Living Radical Polymerization of Styrene in the Presence of 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, and Radical Transformation of the Resulting Polymer by Other Radicals

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Radical polymerization of styrene was performed by benzoyl peroxide (BPO) as an initiator, in the presence of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HTEMPO) at 95 °C for 3.5 h, and then continued at 125 °C for another designated period. The polymerization was found to proceed in the accordance with a living mechanism, because the molecular weight of the polystyrene was in proportion to the conversion and was in inverse proportion to the initial concentration of HTEMPO. Further, it was found that all the resulting polystyrene had the HTEMPO moiety at their chain ends and that the initial concentration of HTEMPO determined the molecular weight of the polymer produced, from ^{1}H NMR analysis. The radical transformation of the HTEMPO-modified polystyrene by 4-methoxy-TEMPO (MTEMPO), was also performed. The transformation proceeded to give the polystyrene with MTEMPO moiety at the chain end, although the degree of the transformation decreased over time. It was found that decomposition of the MTEMPO-modified polystyrene obtained by the reaction occurred during the reaction.

Great interest has been devoted to living radical polymerization in recent years. There are a great number of publications on the polymerization related to experiments which involve the use of various compounds as controlling agents for chain growth. Publications have been released on the polymerization by some organometallic compounds with cobalt,[1)] copper,[2)] and ruthenium.[3)] Braun and co-workers have performed the polymerization of methyl methacrylate (MMA) by 1,1,2,2-tetraphenyl-1,2-diphenoxyethane to obtain living poly(MMA).[4)] Otsu and his group have proposed "iniferter" to achieve the living radical polymerization with *S*-benzyl diethyldithiocarbamate,[5)] while Druliner has found that the radical polymerization with diazonium ions gave living polymers.[6)] Rizzardo has revealed that the radical polymerization in the presence of nitroxyl radicals has resulted in the formation of living polymers.[7)] Among these methods, remarkable progress has been made in the living radical polymerization of styrene using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) since Georges and his group succeeded obtaining a polymer with narrow polydispersity (< 1.3) by the polymerization in the presence of TEMPO.[8)] There are a number of publications on kinetics and mechanisms of the polymerization,[9)] and many publications have also been released on various molecular designs using this polymerization.[10)]

Living polymerization has great advantages not only in that it can conveniently synthesize polymers with molecular weights which are strictly controlled, but also in that it can quantitatively introduce functional groups into the polymer chain ends. There is no paper on synthesis of end-functional polymers by the living radical polymerization. We have already found that all 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 (MTEMPO), rather than that of benzoyl peroxide (BPO), when the radical polymerization of styrene was performed by BPO as an initiator in the presence of MTEMPO.[11)] If TEMPO with a functional group serves as a counter radical in the polymerization, it is expected that polymers which have the functional group at their chain ends can be quantitatively obtained through the radical polymerization. Furthermore, it is also possible to introduce functional groups into the growing polymer chain ends by exchanging the TEMPO moiety attached to the polymer chain end, for other radicals, if the exchange reaction proceeds. In this study, the radical polymerization of styrene was performed by TEMPO which has the hydroxy group. A hydroxy group is the most important group in organic syntheses including polymer syntheses, because it is easily converted into various functional groups. Therefore, polymers with hydroxy moieties are able to be precursors for a number of other end-functional polymers, macromonomers, and block and graft copolymers. This paper describes the radical polymerization of styrene by BPO as an initiator in the presence of 4-hydroxy-TEMPO (HTEMPO), and the radical transformation of the HTEMPO-terminated polystyrene by other radicals.

Experimental

General. ^{1}H NMR spectra were obtained with a Bruker ARX-500 NMR spectrometer. 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 of Toso TSK gel G4000H$_8$ and G2000H$_8$ was used with THF as the eluent at 42 °C. Gas chromatography (GC) was performed with a Shimadzu GC-8A.

Materials. HTEMPO and MTEMPO were prepared by the methods reported previously.[12] BPO was purified by precipitation from chloroform into methanol and then crystallized in methanol at 0 °C. Commercial grade styrene was washed with an aqueous alkaline solution and water, and distilled over calcium hydride. Benzene was washed with sulfuric acid, an alkaline solution and water, and then distilled over sodium. Toluene as an internal standard in GC was distilled over sodium. Pure grade di-α-cumyl peroxide was used without further purification.

