Available online at www.sciencedirect.com
SCIENCE @ DIRECT®

Polymer 44 (2003) 5187–5194

polymer

www.elsevier.com/locate/polymer

‘Living’ radical polymerization of styrene mediated by spiro ring-substituted piperidinyl-*N*-oxyl radicals. The effect of the spiro rings on the control of polymerization

Yozo Miura*, Ayako Ichikawa, Isao Taniguchi

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan

Received 16 April 2003; received in revised form 9 June 2003; accepted 9 June 2003

Abstract

The bulk radical polymerizations of styrene (St) at 80–120 °C in the presence of 6-aza-7,7-dimethyl-9-hydroxyspiro[4.5]decane-6-yloxyl (**1**) and 1-aza-2,2-dimethyl-4-hydroxy[5.5]undecane-1-yloxyl (**2**) were studied. At 100 and 120 °C, the polymerizations were well controlled by those nitroxides to give poly(St)s with narrow polydispersities. On the other hand, the polymerization mediated by **2** at 80 °C showed a good ‘livingness’ of polymerization, but **1** had a poor ability to control the polymerization to give poly(St) with a broad polydispersity of 1.52. The rate constants (k_{act}) for the homolysis of the NO–C bond of the alkoxyamines prepared from **1** and **2** were measured at 333–373 K, and the A_{act}s and E_{act}s values were determined to be 2.8×10^{13} s^{-1} and 128 kJ mol^{-1} (**1**) and 4.0×10^{13} s^{-1} and 125 kJ mol^{-1} (**2**), respectively, from the Arrhenius plots. These results are compared with those for the structurally related piperidinyl-*N*-yloxyl radicals including TEMPO.

Keywords: Living radical polymerization; Nitroxide; Styrene

1. Introduction

Nitroxide mediated ‘living’ radical polymerization [1,2], as well as atom-transfer radical polymerization (ATRP) [3] and radical addition fragmentation chain transfer (RAFT) [4] have provided a robust method which yields well-controlled polymers with low polydispersity indexes (M_w/M_n). Since radical polmerization does not require strict purification of monomers and the strict polymerization conditions, e.g. a thorough exclusion of water and oxygen, different from the ionic polymerizations, the ‘living’ radical method has attracted much attention in the field of the industrial chemistry as well as the polymer chemistry. A variety of stable nitroxides have been investigated to evaluate their abilities to control the radical polymerization for the past decade [1,2], and a large body of the accommodated data indicated that many nitroxides including the commercially available 2,2,6,6-tetramethylpiperidinyl-*N*-oxyl (TEMPO) are effective as the mediator for the polymerization of styrene (St) and styrene derivatives [1,5]. However, some severe problems, i.e. the limitation of the applicable monomers, the low polymerization rates and the high temperature polymerization, were pointed out for the nitroxide-mediated radical polymerization. To solve these problems, many nitroxides were newly prepared, and some excellent nitroxides have been found. For example, *tert*-butyl 1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) [6] and *tert*-butyl 2-methyl-1-phenylpropyl nitroxide (BMPN) [7] are particularly interesting as the mediator for the polymerization of acrylates.

In our continuing study on the nitroxide-mediated ‘living’ radical polymerization [8–10], we prepared the two kinds of spiro ring-carrying piperidinyl-*N*-oxyl, **3** and **4** (see Chart 1). Their abilities to control the radical polymerization of St and the random copolymerization of St and butyl acrylate (BA) and St and MMA were excellent even at the temperature as low as 80 °C [9,10] and a considerable success was obtained for the homopolymerization of BA [10]. In the present work we prepared two kinds of structurally related spiro ring-carrying piperidinyl-*N*-oxyl, **1** and **2** and evaluated their abilities to control the

---

* Corresponding author. Tel.: +81-6-6605-2798; fax: +81-6-6605-2769.
E-mail address: miura@a-chem.eng.osaka-cu.ac.jp (Y. Miura).

