heating at 125 °C, polymeric and stable nitroxyl radicals were formed.



(4)

(5)

In the presence of styrene (St), the produced block copolymers had a controlled molecular weight, since termination reactions were minimized and the equilibrium between the dormant and active species allows controlled growth.

In the present study, we describe our results on the preparation of alkoxyamine-terminated PTHF by end-coupling reactions of living THF. Polymers with an alkoxyamine end-group are expected to give polymeric radicals upon heating which would lead to block copolymers by radical polymerization.

2. EXPERIMENTAL

2.1. Materials

Tetrahydrofuran (THF) was dried over potassium hydroxide and distilled over sodium/benzophenone ketyl just before use. Styrene was washed with 5% alkali solution to remove stabilizers, dried over $CaCl_2$, and distilled over CaH_2. Sodium ascorbate (Fluka), sodium hydride as a 60% dispersion in oil (Aldrich), triethyloxonium tetrafluoroborate (Aldrich), triflic anhydride (Fluka), and 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) (Aldrich) were used as received.

2.2. Synthesis of sodium 2,2,6,6-tetramethylpiperidin-1-oxylate

A suspension of 0.53 g (3.4 mmol) of TEMPO in 5 ml of water was mixed with 0.67 g (3.4 mmol) of sodium ascorbate in 5 ml of water. The reaction mixture was stirred for 15 min. The resulting solution was extracted four times with diethyl ether and the organic layers collected were evaporated until dryness. The crude product was dissolved in 20 ml of freshly distilled THF and 78 mg (2.2 mmol) of NaH was added to this solution and kept under argon.

2.3. Synthesis of monofunctional alkoxyamine-terminated PTHFs

The living cationic polymerization of THF was initiated by adding 0.057 ml (0.4 mmol) of triethyloxonium tetrafluoroborate to 20 ml of freshly distilled THF at 25°C under dry argon. After a certain time, active chain ends were terminated by addition of sodium 2,2,6,6-tetramethylpiperidin-1-oxylate. The mixture was stirred for 3 h at room temperature and poured into ten-fold methanol. The precipitated polymer was filtered off and dried at room temperature *in vacuo*. The molecular weight and polydispersity of the resulting polymer were 24 300 g/mol and 1.32 respectively, as determined by GPC calibrated with standard PTHF.

2.4. Synthesis of bifunctional alkoxyamine-terminated PTHFs

The living cationic polymerization of THF was initiated by adding 0.1 ml (0.6 mmol) of trifluoromethane sulfonic anhydride to 50 ml of freshly distilled THF at 25°C under dry argon. After a certain time, active chain ends were terminated by addition of sodium 2,2,6,6-tetramethylpiperidin-1-oxylate. The mixture was stirred for 3 h

at room temperature and poured into ten-fold methanol. The precipitated polymer was filtered off and dried at room temperature *in vacuo*. The molecular weight and polydispersity of the resulting polymer were 22 000 g/mol and 1.38 respectively, as determined by GPC calibrated with standard PTHF.

2.5. *Thermal block copolymerization of styrene*

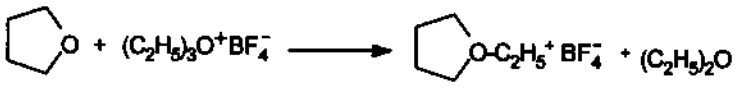
0.7 g of alkoxyamine-terminated PTHF was dissolved in 1 ml (8.70 mmol) of styrene and the system was degassed under high vacuum and disconnected with air. The polymerization reactions were performed at 125 °C for different times. The mixtures were cooled with liquid nitrogen to terminate the polymerization. After dilution of the mixture with dichloromethane, the polymers were precipitated into a large excess amount of methanol. This procedure was repeated several times and finally the filtered polymer was dried *in vacuo*.