General Procedure for Radical Polymerization of Styrene by BPO in the Presence of HTEMPO. Styrene (1.00g, 9.60 mmol), BPO (23.0 mg, 0.0949 mmol), and HTEMPO (19.0 mg, 0.110 mmol) were placed in an ampule. After degassing the content, the ample was sealed in vacuo. The polymerization was carried out at first for 3.5 h at 95 °C, and then continued for another 42 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 to methanol, and finally lyophilized with benzene. The purified polymer (695 mg) was obtained. Conversion of styrene was estimated to be 91% by GC of a dichloromethane solution of the product after addition of toluene as an internal standard.

Radical Transformation of the HTEMPO-Modified Polystyrene by MTEMPO. The HTEMPO-modified polystyrene (300 mg, 0.138 mmol, M_n: 2180, M_w/M_n: 1.15), MTEMPO (29.0mg, 0.156 mmol), and benzene (1 mL) were placed in an ampule. After degassing the content, the ampule was sealed in vacuo. The reaction was carried out at 130 °C for 24 h. It was terminated by cooling with liquid nitrogen. The product was purified by repeated precipitations from dichloromethane to methanol, and finally lyophilized with benzene. The purified polymer (135 mg) was obtained.

Radical Transformation of the HTEMPO-Modified Polystyrene by Di-α-cumyl Peroxide. The HTEMPO-modified polystyrene (502 mg, 0.0831 mmol, M_n: 6040, M_w/M_n: 1.21), di-α-cumyl peroxide (32.0 mg, 0.118 mmol), and benzene (1.5 mL) were placed in an ampule. After degassing the content, the ampule was sealed in vacuo. The reaction was carried out at 125 °C for 24 h. It was terminated by cooling with liquid nitrogen. The product was purified by repeated precipitations from dichloromethane to methanol, and finally lyophilized with benzene. The purified polymer (266 mg) was obtained.

Results and Discussion

Living Radical Polymerization of Styrene in the Presence of HTEMPO. Radical polymerization of styrene was performed in bulk by BPO as an initiator, in the presence of HTEMPO (1.17 molar amounts to BPO) at 125 °C for designated periods, after being held at 95 °C for 3.5 h following Georges' method.[5b] The conversion of styrene were estimated by GC with toluene as an internal standard. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of the resulting polymers were determined by GPC, which was calibrated with standard polystyrenes. The relationships between the molecular weight, conversion, and polymerization time are summarized in Table 1.

Table 1. Polymerization of Styrene in the Presence of HTEMPO[a)]

Time/h	Convn/%[b)]	M_n[c)]	M_w/M_n[c)]
30	23	1970	1.14
34	42	3170	1.22
37.5	85	6860	1.21
42	91	8500	1.21

a) Polymerized under the conditions of HTEMPO/BPO, 1.17 in all the cases. b) Estimated by GC. c) Estimated by GPC based on polystyrene standards.

All the resulting polymers showed unimodal GPC. It is obvious that the molecular weights and conversions increased over the time, and the polydispersity indices were less than 1.3 in the entire region of conversion in the present study. Figure 1 shows plots of the molecular weights versus conversion in the polymerization. The molecular weight linearly increased with an increase of the conversion, suggesting that the polymerization proceeded in accordance with a living mechanism. In a living polymerization system, the ultimate molecular weight of the polymer produced (*MW*p) ought to be defined by Eq. 1.[13)]

$$MW\mathrm{p} = \frac{[\mathrm{M}]}{[\mathrm{P}]} \times MW\mathrm{m} \tag{1}$$

where [M] denotes the concentration of the monomer consumed, [P] the concentration of the growing polymer chain, and *MW*m the molecular weight of the monomer. We have already found in the living radical polymerization of styrene by BPO and MTEMPO, that [P] was equal not to the initial concentration of BPO, but to that of MTEMPO.[11)] Therefore, the molecular weight of the polymer produced is represented by Eq. 2 using the initial concentration of MTEMPO ($[\mathrm{MTEMPO}]_0$) in place of [P].