0032-3861/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00497-X

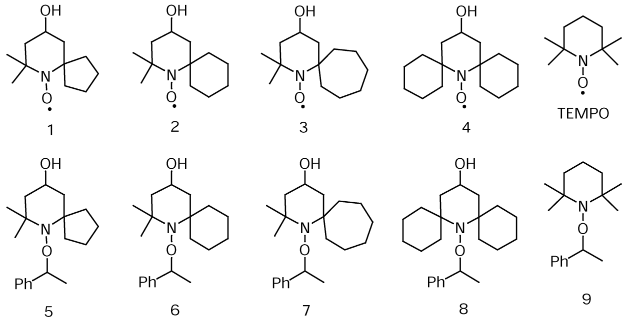


Chart 1.

polymerization of St to compare with those of structurally related **3** and **4**. Furthermore, the kinetic study for the homolysis of the NO–C bond of the alkoxyamines prepared from **1** and **2** was performed. Since the relationship between the structures and the 'livingness' for the structurally related nitroxides has not so far been reported, the data obtained are expected to give useful information about the relationship between the steric factors of nitroxides and the 'livingness' of polymerization.

2. Results and discussion

2.1. Syntheses of nitroxide *1* and *2*

Nitroxides **1** and **2** were prepared according to Schemes 1 and 2, respectively. This method is based on the reported method by Bobbitt et al. [11]. 2,2,4,4,6-Pentamethyl-2,3,4,5-tetrahydropyrimidine (acetonin) monohydrate, **10**·H_2O, were obtained by the reaction of acetone with NH_3 in the presence of NH_4SCN according to the reported method [11]. The reaction of **10** with a large excess of cycopentanone in the presence of NH_4Cl at 60 °C showed the formation of many products. Since the attempted column chromatography was unsuccessful, the desired compound **11** was roughly separated by distillation, and the subsequent semisolid mass was purified by sublimation to give **11** in 6.2% yield as colorless needles. Reduction of **11** with $NaBH_4$ in MeOH gave **12** as colorless plates in 65% yield, and oxidation of **12** with H_2O_2 in the presence of Na_2WO_4 gave **1** as red needles in 78% yield.

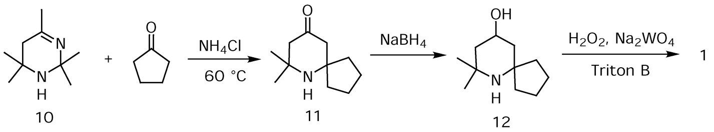
Nitroxide **2** was prepared by the analogous method. The reaction of **10** with a large excess of cyclohexanone in the presence of NH_4Cl at 60 °C again showed the formation of many products. The reaction mixture was first subjected to column chromatography and the fractions containing **13** were distilled to give **13** in 14% yield as a viscous oil. Reduction of **13** with $NaBH_4$ in MeOH afforded **15** in 44% yield as a colorless viscous oil, and oxidation of **15** with H_2O_2 in the presence of Na_2WO_4 gave **2** as red needles in 84% yield.

2.2. Syntheses of alkoxyamines *5* and *6*

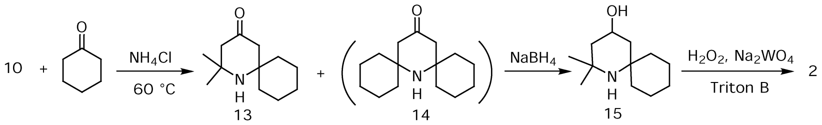
Alkoxyamines **5** and **6** were prepared according to our previously reported method [12,13]. Thus, a mixture of nitroxide and di-*tert*-butyl diperoxyoxalate (DBDPX) in ethylbenzene was heated at 38 °C under a nitrogen stream, and the resultant mixtures were subjected to column chromatography. Since the separated alkoxyamines contained small amounts of impurities which were not able to be removed by chromatography, those were removed with recycle HPLC, and the pure viscous oils of **5** and **6** could be obtained in 30 and 36% yields, respectively. The structures of **5** and **6** were confirmed by the ^{1}H NMR and HABMS spectra and the elemental analyses. Although their ^{1}H NMR spectra were very complex due to the ansymmetric structures, the assignments were satisfactorily made (see: Section 4). The HABMS spectra showed a peak due to $[M + 1]^+$ ion at $m/z = 304$ (**5**) and 318 (**6**), respectively, and an addition of aq KI showed a peak due to $[M + K]^+$ at $m/z = 342$ (**5**) and 356 (**6**), respectively. Although the elemental analyses of **6** provided satisfactory agreements with the calculations, that of **5** showed a small deviation of 0.85 in C% from the calculation, probably due to the oil sample. However, we can safely conclude that the alkoxyamine **6** have the proposed structure on the basis of the satisfactory ^{1}H NMR and MS spectra.

