Synthesis of Poly(tetrahydrofuran) with a Nitroxyl Radical at the Chain End and Its Application to Living Radical Polymerization

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ABSTRACT: The synthesis of poly(tetrahydrofuran (THF)) having 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) moiety at the chain end and its application as a polymeric counter radical to the living radical polymerization of styrene were performed. The TEMPO moiety could be introduced in quantitative efficiency by the reaction of living poly(THF) initiated by methyl trifluoromethanesulfonate with sodium 4-oxy-TEMPO. The resulting polymer could serve as a polymeric counter radical in the radical polymerization of styrene with benzoyl peroxide to give the corresponding block copolymer quantitatively. Furthermore, it was found that this radical polymerization proceeded in accordance with a living mechanism because the molecular weight of the block copolymer linearly increased with increasing conversion of styrene and was inversely proportional to the initial concentration of poly(THF).

Introduction

End-functional polymers have attracted considerable attention as prepolymers for synthesizing block and graft copolymers, star polymers, and polymer networks. There are a number of publications which discuss the synthesis of the end-functional polymers by various methods, including anionic, cationic, and radical polymerizations and chemical modification of polymer ends. Among these, cationic living polymerization of tetrahydrofuran (THF) can be conveniently utilized for the synthesis of polymers with quantitatively functionalized terminals. There are many publications on the synthesis of poly (THF)s, which have such specific terminal groups as amino,[1] mercapto,[2] azo,[3] allyl,[4] and transition metal complex,[5] by reaction of living poly(THF) with the corresponding low molecular weight compound. Publications have also been released on block copolymers and polymer networks using these corresponding prepolymers.

2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO), a stable nitroxyl radical, is known to act as an antioxidant for polyolefins and as a spin labeling agent in ESR study. It is an efficient mediator for the oxidation of monomeric and polymeric alcohols with copper(II),[6] iron(III),[7] or chlorine.[8] In recent years, TEMPO has been found to serve as a "counter radical" in living radical polymerization to give polymers with narrow polydispersities.[9−12] We have recently found that the polymers obtained had an aminoxy moiety at their terminals and that the molecular weights of the polymers were determined by the initial concentration of 4-methoxy-TEMPO rather than that of BPO, when the polymerizations of styrene[13] and of *p*-bromostyrene[14] were performed with BPO as an initiator in the presence of 4-methoxy-TEMPO. Polymers which have the nitroxyl radical at the terminals can be expected to behave not only as mediators for oxidation but also as polymeric counter radicals for propagating polymeric radicals. The use of polymeric counter radicals results in the formation of block copolymers by living radical polymerization. This paper describes the synthesis of poly(THF) having a nitroxyl radical at its chain end by the reaction of living poly(THF) with sodium 4-oxy-TEMPO and the application of it as a counter radical in living radical polymerization.

Experimental Section

Measurement. Gel permeation chromatography (GPC) was performed with a Toso HLC-802A instrument equipped with a Toso CP-8000 chromato processor. A combination of two polystyrene gel columns, Toso TSK Gel G4000H$_8$ and G2000$_8$, was used with THF as the eluent at 42 °C. The molecular weight was determined by calibrating with polystyrene standards. ^{1}H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer, and UV spectra were obtained with a Beckman DU-68 spectrophotometer. ESP spectra were recorded on a JEOL JES-TE 300 ESR spectrometer. Gas chromatography (GC) was performed with a Shimadzu GC-8A.

Materials. THF was purified by refluxing on sodium and then on lithium aluminum hydride for several hours and distilled over lithium aluminum hydride immediately before use. Methyl trifluoromethanesulfonate was distilled over phosphorus pentaoxide under nitrogen. 4-Hydroxy-TEMPO was prepared by the method reported previously.[15] The oil used for storing the sodium hydride was removed by washing with hexane: Sodium hydride (*ca*. 60 wt % in oil) was suspended in hexane and stirred with a magnetic stirrer at room temperature for 5 min, and then hexane was removed by decantation. Finally, the bare sodium hydride was dried *in vacuo* immediately before use. Commercial grade styrene was washed with an aqueous alkaline solution and water and distilled over calcium hydride. Benzoyl peroxide was precipitated from chloroform and then recrystallized in methanol at 0 °C. 4-Methoxy-TEMPO to be used for the calibration of UV absorption intensity was prepared by the method described previously.[16] Toluene as an internal standard in GC was distilled over sodium. Extrapure grade phenylhydrazine for ^{1}H NMR studies was used without further purification.