$$MW\mathrm{p} = \frac{[\mathrm{M}]}{[\mathrm{MTEMPO}]_0} \times MW\mathrm{m} \tag{2}$$

The molecular weight of the polystyrene is supposed to be proportional to the reciprocal of the initial concentration of HTEMPO ($[\mathrm{HTEMPO}]_0$), if the polymerization by

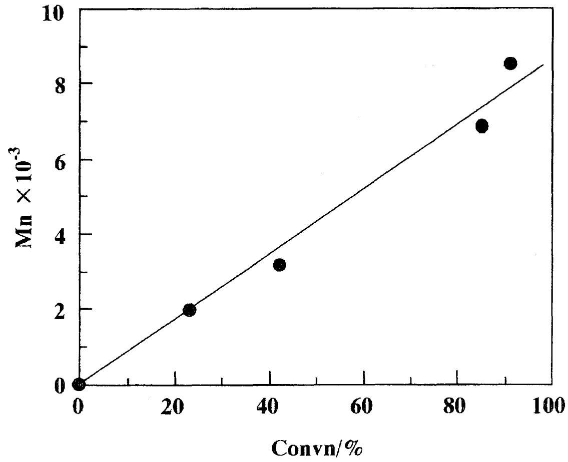


Fig. 1. Conversion-molecular weight plots in the polymerization of styrene by BPO and HTEMPO.

HTEMPO proceeds in the accordance with a living mechanism. The effect of the concentration of HTEMPO on the molecular weight of the resulting polystyrene was studied under the condition that the initial molar ratio of HTEMPO to BPO was 1.17. The results are summarized in Table 2. The conversions were very high in all the cases. It is obvious that the molecular weights decreased with an increase of $[\mathrm{HTEMPO}]_0$. Figure 2 shows the relationship between the molecular weight and the reciprocal of $[\mathrm{HTEMPO}]_0$. The molecular weights were found to be directly proportional to $1/[\mathrm{HTEMPO}]_0$. These results indicate that the polymerization proceeded in the accordance with a living mechanism.

The polystyrene with a lower molecular weight was also examined by ^{1}H NMR, to investigate the structure of the polymer obtained. The polymerization was carried out by BPO and HTEMPO ($[\mathrm{HTEMPO}]_0/[\mathrm{BPO}]_0$: 1.17) for 15 h at 125 °C, after 3.5 h at 95 °C. The polymer produced was purified by repeated precipitations from dichloromethane into methanol, and lyophilized with benzene. The ^{1}H NMR spectrum of the resulting polystyrene (M_n: 2180, M_w/M_n: 1.15) is shown in Fig. 3a. The signals at 1.2—2.5 (a) and 6.2—7.3 ppm (b) were assigned to the methylene and methine protons (a), and aromatic ones of the main chain (b), respectively. A signal was observed at 7.85 ppm (c) originating from the aromatic proton at *ortho* position of the benzoyl moiety, which was attached to the polymer head group. The signal observed at 0.25, 0.35, 0.95, and 1.15 ppm (d) were assigned to the methyl protons from HTEMPO attached to the polymer end group. The signals at 3.7—5.0 ppm (e) were also assigned to the three types of protons; the methylene bonded to the benzoyl moiety, the methine coupled to HTEMPO, and another methine bonded to hydroxy group of HTEMPO. These signals were assigned on the basis of the ^{1}H NMR spectra of authentic compounds.[10c,14] It was found that not all the polymers had the benzoyl moiety at their heads, because the molar ratio of HTEMPO to the benzoyl moiety was 1.16, which was calculated by the intensity ratio of the three types of protons (e) to the aromatic ones (c) located at the *ortho* position of the benzoyl group. This implies that the polymerization occurred not only by the presence of BPO, but also by thermal initiation. The thermal initiation took place probably in the accordance with a Mayo mechanism. Furthermore, this value was almost equal to the initial molar ratio of HTEMPO to BPO, 1.17. Therefore, we proved that one molecule of benzoyl radical was generated from one molecule of BPO. This result agreed with that drawn by Veregin.[9b] The molecular weight of the resulting polystyrene was estimated to be 2220 on the basis of the intensity ratio (Hb/He) of the aromatic protons of styrene (b) to the protons at 3.7—5.0 ppm (e), when the molar ratio of HTEMPO to the benzoyl moiety, 1.16, as described above, was taken into account. This result indicates that all the resulting polymers had a HTEMPO moiety at their chain ends, and that the total amounts of HTEMPO added had engaged in the polymerization. This means that HTEMPO controlled not only the chain growth in the polymerization initiated by BPO, but also that in the thermal polymerization (Scheme 1). These results agreed with our previous work on the living radical