2.3. Bulk polymerization of St initiated by alkoxyamines *5* and *6*

Bulk polymerizations of St initiated by **5** and **6** were carried out at 80, 100, and 120 °C. The concentrations of alkoxyamines were 10.0 mmol dm^{-3} in all the experiments. Fig. 1 shows the $\ln([M]_0/[M]_t)$ vs time plots for the polymerizations at 120 °C. In both cases, the $\ln([M]_0/[M]_t)$ vs time plots are linear up to a high conversion, indicating that a first-order kinetics with respect to the St concentration is established. In Fig. 2, the M_n vs conversion and the M_w/M_n vs conversion plots are depicted. The M_ns increase linearly with conversion and a good agreement between the observed $M_n s$ and the theoretical values calculated by Eq. (1) is observed, in particular, below 40% conversion. A somewhat large discrepancy between them is found above



Scheme 1.



Scheme 2.

~40% conversion, indicating that the permanent termination of the propagating radicals by the side reactions takes place to some extent at 120 °C. Although, as found in Fig. 2b, the observed polydispersity indexes for the resulting poly(St)s decrease with conversion below ~40% conversion, reaching the values below 1.3, they gradually increase with conversion above ~40% conversion, reaching 1.4 at 66–84% conversions. This observation corresponds to the results shown in Fig. 2a, indicating that the influence of the side reactions on M_w/M_n clearly appears above 40% conversion.

$$M_n = [\mathrm{St}]/[\mathrm{alkoxyamine}] \times \mathrm{conversion} \times \mathrm{MW_{St}} \quad (1)$$

The bulk polymerizations of St at 100 °C mediated by **1** and **2** gave the better results than the polymerization at 120 °C. Similar to the polymerizations at 120 °C, the $\ln([M]_0/[M]_t)$ vs time plots (Fig. 3) showed a linear relationship and the M_n vs conversion plots showed a linear relationship. However, different from those at 120 °C, the polydispersity indexes for the polymerizations at 100 °C decreased with conversion, reaching 1.33 (**1**) and 1.20 (**2**). These values are lower than those at 120 °C, indicating that polymerizations mediated by **1** and **2** are well controlled throughout the polymerization. (Fig. 4)

Large differences were observed between the polymerization mediated by **1** and that mediated by **2** at 80 °C. Although both the polymerization systems showed a linear relationship in the $\ln([M]_0/[M]_t)$ vs time plots (see Fig. 5), considerable large differences were observed in the M_n vs conversion and the M_{w}/M_n vs conversion plots. In the polymerization mediated by **2**, the M_ns increase linearly with conversion and the observed M_ns agree with the theoretical values, as found in Fig. 6a. The polydispersity indexes of the resultant poly(St)s showed 1.21–1.25 at 39–46% conversions (Fig. 6b), indicating the polymerization is well controlled, even at 80 °C. In contrast, in the polymerization mediated by **1** the M_n vs conversion plots do not pass the origin and the observed M_ns show a large deviation from the theoretical values already in the initial step of polymerization. Furthermore, the polydispersity indexes decrease with conversion but still show a high value of 1.52 at 32% conversion, indicating a poor 'livingness' for the polymerization at 80 °C mediated by **1**.

For comparison, the literature values for the polymerizations of St mediated by **3**, **4**, and TEMPO are shown in Figs. 5 and 6 [10]. Fig. 5 shows that the rates for the polymerizations mediated by **2**, **3** and **4** are similar to each other, but the polymerizations mediated by **1** and TEMPO show a slower polymerization. The observation that sterically more hindered nitroxides give a higher polymerization rate may be explained by the higher K value for the equilibrium between the dormant and active species ($K =$ [nitroxide][propagating radical]/[dormant species]) [14]. A clear difference is also observed for the poly(St) polydispersity indexes. The polydispersity indexes for the polymerization mediated by **1** are as high as those for the polymerization mediated by TEMPO, while those for the polymerization mediated by **2** are much lower than those for the polymerization mediated by **1** or TEMPO, but slightly higher than those for the polymerization mediated by **3** or **4**. On the basis of the above results, it can be concluded that the abilities of the piperidinyl-N-oxyls to

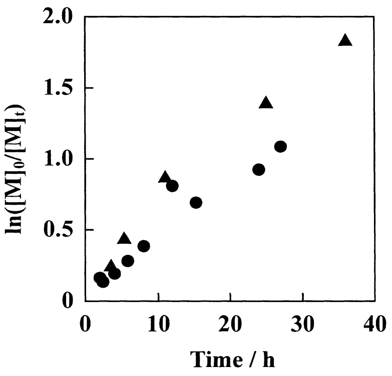


Fig. 1. The $\ln([M]_0/[M]_t)$ vs time plots for the polymerization of St initiated with **5** and **6** at 120 °C. (●) **5**, (▲) **6**; St, 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}.