Reaction of Living Poly(THF) with Sodium 4-Oxy-TEMPO. Cationic polymerization was carried out in a baked flask with a three-way stopcock at room temperature and under a dry nitrogen atmosphere. To 100 mL of THF was added 0.37 mL (3.27 mmol) of methyl trifluoromethanesulfonate at room temperature, and the mixture was stirred at room temperature for 7 min. Sodium 4-oxy-TEMPO was separately prepared as follows: 1.69 g (9.81 mmol) of 4-hydroxy-TEMPO dissolved in 11 mL of THF was added to sodium hydride (352 mg, 14.7 mmol) at room temperature, and the mixture was stirred at room temperature for 2 h under nitrogen. A white suspension of sodium 4-oxy-TEMPO thus prepared was added to the THF solution of the living poly-

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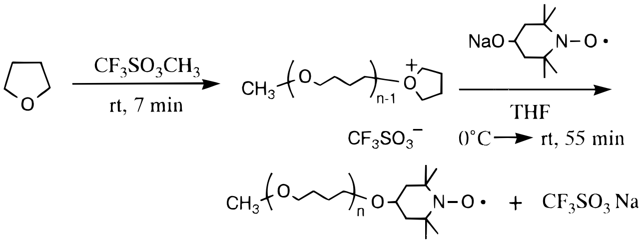
Table 1. Reaction of Living Poly(THF) with Sodium 4-Oxy-TEMPO

					M_n						
						^{1}H NMR					
polymerization time, min	polymer	isolated yield, g	DI[a]	content of TEMPO,[b] mmol/g	UV[c]	OCH_3[d]	TEMPO[e]	GPC[f]	M_W/M_n[f]	g value[g]	A_N,[g] G
7	PT-1	1.53	1.17	1.00	1000	1170	1270	1520	1.38	2.00694	15.82
15	PT-2	4.61	1.24	0.651	1540	1910	2060	3300	1.43	2.00698	15.84
30	PT-3	20.6	1.03	0.180	5560	5730	5870	10600	1.26	2.00700	15.85

[a] Degree of introduction of TEMPO moiety into the polymer chain end. [b] Content of TEMPO attached to the polymer chain end. [c] Estimated by the content of TEMPO. [d] Estimated by ^{1}H NMR based on the intensity ratio of methylene protons at 1.16 ppm to methyl ones at 3.32 ppm. [e] Estimated by ^{1}H NMR based on the intensity ratio of methylene protons at 1.16 ppm to methyl ones at 1.23 and 1.31 ppm. [f] Estimated by GPC based on standard polystyrenes. [f] Estimated by ESR at room temperature in toluene.

Scheme 1



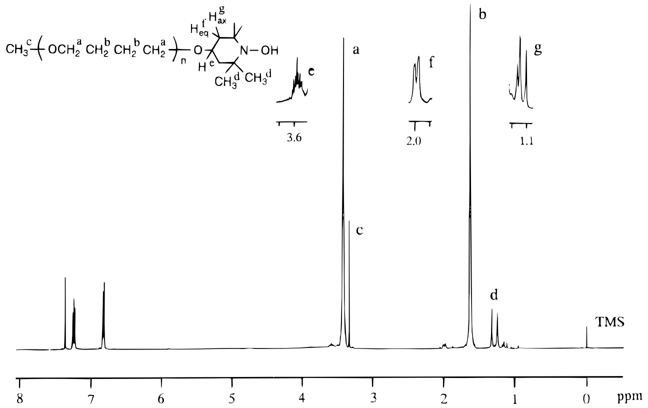


Figure 1. ^{1}H NMR spectrum of the polymer (Table 1, PT-1) obtained by the reaction of the living poly(THF) with sodium 4-oxy-TEMPO (solvent: $CDCl_3$, in the presence of phenylhydrazine).