Table 2. Relationship between Molecular Weights of Polystyrenes and Initial Concentration of HTEMPO[a)]

$[\mathrm{HTEMPO}]_0$ $\mathrm{mol\,dm^{-3}} \times 10^3$	Convn[b)] %	M_n[c)]	M_w/M_n[c)]
26.3	97	27800	1.26
51.3	94	16500	1.21
98.6	91	8500	1.21
209	100	6460	1.44

a) Polymerized for 42 h at 125 °C after 3.5 h at 95 °C under the conditions of HTEMPO/BPO, 1.17 in all the cases. b) Estimated by GC. c) Estimated by GPC based on polystyrene standards.

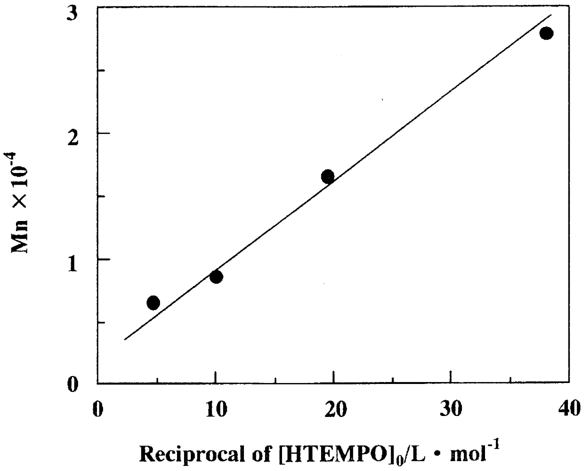


Fig. 2. Plots of the molecular weight versus the reciprocal of the initial concentration of HTEMPO in the polymerization of styrene by BPO and HTEMPO.

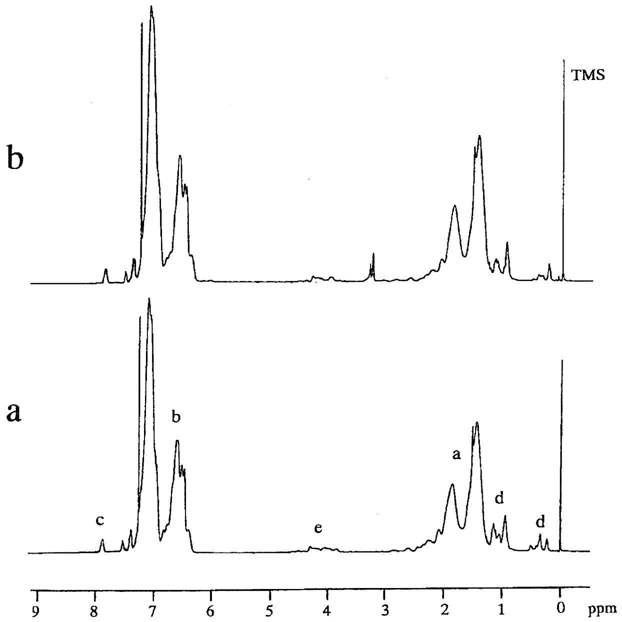
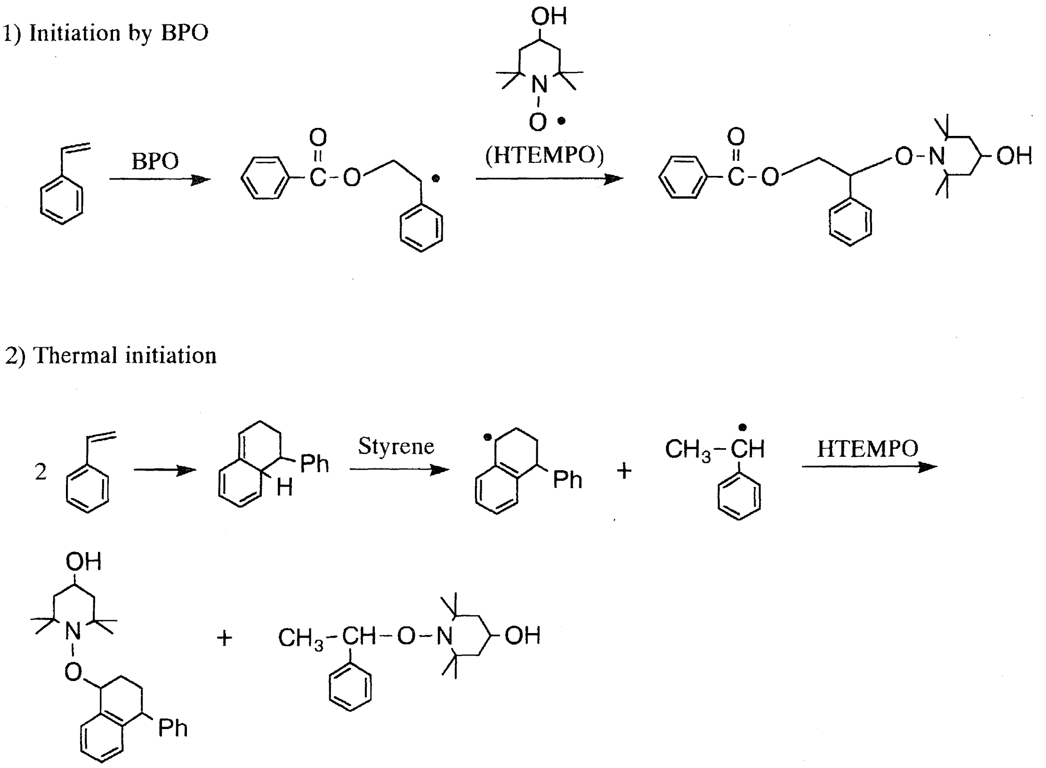


