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Controlled radical polymerization of styrene with an oxazolidinyl-*N*-oxyl stable free radical

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Summary

The bulk polymerization of styrene at 110 °C in the presence of 7-oxo-15-azadispiro[5.2.5.1]pentadecanyl-*N*-oxyl was investigated. The M_n values of poly(St) formed were increased linearly with conversion, and the M_w/M_n values were 1.48-1.54 at 90% conversion. On the basis of the results it was concluded that **1** controlled radical polymerization of St.

Introduction

Nitroxide-mediated "living" free radical polymerization of styrene (St) at elevated temperature gives polymers with a narrow polydispersity (M_w/M_n) (usually <1.3), and the molecular weights of polymers produced increase straight with conversion (1-5). Such a polymer is impossible to be obtained by conventional radical polymerization. By using this method well-controlled macromolecular architectures, including block and graft copolymers, can also be obtained (2-6).

For several stable nitroxide free radicals the abilities to control the polymerization of St have been investigated, and 2,2,6,6-tetramethylpiperidinyl-N-oxyl (TEMPO) (7), 2,5-dimethyl-2,5-diphenylpyrrolidinyl-*N*-oxyl (8), and di-*tert*-butyl nitroxides (9) have been shown to have a clear "living" character. However, there still remain some problems that should be solved. For example, available monomers for the "living" radical polymerization are limited to St or St derivatives, and polymerization temperatures are high (usually 120-140 °C). At such high temperatures, autopolymerization of St must occur to a considerable extent. This leads to a undesirable increase in the polydispersity of poly(St). Consequently, the quest of suitable stable free radicals to solve these problems is important for further advances in the study of "living " free radical polymerization. Standing on this background we have made an effort to search for stable free radicals suitable for the "living" radical polymerization and focused on oxazolidinyl-*N*-oxyl radicals (10,11). This family of radicals are stable at high temperatures and can be readily prepared by condensation of ß-aminoalcohols with ketones, followed by oxidation. Therefore, a

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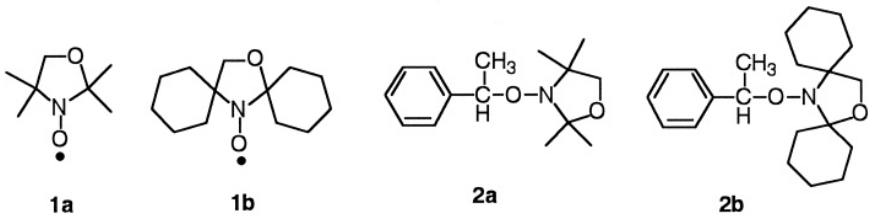
variety of structures can be designed and obtained by choosing the appropriate ß-aminoalcohols and ketones. We first investigated the ability of 2,2,4,4-tetramethyl-oxazolidinyl-*N*-oxyl (**1a**) to control the polymerization of St. However, no significant effects on M_n and M_w/M_n were shown for the poly(St) obtained at 110 °C. That is, M_w/M_n was never below 1.5 until high conversion, and M_n didn't increase straight with increasing conversion. On the other hand, radical polymerization of St in the presence of 7-oxo-15-azadispiro[5.2.5.1]pentadecanyl-*N*-oxyl (**1b**) gave poly(St) with M_w/M_n of ~ 1.5, and M_n was increased straight with increasing conversion. Herein we report the controlled radical polymerization of St mediated by **1b**.

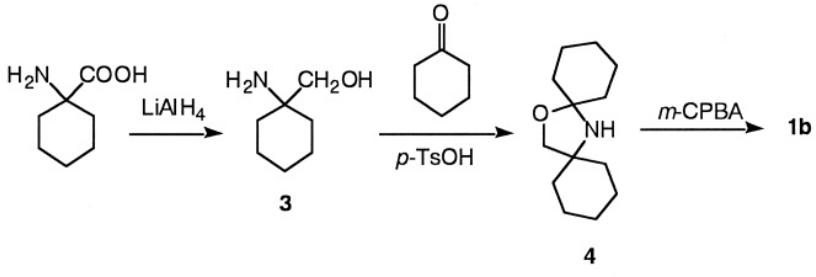
Results and discussion

Synthesis of alkoxyamine initiators 2. In the present study the bulk polymerization of St was performed with the corresponding alkoxyamine nitroxide adducts **2** at 110 °C.

