Living Radical Polymerization by Biradical Compounds of Tetramethylpiperidine-1-oxyl

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ABSTRACT: The polymerization of styrene was performed using two types of biradical compounds derived from 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO). The biradical compounds are diesters of 4-hydroxy-TEMPO with phthalic acid (*o*-TEMPO) and with terephthalic acid (*p*-TEMPO). When the polymerization was carried out by *o*-TEMPO and benzoyl peroxide (BPO) as an initiator, a polymer obtained had showed bimodal GPC. This suggests that dimerization by coupling of the polymers occurred during the polymerization. GPC demonstrated that the polymerization in the absence of BPO suppressed the dimerization and gave a polymer with narrow polydispersity. The polymerization was found to proceed in accordance with a living mechanism, because the molecular weight was directly proportional to the conversion, and was inversely proportional to the initial concentration of the biradical compound. A polystyrene obtained by the polymerization with the biradical compound initiated the polymerization of *tert*-butoxystyrene, giving ABA type of triblock copolymer.

KEY WORDS 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO) / Living Radical Polymerization / Biradical Compounds / Both Growing Chain Ends /

Initiators which give both growing chain ends are of importance in preparing ABA type of block copolymers and polymers with functional groups at both the chain ends. Such initiators were already discovered in ionic polymerizations. For anionic polymerization, aromatic radical-anions such as sodium or potassium naphthalene and sodium biphenyl are well-known as initiators to give both growing chain ends.¹ By using these variety of polymers with functional groups at both the chain ends and symmetric multiblock copolymers were prepared through living anionic polymerizations. In respect of cationic polymerization, aromatic radical-cations of perylene^{2–4} and tropylium ion^{5,6} are used as initiators giving both propagating chain ends. Trifluoromethanesulfonic acid anhydride is also an efficient initiator forming both growing chain ends for living cationic polymerization of THF.^{7,8} Thus, a variety of initiators giving both propagating chain ends were found in ionic polymerizations, while there are not readily available such initiators in radical polymerization. It has been reported by Matyjaszewski that a macroinitiator which has Cu(I)/bipyridyl moieties at the terminals gave polymers with both growing chain ends.^{9,10} A multifunctional radical initiator was found by Hawker and co-workers.¹¹ This initiator composes of a stable nitroxyl radical, tetramethylpiperidine-1-oxyl (TEMPO). TEMPO is well-known to play a role as a counter radical for living radical polymerization. Although

TEMPO has no ability to initiate radical polymerization, this radical has the potential to induce initiation. This is based on the fact that concentration of a growing polymer chain end is determined by the initial concentration of TEMPO.¹² For the preparation of symmetric block copolymers by radical polymerization, difunctional compounds of TEMPO can be substituted for initiators giving both propagating chain ends. In the polymerization using biradical compounds of TEMPO, monomers are inserted between the growing carbon radical and TEMPO, so that the following monomers form the middle segments in symmetric diblock copolymers (Scheme 1). The active species are located at the middle of a polymer in this case. Therefore, mobility of the active species should be restrained as the molecular weight increases. The presence of the active species at the middle is expected to serve to stabilize the species, although the propagation rate may decrease. This is accounted for by the fact that deactivation of the active species is caused by disproportionation of the aminoxy moiety in the styrene polymerization.^{13,14} It has been reported that dispro-

Scheme 1.

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portionation hardly occurred in the polymerization by TEMPO supported on polymer chain end.¹⁵ We have already succeeded in preparing ABA type of triblock copolymers through radical polymerization of styrene using polymers with TEMPO at both the chain ends.^{15,16} In this paper, the living radical polymerization of styrene using biradical compounds of TEMPO and the synthesis of a symmetric triblock copolymer, are described.

EXPERIMENTAL

Measurements

Gel permeation chromatography (GPC) was performed with Tosoh HLC-802A equipped with a RI detector and with a Tosoh CP-8000 chromatoprocessor. Two polystyrene gel columns of Tosoh TSK gel G4000H₈ and G2000H₈ were used with THF as the eluent at 42°C. ¹H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer. Gas chromatography (GC) was performed with a Shimadzu GC-6A.