Fig. 3. ^{1}H NMR spectra of the polystyrene (M_n: 2180, M_w/M_n: 1.15) (a), and of the polystyrene obtained by the transformation by MTEMPO (b). (Solvent: $\mathrm{CDCl_3}$).

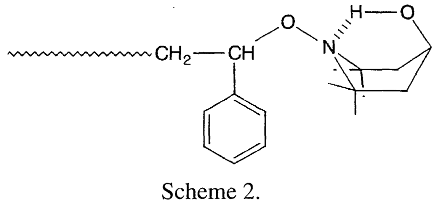


Scheme 1.

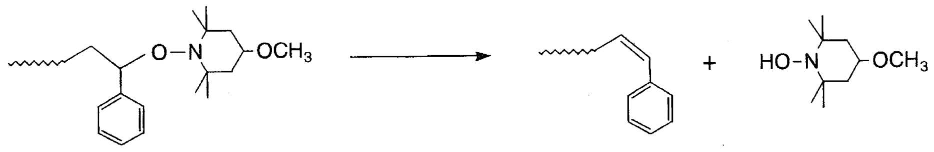
polymerization of styrene by BPO and MTEMPO.[11)]

Radical Transformation of the Polystyrene with HTEMPO Moiety by Other Radicals. The TEMPO moiety attached to the polymer chain end can be exchanged for other radicals with functional groups, if the exchange reaction proceeds. The radical transformation of the HTEMPO-terminated polystyrene obtained by the polymerization was performed by MTEMPO, to investigate the possibility of the exchange reaction. MTEMPO can be regarded as a model compound for TEMPO-supported polymers which give block or graft copolymers by the radical transformation. The transformation of the HTEMPO-modified polystyrene was carried out by MTEMPO in benzene at 130 °C for 24 h. The polystyrene with a lower molecular weight (M_n, 2170 and M_w/M_n, 1.15) was used for the reaction. Figure 3b shows the ^{1}H NMR spectrum of the product obtained by the reaction. The signal was discerned at 3.25 ppm, assigned to the methoxy protons from MTEMPO, in the spectrum of the resulting polymer, although no signal was observed at 3.25 ppm in that of the polymer before the reaction. Further, the signals of the methyl protons from HTEMPO or MTEMPO were observed at 0.2—0.6 and 0.8—1.2 ppm, in the spectra of the polystyrenes both before and after the reaction. These results indicate that the radical transformation of the HTEMPO-modified polystyrene was caused by MTEMPO. The degree of transformation was estimated to be 79% by the intensity ratio of the methoxy protons to the aromatic ones located at *ortho* position of the benzoyl moiety, when the molar ratio of HTEMPO to the benzoyl moiety, 1.16, was taken into consideration. This result suggests that the HTEMPO-modified polystyrene releases HTEMPO more easily than the MTEMPO-modified one releases MTEMPO, because in the former polystyrene, the intramolecular hydrogen bonding can be formed between the N atom and the hydroxy group of the HTEMPO moiety (Scheme 2). In addition, it was found that the coupling between the polystyrenyl radicals did not occur at all during the reaction, because the resulting polymer showed a unimodal GPC and its molecular weight and polydispersity index (M_n: 2540, M_w/M_n: 1.12) were similar to those of the prepolymer (M_n: 2170, M_w/M_n: 1.15).