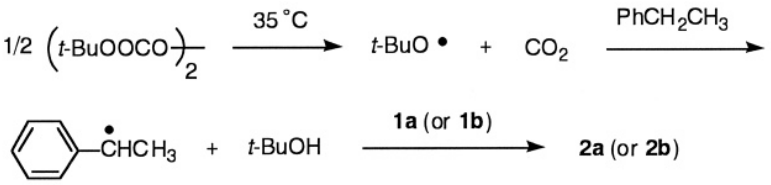
Nitroxide **1a** was prepared according to the reported method (12). Nitroxide **1b** was prepared according to Scheme 1. Thus, 1-amino-1-cyclohexanecarboxylic acid was reduced with an excess of $LiAlH_4$ (13), and condensation of **3** with cyclohexanone in the presence of TsOH yielded **4** (14). Treatment of **4** with *m*-chloroperbenzoic acid (*m*-CPBA) in CH_2Cl_2 gave **1b** as red needles after column chromatographic separation. The purity of the radical determined by ESR using TEMPO as reference was ~ 100%.



Synthesis of alkoxyamines **2a** and **2b** is shown in Scheme 2 (6,15). A mixture of 1 equiv of **1** and 1 equiv of di-*tert*-butyl diperoxyoxalate (16) in ethylbenzene was stirred at ~36 °C under nitrogen. After the characteristic red color due to **1** disappeared (2 h), the reaction mixture was evaporated at room temperature under reduced pressure and the residue chromatographed on silica gel at 0 °C to give **2a** in 78% yield and **2b** in 87% yield as a colorless oil.



Scheme 1



Scheme 2

Their structures were confirmed on the basis of mass (EI or CI) and ^{1}H NMR spectra. In the mass spectrum (CI) of **2a**, (M^+ + 1) ion was observed at *m/z* 250 (100%), along with ions at *m/z* 178 (22), 145 (13), and 105 (37%), and in that (EI) of **2b** (M^+ - 1) ion was observed at m/z 328 (64%), along with ions at *m/z* 224 (100) and 105 (70%). The ions appearing at m/z 224, 145, and 105 correspond to $\overline{ONC[(CH_2)_5]OCH_2C}[(CH_2)_5]^+$, $[\overline{ONC(ME_2)OCH_2C(Me_2)} + H]^+$, and $PhCH(Me)^+$, respectively. In the ^{1}H NMR spectrum of **2a** eight singlets (12 H) were observed in the region 0.77-1.44 ppm, two doublets (3 H) at 1.47 and 1.48 ppm, four doublets (2 H) at 3.47, 3.503, 3.512, and 3.53 ppm, a quintet (1 H) at 4.61 ppm, and multiplets (5 H) at 7.26-7.33 ppm, and they were assigned to the four methyl groups at the 2,2,4,4-positions of the oxazolinzine ring, -CH(C**H**$_3$)-, -$CH_2$0-, -C**H**(CH_3)-, and the aromatic protons, respectively. In the case of **2b** multiplets (20 H) were observed in the region 0.675-1.90 ppm, two doublets (3 H) at 1.478 and 1.484 ppm, four doublets (2 H) at 3.55, 3.57, 3.67, and 3.72 ppm, two quintets (1 H) at 4.61 and 4.65 ppm, and multiplets (5 H) at 7.26-7.34 ppm, and they were assigned to the cyclohexyl protons, -CH(C**H**$_3$)-, -OCH_2-, -C**H**(CH_3)-, and the aromatic protons, respectively.

Radical polymerization of St with 2. Radical polymerization of St in the presence of **2** was carried out at 100-120 °C using the sealed tube method. After a prescribed time, the polymerization mixture was poured into a large excess of MeOH and, after ca 6 h, the precipitated polymer was filtered and dried. The conversions were calculated from the weights, and M_n and M_w/M_n of poly(St) were determined by GPC.

The results of the polymerization of St in the presence of **2a** are shown in Table 1. Although the polymerization was carried out in a variety of concentrations of **2a** (28-169 mM) in the temperature range 100-120 °C, no significant effects on M_n and M_w/M_n of the poly(St) obtained were observed, indicating **2a** has no significant ability to control the radical polymerization of St. We assumed that the C-O bond in **2a** or in the corresponding domant species were too strong to control the polymerization of St. In this case a considerable part of poly(St) seems to be formed by the conventional radical polymerization.