(THF) at 0 °C. The mixture was stirred at 0 °C for 5 min, kept at room temperature for the following 55 min, and then quenched with water. The THF remaining in the product was removed by evaporation under a reduced pressure, and the residue was dissolved in hexane. This hexane solution was washed with water several times, dried over anhydrous magnesium sulfate, and then evaporated to remove hexane. The product was dried *in vacuo* at 50 °C for several hours, yielding 1.53 g of the polymer.

Radical Polymerization of Styrene in the Presence of PT-1. Styrene (1.0 mL, 8.70 mmol), BPO (21 mg, 0.0866 mmol), and PT-1 (115 mg, containing 0.115 mmol of the TEMPO moiety) were placed in an ampule. After degassing, the ampule was sealed *in vacuo*. The polymerization was carried out for 3.5 h at 95 °C and then continued for another 64 h at 125 °C. It was terminated by cooling with liquid nitrogen. The product was dissolved in 10 mL of dichloromethane, purified by repeated precipitations from dichloromethane into methanol, and finally lyophilized with benzene, yielding 886 mg of the block copolymer. After addition of toluene as an internal standard, the dichloromethane solution was subjected to GC to estimate the conversion of styrene.

Results and Discussion

Synthesis of Poly(THF) with TEMPO at the Chain End. Living poly(THF) was prepared by cationic polymerization of THF by methyl trifluoromethanesulfonate as an initiator in bulk at room temperature for 7 min under nitrogen. The living cationic poly(THF) thus obtained was subjected to the reaction with sodium 4-oxy-TEMPO, which was prepared by the reaction of 4-hydroxy-TEMPO with sodium hydride in THF (Scheme 1 and Table 1, PT-1). The polymer, isolated and purified by repeated washing of the hexane solution of the product with water, was highly viscous and red, indicating the presence of the living nitroxyl radical.

The molecular weight and polydispersity index of the resulting polymer were determined by GPC, being calibrated with standard polystyrenes. The polymer obtained showed a unimodal GPC curve, which gave the molecular weight and the polydispersity index as 1520 and 1.38, respectively. Since TEMPO can be easily reduced by hydrazines to the corresponding hydroxylamine,[17] ^{1}H NMR measurement was performed for the poly(THF) modified with 4-hydroxy-TEMPO in the presence of a small amount of phenylhydrazine. The ^{1}H NMR spectrum recorded is shown in Figure 1. The signals at 6.8 and 7.2 ppm are due to the phenylhydrazine added. Two signals at 3.39 (a) and 1.61 ppm (b) could have originated from two types of methylene protons; one was attributed to the methylene bonding to the oxygen atom (a) and the other to the methylene group (b) in the main chain. In addition, a singlet signal was observed at 3.32 ppm (c), assigned to methoxy protons (c) attached to the polymer head group. Another two singlet signals were observed at 1.23 and 1.31 ppm, assigned to methyl (d) protons. Further, methine (e) and two types of proton signals of methylene, equatorial (f) and axial (g), could be discerned at 3.6 (e), 1.98 (f), and 1.12 ppm (g), respectively. These signals were due to the TEMPO moiety attached to the polymer chain end. The intensity ratio of methylene protons at 1.61 ppm (b) to the methyl ones at 3.32 ppm (c) allowed us to calculate a number-average molecular weight. The molecular weight thus calculated was 1170, which was about 20% smaller than that estimated by GPC. It was possible to calculate another molecular weight using the intensity ratio of methylene protons at 1.61 ppm (b) to methyl ones at 1.23 and 1.31 ppm (d). The molecular weight thus calculated was 1270, which was almost equal to 1170. This suggests that TEMPO was quantitatively introduced into the polymer chain end.