The variation of the degree of transformation with time was shown in Fig. 4. The degree reached 80% and then, decreased over the time. This result could be accounted for by the fact that the decomposition of the MTEMPO moiety attached to the chain end had occurred. The decomposition was suggested to take place in the accordance with the mechanism shown in Scheme 3, because the signals of the protons from the olefin which was produced by the decomposition were observed in the ^{1}H NMR spectra of the resulting polymers. Figure 5 shows the parts of the ^{1}H NMR spectra obtained from the polymers after the reaction. The signals which were discerned at 5.9—6.2 ppm originating from the



Scheme 2.



Scheme 3.

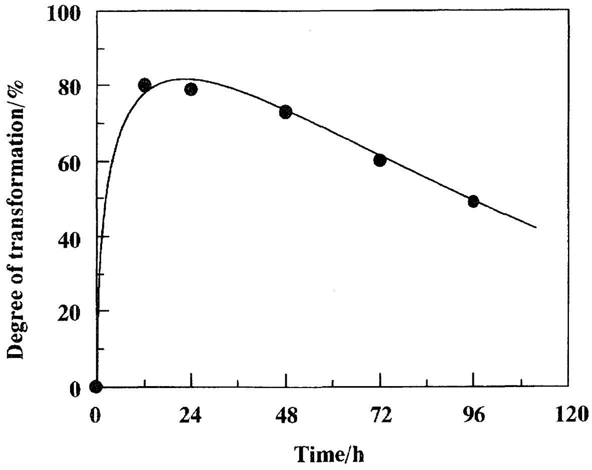


Fig. 4. Time-degree plots in the transformation of the HTEMPO-modified polystyrene by MTEMPO.

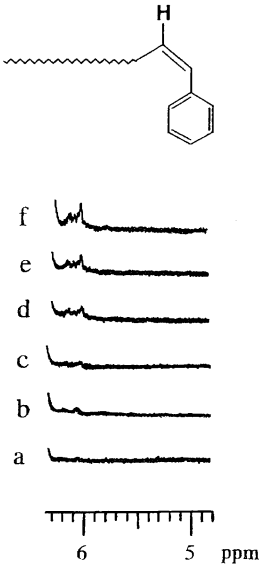


Fig. 5. ^{1}H NMR spectra of the polystyrenes obtained by the transformation for 0 h (a), 12 h (b), 24 h (c), 48 h (d), 72 h (e), and 96 h (f). (Solvent: $CDCl_3$).

Table 3. Degrees of Transformation and Decomposition

Time	Degree/%	
h	Transformation	Decomposition
12	80	17
24	79	18
48	73	25
72	60	38
96	49	56

one of the olefin protons. It is obvious that the intensity of the signals increased over the time. This implies that the degree of the decomposition increased over the time. The degrees of transformation and decomposition with time are summarized in Table 3. It was found that the degrees of transformation and decomposition showed good agreement in their material balances, in all the cases. Therefore, we can deduce that the decrease of the degree of transformation was caused by the decomposition of the MTEMPO moiety in the accordance with the mechanism shown in Scheme 3. These results support the mechanism proposed by Priddy for the decomposition of the growing polymer chain end, during the polymerization of styrene by BPO and TEMPO.[9g]