2.6. *Analysis of the polymers*

^{1}H-NMR spectra were taken on a Bruker-200 spectrometer in $CDCl_3$ solution. GPC analysis was performed with a set-up consisting of a Bischoffs HPLC pump and four Waters Styragel HR columns with porosities of 10^6, 10^5, 5×10^3, and 10^3 Å. $CHCl_3$ was used as the eluant at a flow rate of 1 ml/min and detection was carried out with a Bischoffs differential refractometer (model 8110). Molecular weights were calculated with the aid of PTHF and polystyrene standards.

3. RESULTS

The living PTHF was prepared by cationic polymerization of THF using triethyloxonium tetrafluoroborate as initiator in bulk at room temperature for 1 h under argon, according to reactions (6) and (7). The living propagating chain end was quenched with previously prepared sodium 2,2,6,6-tetramethylpiperidin-1-oxylate according to reactions (8) and (9).



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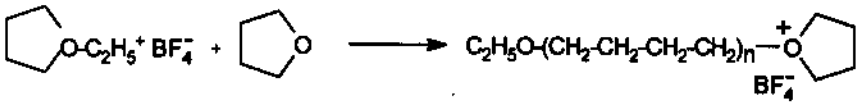
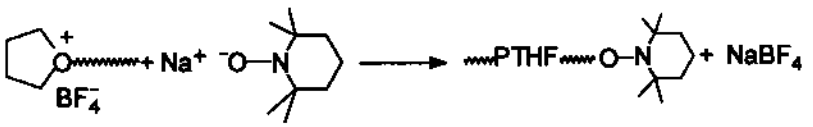


(7)

The isolated polymer was purified by precipitation and washing with *n*-hexane several times; yield 15% PTHF.

The ^{1}H-NMR spectrum of a typical PTHF (Fig. 1) displays signals at 3.4 ppm (a) and 1.7 ppm (b) corresponding to two different types of methylene protons, one of

which was attributed to the methylene bonding to the oxygen atom and the other to the methylene group in the main chain. Two other singlets were observed at 1.1 and 1.2 ppm belong to methyl protons (c). The methyl protons in the cycle coupled with methylene protons in the main chain.



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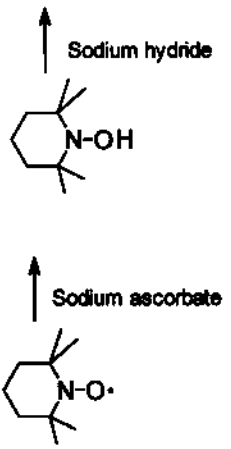

(9)

To confirm the possibility of transformation of living cationic to living free radical polymerization, radical polymerization of styrene was carried out with alkoxyamine-terminated PTHF. The results are shown in Table 1. The polymerization was carried out in bulk at 125°C. Initial thermolysis at 95°C for 3.5 h, which is used in the usual procedure of nitroxyl radical-mediated living polymerization with low molar mass initiators, was excluded since the polymer chains possess terminal alkoxyamine groups in the beginning. The increase in conversion with increasing polymerization time and polydispersity of the resulting polymers was close to that of the prepolymer ($M_w/M_n = 1.33$). Figure 2 illustrates typical GPC profiles obtained for different polymerization times.

As can be seen from the GPC chromatograms, all block copolymers give unimodal peaks and as the polymerization time increases, the peaks shift to lower elution volume, i.e. the higher molecular weight side. Alkoxyamine-terminated PTHF initiates the polymerization with a somewhat controlled mechanism. As can be seen from Fig. 3, the molecular weight of the polymer produced is in proportion to the conversion. However, the molecular weights of the block copolymers are higher than expected. This may be due to the presence of non-functionalized PTHF and the relatively slow decomposition and initiation of alkoxyamine attached to unsubstituted methylene groups. The poor efficiency of ω-alkoxyamine PTHF is not surprising: a recent article by Hawker *et al.* [15] indicates that alkoxyamines containing an unsubstituted carbon atom are very slow to decompose and initiate polymerization. The