Figure 2 shows the UV spectrum of the resulting polymer. It was found that the polymer had a characteristic absorption λ_{max} at 460 nm due to the nitroxyl radical. The degree of introduction of TEMPO was estimated to be 1.17 based on the molecular weight of the polymer ($M_n = 1170$) calculated from ^{1}H NMR, and the absorbance intensity at 460 nm, which was calibrated with 4-methoxy-TEMPO. Furthermore, the content of TEMPO attached to the polymer chain end could be calculated by the absorbance at 460 nm. The content of TEMPO per gram of polymer was 1.00 mmol/g. Therefore, the molecular weight was also calculated by

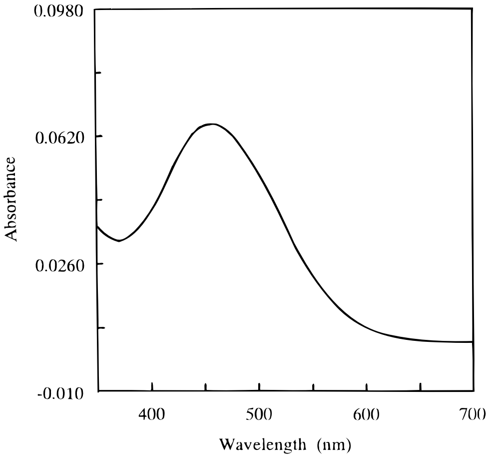


Figure 2. UV spectrum of the resulting polymer (Table 1, PT-1) obtained by the reaction of the living poly(THF) with sodium 4-oxy-TEMPO (solvent:toluene).

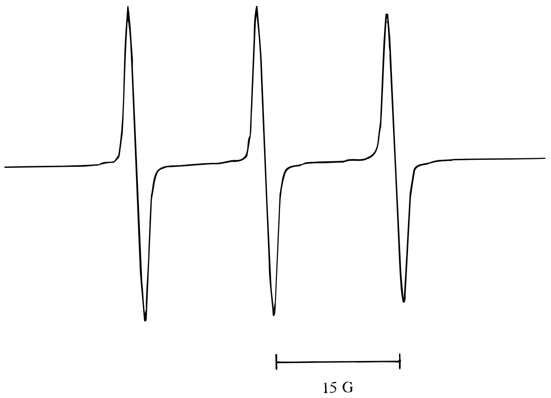


Figure 3. ESR spectrum of PT-1 (solvent: benzene, at room temperature).

this value. The molecular weight thus calculated was 1000, which was almost equal to 1170. On the basis of these UV analyses, we concluded that it is possible to introduce TEMPO into the polymer chain end in quantitative efficiency by the reaction of the living poly(THF) with sodium 4-oxy-TEMPO.

When the polymerization of THF was conducted for 15 or 30 min, red polymers were obtained in a solid state (Table 1, PT-2 and -3). For both polymers, unimodal GPC curves were obtained and TEMPO could be quantitatively introduced into the polymer chain ends on the basis of the degrees of introduction estimated from the UV studies of the polymers.

Figure 3 illustrates a typical ESR spectrum of PT-1. All the resulting polymers showed three sharp signals, and these g values and hyperfine coupling constants (A_N) were almost identical to those of 4-methoxy-TEMPO ($g = 2.00699$, $A_N = 15.81$ G) or 4-hydroxy-TEMPO ($g = 2.00704$, $A_N = 15.88$ G). This suggests that the stability of TEMPO attached to the polymer chain end was not affected by the polymer main chain under these conditions, and therefore, these polymeric TEMPOs have the potential to serve as counter radicals in living radical polymerization in the same manner as monomeric TEMPO.

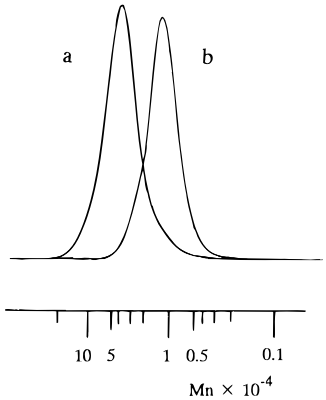


Figure 4. GPC profiles of the block copolymer, PTS-3 (a), and the prepolymer PT-3 (b).