Materials

4-Hydroxy-TEMPO was prepared by the method reported previously.¹⁷ THF and toluene were purified by refluxing on sodium for several hours and distilled over sodium. Pyridine and trifluoroethanol were purified by refluxing on calcium hydride and distilled. Commercial grade styrene was washed with aqueous alkaline solution and water, and distilled over calcium hydride. 4-*tert*-Butoxystyrene was distilled over calcium hydride. Benzoyl peroxide (BPO) was precipitated from chloroform into methanol and recrystallized at 0°C. Extrapure grade phthaloyl chlorolide, terephthaloyl chlorolide, benzoyl chlorolide, trifluoromethanesulfonic acid, and phenylhydrazine for ¹H NMR studies were used without further purification.

Synthesis of Bis[4-(2,2,6,6-tetramethylpiperidine-1-oxyl)] Phthalate (*o*-TEMPO)

Pyridine (0.94 mL, 11.6 mmol) and phthaloyl chlorolide (0.56 mL, 3.89 mmol) was added at 0°C to a solution of 4-hydroxy-TEMPO (2.00 g, 11.6 mmol) in THF (20 mL). The mixture was kept at room temperature being stirred. After 24 h, white precipitate in the mixture was filtered off with suction. Ether (100 mL) was added to the filtrate and the mixture was washed with 50 mL of water three times. The ether layer was dried with anhydrous magnesium sulfate, and evaporated to remove the ether. The residue was dried *in vacuo* for several hours. A crude product (2.00 g) was obtained. *o*-TEMPO was separated by a silicagel

column with a mixed solvent (benzene: ethyl acetate = 5:1 v/v) as the eluent. *o*-TEMPO was purified by recrystallization from cyclohexane. *o*-TEMPO (1.48 g, yield 80%) was obtained as needle and red crystals.

Bis [4-(2,2,6,6-tetramethylpiperidine-1-oxyl)] terephthalate (*p*-TEMPO) and 4-benzoyl-2,2,6,6-tetramethylpiperidine-1-oxyl were prepared by the same method.

Radical Polymerization of Styrene by BPO and *o*-TEMPO

Styrene (1.0 mL, 8.73 mmol), BPO (21 mg, 0.0866 mmol), and *o*-TEMPO (27 mg, 0.0569 mmol) were placed in an ampule. After degassing, the ampule was sealed *in vacuo*. Polymerization was carried out at 125°C for 16 h, following at 95°C for 3.5 h. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitation from dichloromethane into methanol, and dried *in vacuo* for several hours. A polymer (724 mg, yield 80%) was obtained.

Radical Polymerization of Styrene by *o*-TEMPO:

General Procedure

Styrene (1.0 mL, 8.73 mmol) and *o*-TEMPO (10 mg, 0.0211 mmol) were placed in an ampule. After degassing, the ampule was sealed *in vacuo*. Polymerization was carried out at 125°C for 136 h, and terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitation from dichloromethane into methanol, and dried *in vacuo* for several hours. A polymer (799 mg, yield 88%) was obtained. After the addition of toluene as the internal standard, the dichloromethane solution was subjected to GC to estimate the conversion of styrene.

Block Copolymerization of 4-*tert*-Butoxystyrene by Polystyrene Having *o*-TEMPO Moieties

4-*tert*-Butoxystyrene (1.12 mL, 5.95 mmol) and polystyrene (167 mg, $M_n = 31000$, $M_w/M_n = 1.25$) were placed in an ampule. After degassing, the ampule was sealed *in vacuo*. Polymerization was carried out at 125°C for 18 h, and terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitation from dichloromethane into methanol, and dried *in vacuo* for several hours. A polymer (850 mg, yield 70%) was obtained.

Hydrolysis of a Block Copolymer of Styrene and 4-*tert*-Butoxystyrene

A block copolymer (62 mg) was dissolved in 5 mL of toluene. A few drops of trifluoroethanol was added to the solution. Trifluoromethanesulfonic acid (2 drops) was added to the mixture at -5°C , and the mixture was stirred at the temperature for 15 min. The mixture was poured into hexane (500 mL) to isolate a polymer. Precipitate was collected by filtration, and dried *in vacuo* for several hours. A polymer (41 mg, yield 66%) was obtained.