In contrast, the addition of **2b** to the polymerization system showed clear effects on M_n and M_w/M_n of poly(St). Figure 1 shows plots of $1n([M]_0/[M]_t)$ vs time for the polymerization of St in the presence of **2b** (20, 39, and 78 mM). All plots are on the same straight line passing through the origin, and no significant deviation from the line was observed even at 90% conversion in any concentration of **2b**. This result indicates that the polymerization rate is independent of the concentration of **2b** and the number of the

Table 1. Bulk polymerization of styrene in the presence of **2a**[a)]

Run No.	Concentration of **2a**, mM	Temperature °C	Time h	Conversion %	M_n[a)]	M_w/M_n[b)]
1	28	100	52	63	62900	2.28
2	89	100	70	62	13400	2.51
3	28	110	52	77	37600	2.37
4	89	110	62	66	9280	2.33
5	169	110	62	64	5810	2.13
6	28	120	52	89	28400	1.89
7	89	120	39	65	7470	2.12
8	169	120	39	68	4820	1.96

a) Styrene 3 ml (2.73 g). b) Determined by GPC.

growing chains remains constant during the polymerization process. This behavior of polymerization is characteristic of the "living" free radical polymerization.

As found in Figure 2, M_n increases straight with increasing conversion. However, any line doesn't pass the origin, suggesting that the control process of the polymerization is not sufficient in the low conversion. If the polymerization proceeds in a "living" manner, the molecular weights of poly(St) obtained can be simply estimated by eq. 1,

$$M_n = \frac{\text{Molar quantity of the consumed monomer}}{\text{Molar quantity of the initiator}} \times MW_{St}, \qquad (1)$$

where MW_{St} is the molecular weight of St. The M_n values observed are 32300 (**2b**, 20.0 mM; conversion, 91%), 20600 (39 mM; 89%), and 9400 (78 mM; 90%), which are in good agreement with the calculated ones (41400, 20700, and 10500, respectively).

Figure 3 shows plots of M_w/M_n vs conversion. Although the M_w/M_n values are high (1.56-2.01) in the low conversion, they reduce gradually with increasing conversion and go down to 1.54 (**2b**, 20), 1.54 (39), and 1.48 (78 mM), respectively, at 90% conversion. The higher values in the low conversion are the results from an insufficient control of the polymerization by **1b**, which being in accordance with the profile of M_n vs conversion plots.

On the basis of the above observations it is concluded that **1b** has an ability to control the radical polymerization of St at 110 °C, and the polymerization proceeds in a "living" manner.

Experimental section

General. ^{1}H NMR spectra were obtained with a JEOL α-400 NMR spectrometer: chemical shifts are express in ppm downfield from TMS as an internal standard. Mass spectra were recorded with a JEOR AX-500 spectrometer. GPC measurements were performed with a Tosoh GPC 8020 series equipped with TSKguard columnH_{HR}-H

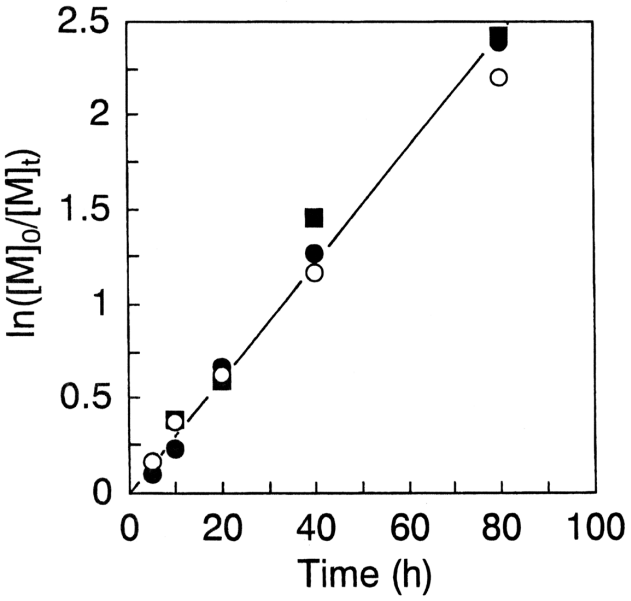


Figure 1. Dependence of $\ln([M]_0/[M]_t)$ on polymerization time for bulk polymerization of St at 110 °C: [**2b**], 78 (●); 39 (○); 20 mM (■).