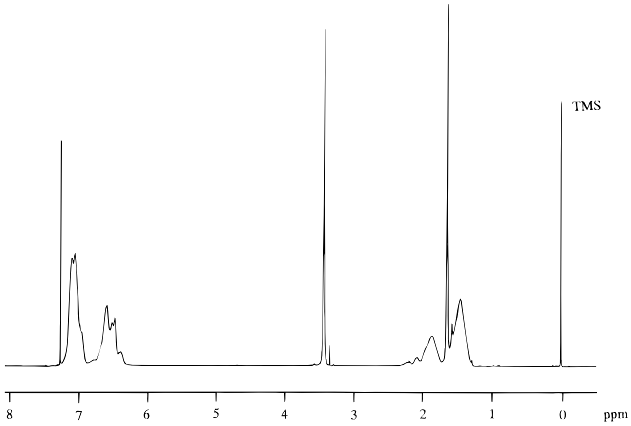


Figure 5. ^{1}H NMR spectrum of PTS-3 obtained by the radical polymerization of styrene by BPO and PT-3 (solvent: $CDCl_3$).

Table 2. Radical Polymerization of Styrene by BPO and PT

pre-polymer	time, h	conv,[b] %	yield, mg	product		units[c]		co-polymer
				M_n[a]	M_W/M_n[a]	THF	St	
PT-1	72	88	886	9690	1.22	14	103	PTS-1
PT-2	24	88	850	12600	1.25	24	112	PTS-2
PT-3	21	94	3360	38800	1.40	77	337	PTS-3

[a] Estimated by GPC based on standard polystyrenes. [b] Calculated by GC. [c] Estimated by ^{1}H NMR.

Living Radical Polymerization of Styrene in the Presence of Poly(THF) with a TEMPO Moiety at the Chain End. Radical polymerization of styrene was performed with BPO as an initiator in the presence of PT. The polymerization was carried out in bulk at 125 °C after being held at 95 °C for 3.5 h following Georges' method.[9] The results are shown in Table 2. The conversion of styrene was estimated by gas chromatography (GC) using a dichloromethane solution of the product. The solution contained a small amount of toluene as an internal standard. The conversions were very high, and the polydispersity indices of the resulting copolymers were similar to those of the prepolymers.

Figure 4 illustrates a typical GPC profile obtained for the product before precipitation. The resulting copolymer showed a unimodal GPC curve, and no peak due to the prepolymer was observed. Furthermore, the prepolymer was not detected at all, even from a filtrate of methanol used to isolate the resulting copolymer by precipitation. These results indicate that all the PTs had the TEMPO moiety at their chain ends and that all the TEMPO moieties were engaged in this polymerization.

Figure 5 shows a ^{1}H NMR spectrum of the resulting copolymer. It is obvious that the signals at both 1.6 and 3.4 ppm originated from THF, while those at 1.2−2.3 and 6.3−7.4 ppm could be attributed to styrene. The number-average degree of polymerization of the respective units in the copolymer was also estimated from the

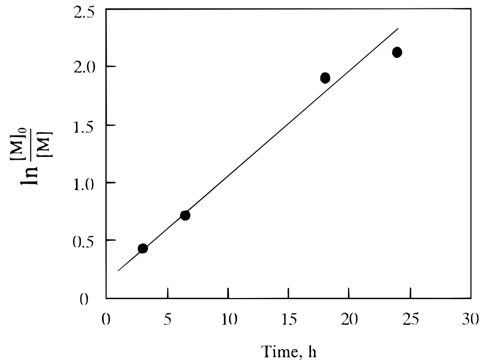


Figure 6. First-order time−conversion plots in the polymerization of styrene by BPO and PT-2.