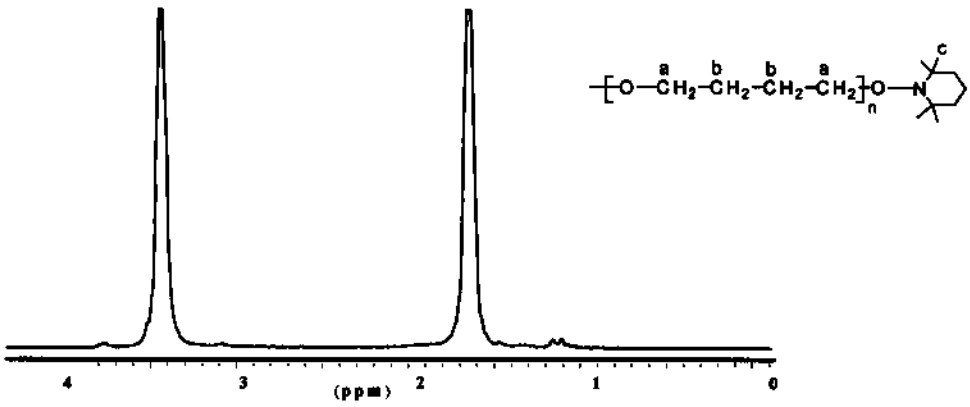

Figure 1. ^{1}H-NMR spectrum of a typical PTHF obtained by the reaction of living PTHF with sodium 2,2,6,6-tetramethylpiperidin-1-oxylate in $CDCl_3$.

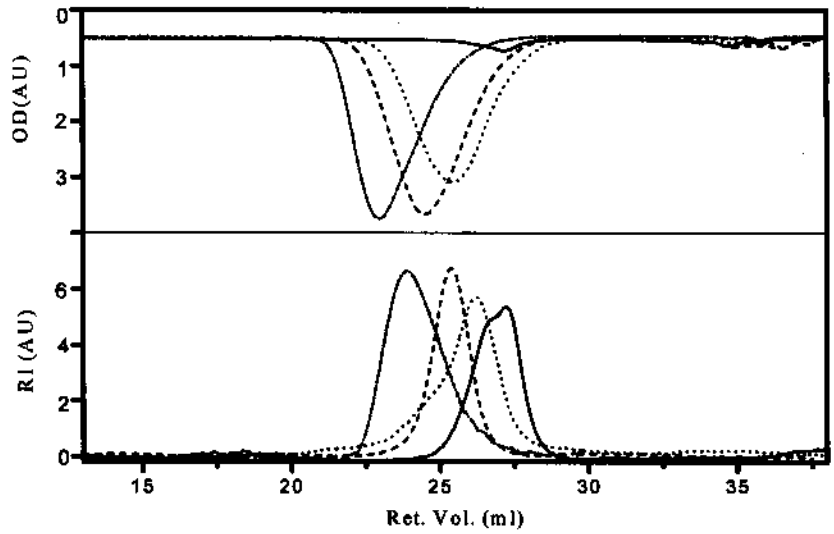

Figure 2. GPC profiles of PTHF (—) and PTHF–PSt block copolymer after 1 h polymerization (····), 2.5 h polymerization (---), and after 8 h polymerization (-·-·-).

Table 1.
Radical polymerization of styrene by alkoxyamine-terminated polytetrahydrofuran

Code	Time (h)	Conversion (%)	M_n	M_w/M_n	Units	
					THF	St
PTS1	1	5	86700	1.48	361	530
PTS2	2	12	107000	1.42	361	725
PTS3	8	38	419000	1.51	361	3600
PTS4	8	42	320000	1.89	305	2600