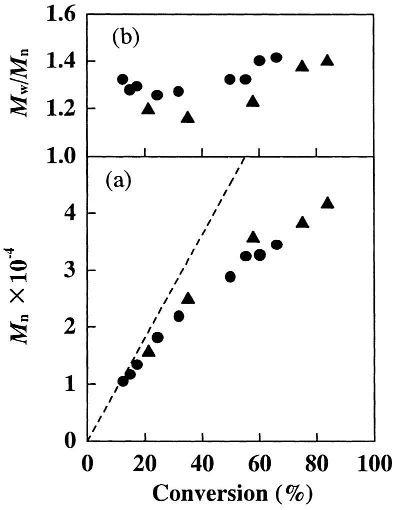


Fig. 2. (a) The M_n vs conversion and (b) the M_w/M_n vs conversion plots for the polymerization of St initiated with **5** and **6** at 120 °C. (●) **5**, (▲) **6**; St 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}. The theoretical values are shown by a dotted line.

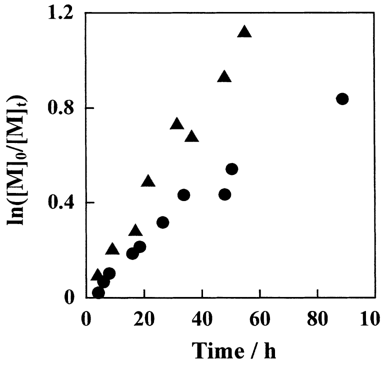


Fig. 3. The $\ln([M]_0/[M]_t)$ vs time plots for the polymerization of St initiated with **5** and **6** at 100 °C. (●) **5**, (▲) **6**; St, 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}.

control the polymerization of St evaluated from Fig. 6 are in the following order: **4** ≈ **3** > **2** ≫ **1** ≈ TEMPO.

2.4. Measurements of the rate constants (k_{act}) for the homolysis of the NO–C bond of the akloxyamines 5 and 6

One of the basic requirements for attaining low polydispersities is large activation rate constants for dormant species, which largely depend on the structures of the nitroxide moieties in alkoxyamines. Many kinetic studies have been carried out to determine the rate constants (k_{act}) for the NO–C bond homolysis of a variety of alkoxyamines to clarify the relationship between the nitroxide structures and 'livingness' [7,15–21]. In a previous paper [10] we reported the k_{act}s for the NO–C bond homolysis of the alkoxyamines **7–9** using the method of Bon, et al. [17] and concluded that the steric factors of nitroxides are reflected mainly on the activation parameters (E_{act}). In the present work we measured the k_{act}s for the NO–C bond homolysis of **5** and **6** using the same method. A combination of the data in the previous and present works makes the direct comparison for the five structurally related piperidinyl-*N*-oxyl radicals possible, which may provide useful information for attaining the more satisfactory control of the nitroxide-mediated radical polymerization of vinyl monomers.

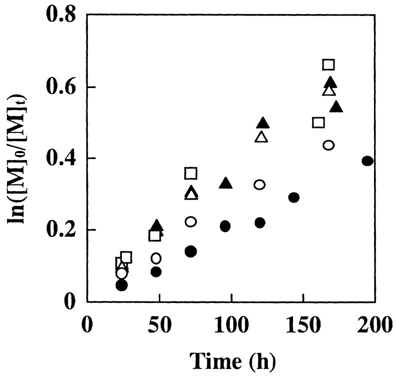


Fig. 5. The $\ln([M]_0/[M]_t)$ vs time plots for the polymerization of St mediated by **5** and **6** at 80 °C. (●) **5**, (▲) **6**, (△) **7**, (□) **8**, (○) **9**; St 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}.

$$\mathrm{PhCH(Me)ONR} \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} \mathrm{Ph\dot{C}H(Me)} + \mathrm{RNO}^{\cdot} \qquad (2)$$