The radical transformation of the HTEMPO-modified polystyrene by di-α-cumyl peroxide was also performed. The polystyrene with the molecular weight, 6040 and the polydispersity, 1.21 was used for the reaction. The transformation was carried out in benzene at 125 °C for 24 h. The ^{1}H NMR spectra of the polystyrene before and after the reaction, are shown in Fig. 6. The signals observed at 0.25, 0.35, 0.95, and 1.15 ppm from HTEMPO disappeared after the reaction. This result suggests that the transformation of the polystyrene took place by di-α-cumyl peroxide. However,

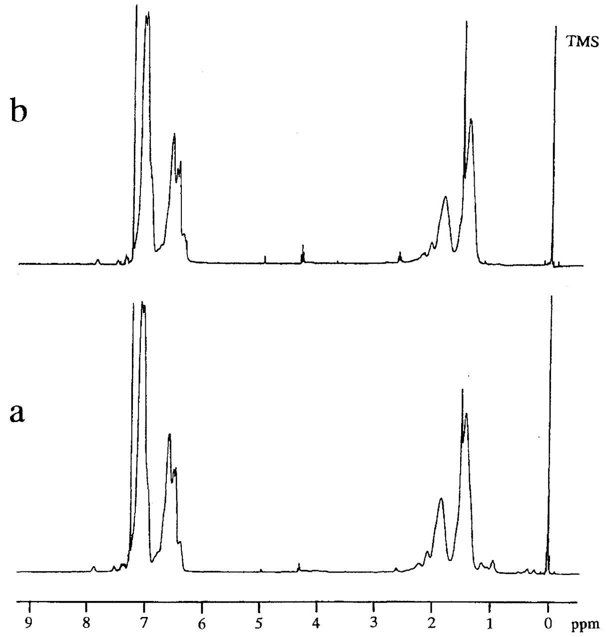


Fig. 6. ^{1}H NMR spectra of the polystyrene (M_n: 6040, M_w/M_n: 1.21) (a), and of the polystyrene obtained by the transformation by di-α-cumyl peroxide (b). (Solvent: $CDCl_3$).

the product obtained showed a bimodal GPC, in contrast to a sharp unimodal curve of the prepolymer (Fig. 7). It was found that coupling between the polystyrenyl radicals occurred during the transformation, because the molecular weight on the higher molecular weight side in the GPC, was estimated to be 13200. This means that the molecular weight, thus calculated, corresponded to almost twice that of the prepolymer (M_n: 6040). The coupling occurred probably in the accordance with the following mechanism (Scheme 4), when the reaction of TEMPO and peroxides was taken into consideration. Further studies on the mechanism and the radical transformation by other compounds are in progress.

Conclusion

The radical polymerization of styrene by BPO as an initiator in the presence of HTEMPO was found to proceed in accordance with a living mechanism, because the molecular weight of the polymer linearly increased with an increase of the conversion of styrene, and was proportional to the reciprocal of the initial concentration of HTEMPO. It was also found that all the molecules of HTEMPO were attached to the polymer chain end. Therefore, the initial concentration of HTEMPO determined the molecular weight of the polystyrene. The radical transformation of the HTEMPO-modified polystyrene proceeded by MTEMPO, resulting in the formation of the MTEMPO-modified polystyrene. This result suggests that an exchange reaction occurs between the molecules of HTEMPO at the growing polymer chain end, during the polymerization in the presence of HTEMPO. This is because the propagation proceeds via the homolytic scission of the C–O bond of the aminoxy moiety, giving the polystyrenyl radical and HTEMPO. The coupling be-