RESULTS AND DISCUSSION

Two types of biradical compounds of TEMPO, *o*-TEMPO, and *p*-TEMPO were used as counter radicals for radical polymerization of styrene. *o*-TEMPO is a diester of 4-hydroxy-TEMPO with phthalic acid, and has the TEMPO moieties at *ortho* positions. *p*-TEMPO is also a diester with 4-hydroxy-TEMPO with terephthalic acid, and has the TEMPO moieties at *para* positions (Scheme 2). While *p*-TEMPO is expected to give linear polymers, *o*-TEMPO has the potential to produce a hairpin type of polymer due to the structure of the counter radical. Radical polymerization of styrene was carried out by BPO as an initiator and *o*-TEMPO. The polymerization was performed in bulk at 125°C for 16 h, after being held at 95°C for 3.5 h. Figure 1a shows a GPC profile of the product. A molecular weight and polydispersity of the product were estimated to be 12000 and 1.77, respectively. The GPC demonstrated that the product contained two kinds of polymers with different molecular weights. The molecular weights at the peak maxima for the respective peaks were estimated to be 35000 and 16000. The larger molecular weight corresponds to be approximately twice the smaller. This suggests that the polymer with the larger molecular weight was generated through dimerization by coupling of the polymers with the smaller molecular weight. In the initiation process for the polymerization of styrene by benzoyl radical, it has been reported that aromatic substitution by benzoyl radical competitively occurs with addition of benzoyl radical to the vinyl group.^{18, 19} Benzoyl radical

Scheme 2.

attacks the aromatic ring to give a radical on the aromatic ring. It is expected that radicals are easily formed on aromatic rings having electron-withdrawing groups by attack of initiator radicals, because radicals on the aromatic rings are stabilized through delocalization by the electron-withdrawing groups.^{20, 21} In addition, formation of one-sided growing chain end is denied to elucidate the reason for observation of the bimodal GPC. This is accounted for by the fact that a peak of a polymer generated from one-sided growing species is generally observed as a shoulder at lower molecular weight side than a main peak in GPC.

We have already reported that TEMPO induces formation of initiator radicals for autopolymerization of styrene.¹² Although TEMPO has no ability to initiate radical polymerization of styrene, TEMPO serves as a counter radical for the autopolymerization to give a polymer with narrow polydispersity. In order to avoid dimerization of the polymers, the polymerization was carried out without BPO at 125°C (Scheme 3). The red color due to N–O radical faded out, after starting the polymerization. After 90 h, viscosity of the reaction system became high, and rotation of a stirrer bar ceased. The polymer with a molecular weight of 14000 and polydispersity of 1.41 was obtained. The

Figure 1. GPC profiles of polymers obtained through the polymerization of styrene by *o*-TEMPO with (a) and without BPO (b).

R: Thermal initiator

Scheme 3.

polydispersity of the product was narrower than that of the polymer obtained from the polymerization in the presence of BPO. GPC demonstrated that the dimerization was suppressed during the polymerization, because the polymer gave unimodal GPC.

The polymerization was explored in detail using *o*-TEMPO, *p*-TEMPO, and a mono radical compound (mo-TEMPO), in order to investigate living nature of the polymerization. mo-TEMPO is an ester of benzoic acid and 4-hydroxy-TEMPO. The results are shown in Table I. In all the cases, molecular weights increased over time, and with an increase of conversion. Polydispersities of the polymers obtained from *o*-TEMPO and *p*-TEMPO were somewhat broader than that of the polymer produced from mo-TEMPO. The very narrow polydispersities of the oligomers prepared were probably caused by not such a good resolution of GPC for such low molecular weight products.

In order to investigate the structure of polymers obtained from *o*- and *p*-TEMPO, the oligomers were subjected to ^1H NMR analysis. Figure 2 shows a ^1H NMR spectrum of a styrene oligomer produced by the polymerization with *o*-TEMPO. This oligomer was obtained from the polymerization carried out for 48 h. In addition of the main signals (1.3–2.5 ppm and 6.3–7.4 ppm) due to the styrene units, signals originating from *o*-TEMPO are discerned. The signals at 0.24 and 0.40 ppm are attributed to the tetramethyl protons of TEMPO moieties. The signals at 1.02 and 1.23 ppm are also due to the tetramethyl protons. The former two signals are observed when TEMPO moiety occupies the boat conformation, while the later are for chain conformation. The signal at 5.12 ppm is also based on TEMPO, and assigned to the methine

proton attached to the ester group. A signal originating from the methine bound to *o*-TEMPO is discerned at 3.97 ppm. The two signals observed at 7.4–7.7 ppm are due to the aromatic protons of *o*-TEMPO moiety. The signal at 7.48 ppm is attributed to the protons located at 3- and 4-positions, and the signal at 7.60 ppm is due to the protons at 5- and 6-positions. The oligomers obtained from the polymerization using *p*- and mo-TEMPO showed similar spectra to the spectrum for *o*-TEMPO, with the exception of the signals for the aromatic protons of the bi- or mono radical compounds. Spectra for the aromatic protons are shown in Figure 3. For the oligomer ($M_n = 1800$) obtained from *p*-TEMPO, only one signal is observed at 8.00 ppm (Figure 3b). Three types of signals are discerned for an oligomer ($M_n = 5900$) obtained from mo-TEMPO: the signal at 7.41 ppm originates from the proton located at 4-position on the ring of the benzoate,