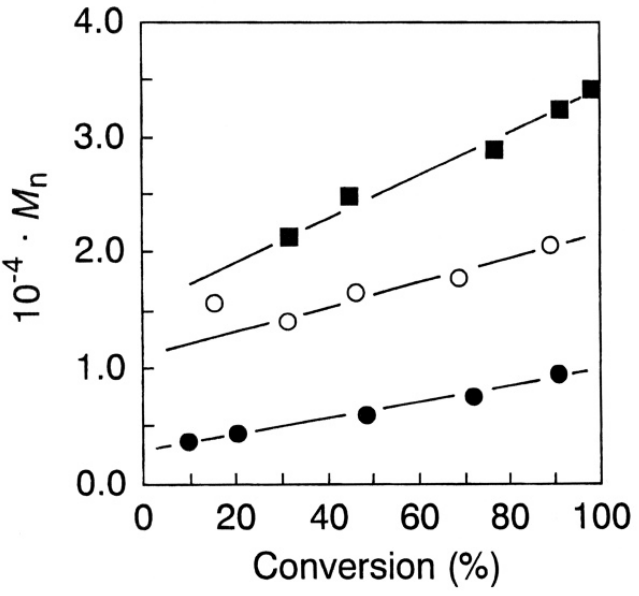


Figure 2. Dependence of M_n on conversion for bulk polymerization of St at 110 °C: [**2b**], 78 (●); 39 (○); 20 mM (■).

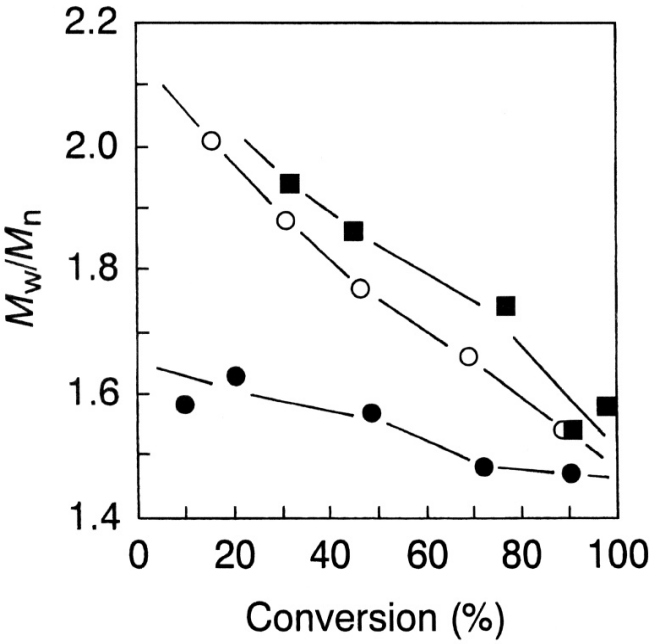


Figure 3. Dependence of M_w/M_n on conversion for bulk polymerization of St at 110 °C: [**2b**], 78 (●); 39 (○); 20 mM (■).

TSKgekG5000H_{HR}, and TSKgelGMH_{HR}-L columns calibrated with polystyrene standards, using THF as eluant. Detection was made with a Tosoh refractive-index detector RI8020. Silica gel column chromatography was carried out with Fuji Silysia Chemical BW-127ZH silica gel, and alumina column chromatography was performed with Merck aluminium oxide 90.

Materials. 2,2,4,4-Tetramethyloxazolidinyl-*N*-oxyl (**1a**) was prepared by the reported method and purified by column chromatography on silica gel (12). 1-Amino-1-cyclohexanemethanol (**3**) was prepared by reduction of 1-aminocyclohexanecarboxylic acid with an excess of $LiAlH_4$ in THF (13), and 7-oxo-15-azadispiro[5.2.5.1]pentadecane (**4**) was obtained by condensation of **3** with cyclohexanone in benzene in the presence of a catalytic amount of TsOH (14). These compounds were used in the next reaction without distillation. Di-*tert*-butyl diperoxyoxalate (Caution! don't scrape the crystals) was obtained according to the reported method (16). *m*-Chloroperbenzoic acid (*m*-CPBA) (70% purity) was commercially available.