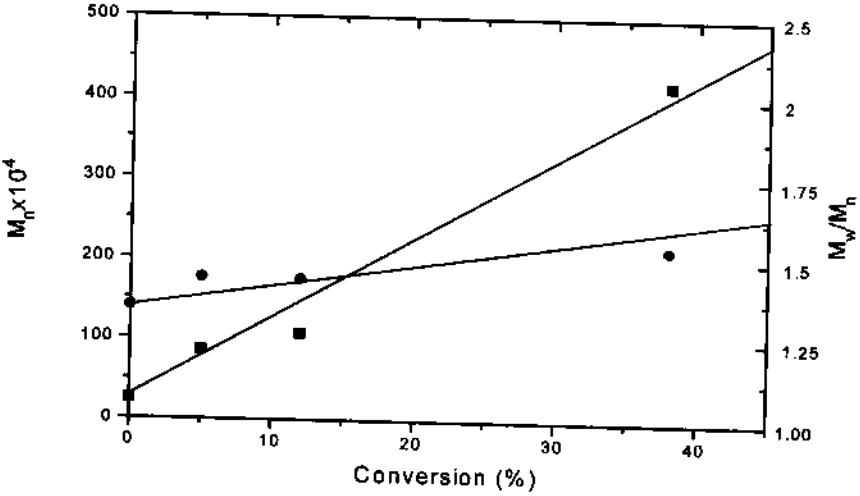

Figure 3. Conversion–molecular weight and polydispersity index plots in the polymerization of styrene initiated by alkoxyamine-terminated PTHF.

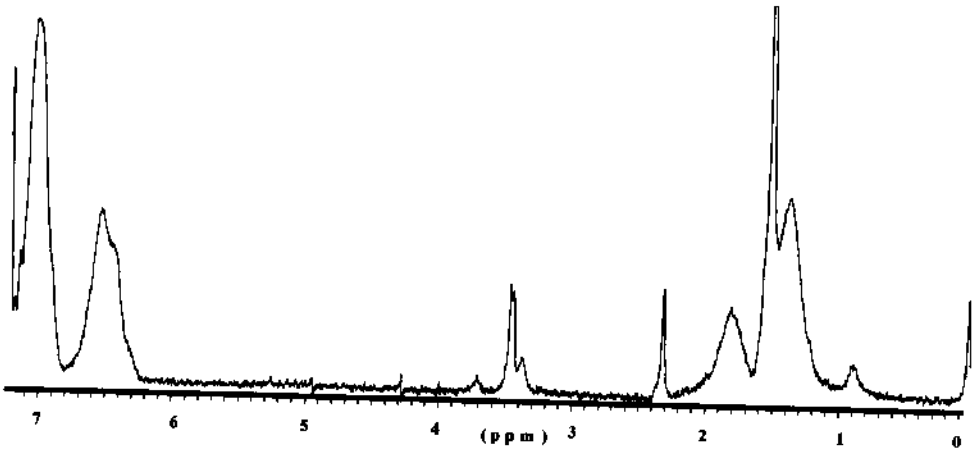

Figure 4. ^{1}H-NMR spectrum of polytetrahydrofuran-*b*-polystyrene (PTS1).

article also reports that for benzylic derivatives an α-methyl group is essential for the free radical polymerization to proceed with a truly living character.

In order to confirm the structures of the PTHF–PSt block copolymer, the polymers were characterized by ^{1}H-NMR. Figure 4 shows a ^{1}H-NMR spectrum of a typical block copolymer (Table 1, PTS1). It is seen that the signals originating from THF resonate at both 1.7 and 3.5 ppm, while signals originating from styrene appear at 6.3–7.2 ppm. The number-average degree of polymerization of the respective blocks in the copolymer was also estimated from the intensity ratio of methylene protons to aromatic protons. These results indicate the formation of block copolymers.

When the free radical polymerization of styrene was carried out with bifunctional alkoxyamine-terminated PTHF, which was obtained by cationic polymerization of

THF by trifilic anhydride (see Section 2), ABA-type block copolymers were obtained. Notably, the polydispersity index of the resulting block copolymer was higher (Table 1, PTS4).

4. CONCLUSION

Mono- and bi-functional alkoxyamine-terminated PTHFs have been prepared by quenching of the living PTHF with sodium 2,2,6,6-tetramethylpiperidin-1-oxylate. When these polymers are used to polymerize styrene, diblock and triblock copolymers are obtained, according to the number of functionalities of polytetrahydrofuran. It was also demonstrated that sodium alkoxyamine can be regarded as an active site agent for the transformation from living cationic polymerization to controlled radical polymerization.

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