Figure 2. ^1H NMR spectrum of the oligomer (conversion = 12%, $M_n = 1900$, and $M_w/M_n = 1.22$) obtained from *o*-TEMPO (solvent: CDCl_3). The polymerization was carried out at 125°C for 48 h.

Figure 3. ^1H NMR spectra of the oligomers obtained from *o*-TEMPO (a, $M_n = 1900$), *p*-TEMPO (b, $M_n = 1800$), and mo-TEMPO (c, $M_n = 5900$) (solvent: CDCl_3). The polymerization was carried out at 125°C for 48, 62, and 62 h by *o*-TEMPO, *p*-TEMPO, and mo-TEMPO, respectively.

Table I. Radical Polymerization of Styrene by *o*-, *p*-, and mo-TEMPO

	Time h	Conversion ^a %	M_n^b	M_w/M_n^b
<i>o</i> -TEMPO ^c	24	6	900	1.03
	48	12	1900	1.22
	72	45	8100	1.40
<i>p</i> -TEMPO ^c	90	82	14000	1.41
	62	16	1800	1.04
	70	38	7200	1.36
mo-TEMPO ^d	85	74	12000	1.33
	86	87	16000	1.29
	26	14	600	1.01
	62	40	5900	1.27
	70	64	8000	1.21
	89	81	9300	1.28
	95	87	12000	1.22

^aCalculated by GC. ^bEstimated by GPC based on polystyrene standards. ^c $[\text{St}]_0 = 8.73$ mmol, $[\text{o- or p-TEMPO}] = 0.0421$ mmol. ^d $[\text{St}]_0 = 3.75$ mmol, $[\text{mo-TEMPO}] = 0.0365$ mmol.

the signal at 7.54 ppm from the protons at 3- and 5-positions, and the signal observed at 7.99 ppm from the protons at 2- and 6-positions. We have already found in the TEMPO-mediated polymerization, that all the polymer chains obtained have TEMPO moiety at the chain end.¹² The absolute molecular weights of the oligomers were estimated based on intensity of the aromatic protons of styrene units and the TEMPO derivatives. The molecular weights were summarized in Table II.

Figure 4 shows time-conversion plots in the polymerizations by *o*-, *p*-, and mo-TEMPO. The conversions equally increased over time, although they had some difference in degree of acceleration. The difference may be based on mobility of the TEMPO moieties and on rate of the formation of the initiator radicals. Figure 5 shows the relationship between molecular weight and conversion. The molecular weight linearly increased with increasing the conversion. This suggests that the polymerization proceeded in accordance with a living mechanism. The molecular weights of the polymers obtained from *o*- and *p*-TEMPO were estimated to be smaller than calculated values, while those of the polymers from mo-TEMPO were larger. This may be accounted for because the aminoxy and ester groups located at the middle of the polymers have some influence on the poly-

mer conformation. When the initial concentrations of TEMPO radicals are identical for the three compounds of TEMPO, the molecular weight of the polymer produced from mo-TEMPO should be half the molecular weights of polymers obtained from *o*- and *p*-TEMPO. It was found that the molecular weight of the polymer obtained from mo-TEMPO was larger than half the molecular weights of the polymers obtained from *o*- and *p*-TEMPO. It was estimated to be 1.36 times larger than the half.

Study of relationship between molecular weight and the initial concentration of the biradical compound also demonstrated that the polymerization proceeded in accordance with a living mechanism. The results are listed in Table III. While the polydispersities maintained around 1.4, the conversions were high enough to compare molecular weights. Figure 6 shows plots of the molecular weights vs. the reciprocal of the initial concentration of *o*-TEMPO. It is obvious that the molecular weight is in inverse proportion to the initial concentration of *o*-TEMPO. These results indicate that the polymerization can control molecular weights of

Table II. Molecular Weights Estimated by GPC and ¹H NMR

	GPC ^a	¹ H NMR
<i>o</i> -TEMPO	1900	3380
<i>p</i> -TEMPO	1800	2390
mo-TEMPO	5900	5740

^aEstimated by GPC based on polystyrene standards.