7-Oxo-15-azadispiro[5.2.5.1]pentadecanyl-*N*-oxyl (1b). To a stirred solution of 6.01 g of **4** (crude) in 340 ml of ether at 0 °C was added dropwise a solution of 17.3 g of *m*-CPBA in 100 ml of ether was added. After the mixture was stirred at room temperature for 1 d, it was washed with 10% aqueous $NaHCO_3$ and brine, and dried ($MgSO_4$). After evaporation, the residue was chrmatographed on alumina with 1 : 5 ether-hexane to give **1b** in 28% yield (4.15 g, 18.5 mmol) (based on **3**). Recrystallization

from hexane gave light red needles with mp 60-62 °C. Anal. Calcd for $C_{13}H_{22}NO_2$: C, 69.44; H, 9.44; N, 6.24. Found: C, 69.61; H, 9.89; N, 6.24.

***N*-(α-Methylbenzyloxy)-2,2,4,4-tetramethyloxazolidine (2a).** A solution of 0.450 g (3.12 mmol) of **la** and ~0.76 g (3.2 mmol) of di-*tert*-butyl diperoxyoxalate in 20 ml of ethylbenzene was stirred at 35-38 °C for 2 h under nitrogen to give a pale yellow solution. The resulting light yellow mixture was then concentrated to ~1 ml at room temperature under reduced pressure, and the residue was chromatographed on silica gel with 1 : 5 ethyl acetate-hexane at 0 °C to give **2a** in 78% yield (0.61 g, 24.5 mmol) as a colorless oil. MS (CI, 200 eV): *m/z* 250 (M^+ + 1, 100), 178 (22), 145 (13), 105 (37%); ^{1}H NMR ($CDCl_3$): δ 0.77, 0.82, 1.08, 1.19, 1.27, 1.28, 1.42, and 1.44 (each s, CH_3, 12 H), 1.47 and 1.48 (each d, *J* = 6.8 Hz, CHC**H**$_3$, 3 H), 3.47, 3.503, 3.512, and 3.53 (each d, *J* = 8.3 Hz, OCH_2, 2 H), 4.61 (*q*, *J* = 6.8 Hz, C**H**CH_3, 1 H), 7.26-7.33 (m, aromatic, 5 H).

***N*-(α-Methylbenzyloxy)-7-oxo-15-azadispiro[5.2.5.1]pentadecane (2b).** A solution of 2.22 g (9.9 mmol) of **1b**, ~2.59 g (11.0 mmol) of di-*tert*-butyl diperoxyoxalate in 20 ml of ethylbenzene was stirred at 35-38 °C for 2 h under nitrogen. The resulting light yellow mixture was concentrated to 1 ml at room temperature under reduced pressure, and the residue (oil) was chromatographed at 0 °C on silica gel with ethyl 1 : 5 acetate-hexane to give **2b** in 87% yield (2.89 g, 8.77 mmol) as a colorless oil. MS (EI, 70 eV): *m/z* 328 (M^+ - 1, 64), 224 (100), 105 (70%); ^{1}H NMR ($CDCl_3$): δ 0.675-1.90 (m, $(CH_2)_5$, 20 H), 1.478 and 1.484 (each d, *J* = 6.8 Hz, CHC**H**$_3$, 3 H), 3.55, 3.57, 3.67, and 3.72 (each d, *J* = ~8.5 Hz, OCH_2, 2 H), 4.61 and 4.65 (each q, *J* = 6.8 Hz, CH_3C**H**, 1 H), 7.26-7.34 (m, aromatic, 5 H).

Polymerization of St. The polymerization of St was carried out in sealed glass tubes. St (2.73 g, 3.00 ml) containing the appropriate molar quantity of the initiator (**2**) was placed in Pyrex tubes, and the tubes were degassed by three freeze-pump-thaw cycles and sealed off from a vacuum system. They were then heated to 110 °C and, after a prescribed time, the polymerization mixtures were poured into a large excess of MeOH. The poly(St) precipitated was collected by filtration, dried in a vacuum oven overnight at 50 °C, and weighed.

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