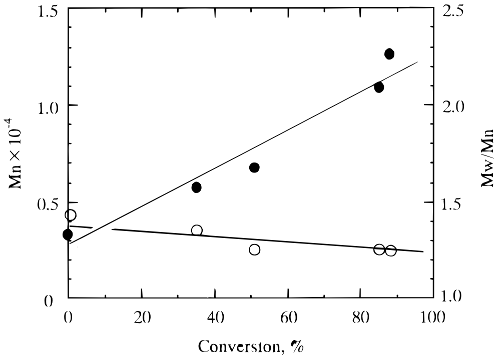
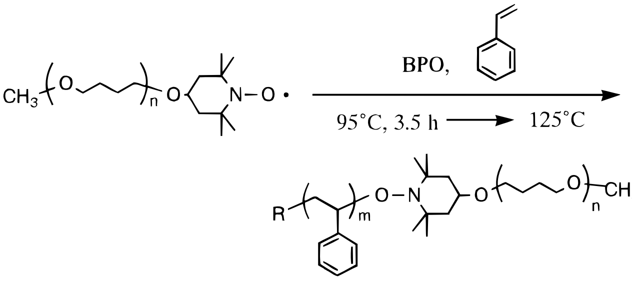


Figure 7. Conversion−molecular weight and polydispersity index plots in the polymerization of styrene by BPO and PT-2.

Scheme 2



intensity ratio of methylene protons at 3.4 ppm to phenyl ones at 6.3−7.4 ppm. These results are indicative of the quantitative formation of poly(THF)-*block*-polystyrene (PTS) (Scheme 2).

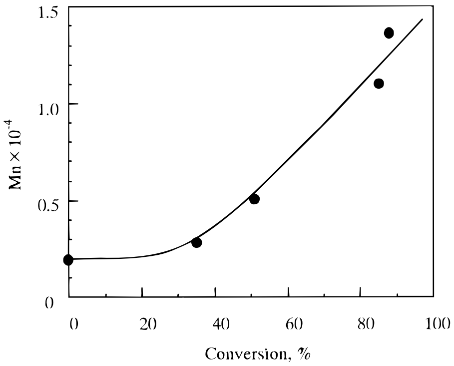


Figure 8. Conversion−molecular weight plots in the polymerization of styrene by BPO and PT-2.

Table 3. Radical Polymerization of Styrene by BPO and PT-2[a]

$[\text{TEMPO-PT}]_0$,[b] $\times 10^3$ mol/L	time, h	conv,[c] %	product		$1/[\text{TEMPO-PT}]_0$, L/mol
			M_n[d]	M_w/M_n[d]	
182	163	100	5750	1.40	5.49
91.1	163	94	11100	1.29	11.0
47.1	48	97	18700	1.27	21.2
25.9	48	99	27000	1.37	38.6

[a] $[\text{TEMPO-PT}]_0/[\text{BPO}]_0$: 1.3, in all cases. [b] The initial concentration of the TEMPO moiety attached to PT-2. [c] Calculated by GC. [d] Estimated by GPC based on standard polystyrenes.

The relation between the molecular weight of the polymer produced and the conversions of styrene was investigated to confirm whether this radical polymerization proceeds in accordance with a living mechanism. The first-order time-conversion, conversion−molecular weight, and polydispersity index plots in the polymerization with PT-2 are shown in Figures 6 and 7, respectively. It is clear that $\ln[M]_0/[M]$ linearly increases with increasing time and that the molecular weight is in proportion to the conversion. The molecular weights were not real because they were estimated by GPC based on standard polystyrenes. The molecular weights of the copolymers could be estimated by NMR analysis and the molecular weight of the prepolymer. Figure 8 shows another conversion−molecular weight plot thus calculated. A straight line was not obtained below 35% conversion, although the plots almost showed a straight line above 35% conversion. This may be accounted for by the fact that below 35% conversion, styrene was consumed during formation of the thermal initiator or thermal polymerization and that the low molecular weight product thus produced was removed by freeze-drying, but this is not clear. In a living polymerization system, the ultimate degree of polymerization (DP) ought to be defined by eq 1.[18]