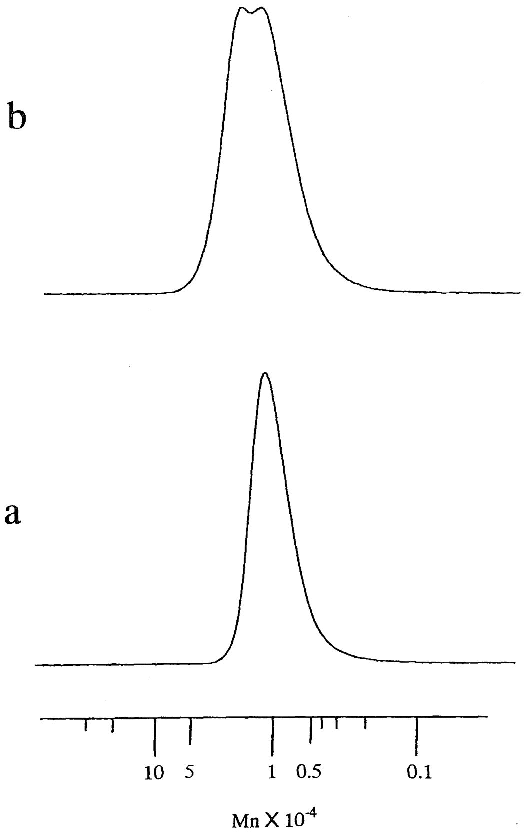
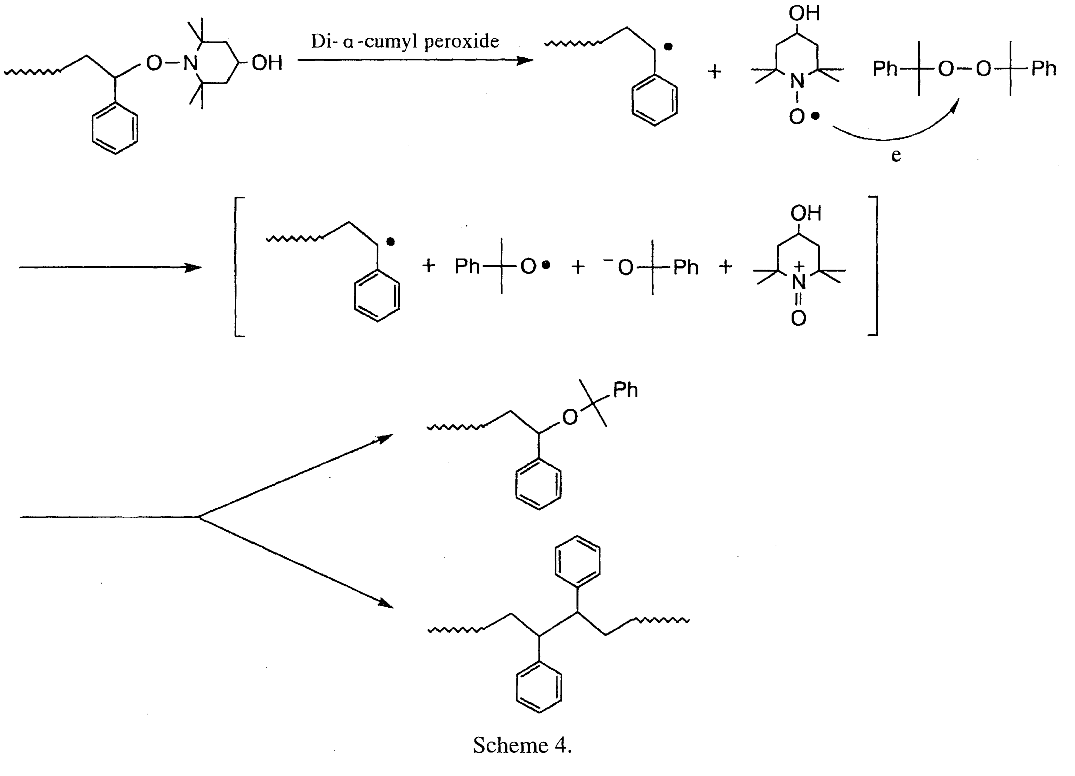


Fig. 7. GPC profiles of the polystyrene (M_n: 6040, M_w/M_n: 1.21) (a), and of the polystyrene obtained by the transformation by di-α-cumyl peroxide (b).



Scheme 4.

tween the polystyrenyl radicals did not occur at all during the transformation by MTEMPO, while it occurred competitively with the transformation when the reaction was carried out by di-α-cumyl peroxide. This means that this radical transformation has the potential to give desirable polymers, if suitable compounds, for which the TEMPO moiety attached to the chain end is exchanged, are chosen.

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