Figure 4. Time-conversion plots for the polymerization of styrene using *o*-TEMPO (○), *p*-TEMPO (△), and mo-TEMPO (□). [St]₀ = 8.73 mmol for [*o*- or *p*-TEMPO]₀ = 0.0421 mmol, and [St]₀ = 3.75 mmol for [mo-TEMPO]₀ = 0.0365 mmol.

Figure 5. Plots of molecular weight vs. conversion in the polymerization of styrene using *o*-TEMPO (○), *p*-TEMPO (△), and mo-TEMPO (□). [St]₀ = 8.73 mmol for [*o*- or *p*-TEMPO]₀ = 0.0421 mmol, and [St]₀ = 3.75 mmol for [mo-TEMPO]₀ = 0.0365 mmol.

Table III. Relation between Molecular Weight and Initial Concentration of *o*-TEMPO^a

[<i>o</i> -TEMPO] ₀ 10 ² × mol L ⁻¹	Time h	Conversion ^b %	M_n^c	M_w/M_n^c
2.11	136	97	46000	1.43
2.34	142	100	34000	1.35
4.21	186	84	15000	1.45
8.43	144	79	10000	1.40

^a[St]₀ = 8.73 mmol. ^bCalculated by GC. ^cEstimated GPC based on polystyrene standards.

Figure 6. Plots of molecular weight vs. reciprocal of the initial concentration of *o*-TEMPO in the polymerization of styrene. [St]₀ = 8.73 mmol.

polymers by choice of the initial concentration of the biradical compounds.

The biradical compound has the potential to give symmetric block copolymers. 4-*tert*-Butoxystyrene (BSt) has similar reactivity to styrene in radical polymerization, and it has already found that the polymerization of BSt by TEMPO proceeded in accordance with a living mechanism.²² A polymer of BSt is easily converted by acid-catalyzed hydrolysis into poly(vinyl phenol). The polymerization of BSt was carried out in bulk at 125°C for 18 h, using a polystyrene as an initiator (Scheme 4). The polystyrene was obtained through the polymerization by *o*-TEMPO, and had a molecular weight of 31000 and polydispersity of 1.25. GPC analysis demonstrated that the polystyrene initiated the polymerization of BSt efficiently to give an ABA type of triblock copolymer (Figure 7). The copolymer was found to have 91000 as a molecular weight and 1.54 as polydispersity. The unit ratio of BSt to styrene was estimated by ¹H NMR as BSt/styrene = 0.75/0.25. The hydrolysis of the copolymer was performed at -5°C for 15 min with trifluoromethanesulfonic acid in a mixed solvent of toluene and trifluoroethanol. An insoluble polymer in THF was obtained, and the degree of hydrolysis was estimated as 57% based on ¹H NMR analysis.

CONCLUSIONS

The results obtained in this study give some significant suggestion. Firstly, it is that this polymerization occurred without adding initiators. This implies that initiator radicals were formed through

Scheme 4.

Figure 7. GPC profiles of a block copolymer (a) and a prepolymer (b).

spontaneous reaction between styrene molecules, because TEMPO has no ability to initiate the radical polymerization of styrene. It is expected that the formation of the initiator radicals was induced by the TEMPO compounds, based on our previous study.¹² The study demonstrated that concentration of the growing chain end was identical to the initial concentration of TEMPO and that all the polymer chains had TEMPO moiety at the chain end. It can be regarded that the TEMPO compounds are a kind of thermal-latent initiators when it is taken into account that the formation of initiator radicals were thermally induced by TEMPO having no ability to initiate the polymerization. Polymerization using initiators formed from monomers through induction by the counter radical has an advantage in preservation for a long period, over conventional polymerizations where initiators need to be added separately.

In the second place, it is that the TEMPO-based biradical compounds can be substituted for initiators which give both growing chain ends. The polymerization by the biradicals produces symmetric multiblock copolymers. It is interesting that the following monomers form the middle segments in symmetric block copolymers. The presence of the propagating species located at the middle of a copolymer is significant to protect the active species in preparing multiblock copolymers quantitatively.

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