$$\text{DP} = [M]/[I] \tag{1}$$

where [M] denotes the initial concentration of the monomer, and [I] the concentration of the growing polymer chain. We have already found in the living radical polymerization of styrene by BPO and 4-methoxy-TEMPO that [I] was determined not by the initial concentration of the initiator but by that of the corresponding nitroxyl radical.[13] Therefore, the molecular weight of the polymer produced (MW_P) is supposed to be proportional to the reciprocal of the initial concentration of TEMPO attached to the polymer chain end ($[\text{TEMPO-PT}]_0$) in this system as is given by eq 2.

$$MW_P = \frac{[M]}{[\text{TEMPO-PT}]_0} \times MW_M \tag{2}$$

where MW_M denotes the molecular weight of the monomer. The relation between the molecular weight and $[\text{TEMPO-PT}]_0$ was explored using PT-2. The results are summarized in Table 3. The conversions were very high in all cases and the molecular weight inversely decreased by an increase of $[\text{TEMPO-PT}]_0$. Figure 9 shows the plots of the molecular weight versus the reciprocal of $[\text{TEMPO-PT}]_0$. It was found that the molecular weight of the copolymer was directly proportional to $1/[\text{TEMPO-PT}]_0$ and could be controlled by the molar ratio of the monomer to this polymeric counter radical.

Conclusions

The synthesis of poly(THF) with a nitroxyl radical at the chain end was performed by the reaction of sodium 4-oxy-TEMPO with living poly(THF), which was obtained by cationic polymerization of THF by methyl trifluoromethanesulfonate as an initiator. The TEMPO

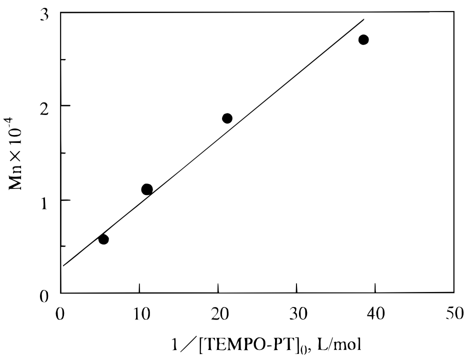


Figure 9. Plot of the molecular weight versus the reciprocal of $[\text{TEMPO-PT}]_0$ in the polymerization of styrene by BPO and PT-2.

moiety was found to be introduced to the polymer chain end in quantitative efficiency. The resulting polymers were able to act as polymeric counter radicals in the polymerization of styrene by BPO used as an initiator to give the corresponding block copolymer. Furthermore, it was found that the radical polymerization proceeded in accordance with living mechanisms, because the molecular weight of the block copolymer increased by an increase of the conversion of styrene, and was directly proportional to the reciprocal of the initial concentration of TEMPO-PT. Therefore, sodium 4-oxy-TEMPO can be regarded as a transforming agent from living cationic to living radical polymerization. A few transformation reactions from cationic to radical polymerization have already been studied by some investigators. One of the authors has reported on the transformation from cationic polymerization of 2-benzylidene-1,3-dioxane to radical polymerization of methyl methacrylate (MMA) by 4-methoxy-2,2,6,6-tetramethylpiperidinium hexafluoroantimonate, which occurred by one-electron oxidation of 4-methoxy-TEMPO.[19] On the other hand, Goethals and co-workers have described that the azo-containing poly(THF) prepared by the reaction of a living cationic poly(THF) with disodium 4,4′-dicyano-4,4′-azodivalerate was utilized for a block copolymerization with either styrene or MMA.[3] It is, however, difficult to control the molecular structure of the block copolymers using these procedures, because chain transfer reactions occurred in both cases. Therefore, this transformation from living cationic to living radical polymerization with sodium 4-oxy-TEMPO is useful to give well-defined block copolymers and can be regarded as the first attempt to achieve transformation from living cationic to living radical polymerization.

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