Since the NO–C bond homolysis experiments of **5** and **6** were carried out under the atmospheric conditions, the pseudo first-order kinetics with respect to the nitroxide concentrations can be established because the atmospheric oxygen serves as a scavenger for the carbon-centered radicals. In Fig. 7, the nitroxide concentrations, determined by the ESR spectroscopic method using TEMPO as the reference, are plotted as a function of time. The k_{act}s determined from the slopes of the plots are summarized in Table 1, together with those for **7–9**. Table 1 shows that the

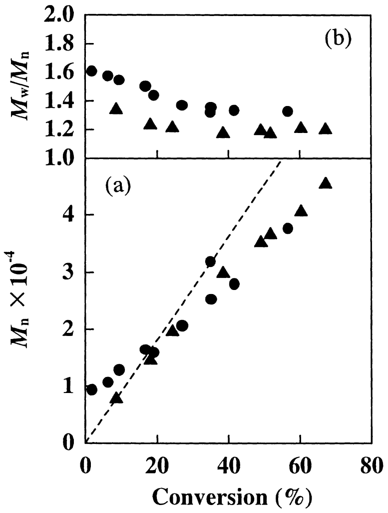


Fig. 4. (a) The M_n vs conversion and (b) the M_w/M_n vs conversion plots for the polymerization of St initiated by **5** and **6** at 100 °C. (●) **5**, (▲) **6**; St 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}. The theoretical values are shown by a dotted line.

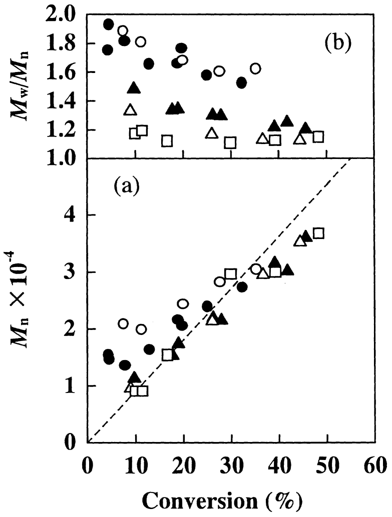


Fig. 6. (a) The M_n vs conversion and (b) the M_w/M_n vs conversion plots for the polymerization of St initiated with **5–9** at 80 °C. (●) **5**, (▲) **6**, (△) **7**, (□) **8**, (○) **9**; St, 1.0 cm^3; alkoxyamine, 10.0 mmol dm^{-3}. The theoretical values are shown by a dotted line.

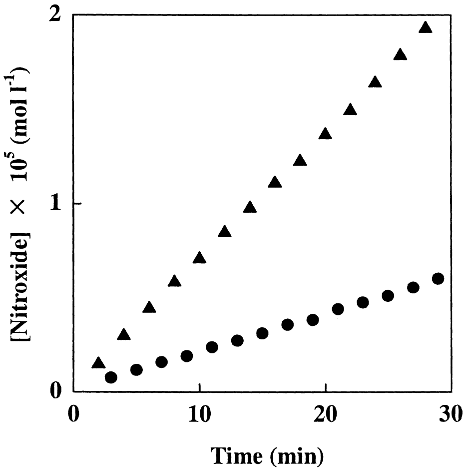


Fig. 7. Pseudo first-order plots for the NO–C bond homolysis of the alkoxyamines **5** and **6** in toluene at 80 °C under the atmospheric conditions. (●) **5**, (▲) **6**, 10.0 mmol dm^{-3}.

order of decreasing k_{act}s for the piperidinyl-*N*-oxyls are **8** > **7** > **6** > **9** ≥ **5** at any temperature measured. This order agrees with that for the 'livingness' indicated by the polydispersity indexes for the poly(St)s obtained, supporting that large activation rate constants of the dormant species is one of the most important requirements for attaining low polydispersities. Although **1**–**4** have a hydroxy group at the 4-position of the piperidine ring, different from TEMPO, the influence of the OH group on k_{act} was previously reported to be minor [20].

In Fig. 8, the Arrhenious plots for k_{act}s are depicted, and the preexponential factors (A_{act}) and E_{act} are determined from the intercept and the slope. In Table 2, the A_{act}s and E_{act}s are summarized, together with those for **7**–**9**. We previously reported that our A_{act} and E_{act} values for **9** agreed with the reported values [10], indicating our procedure was reliable. Table 2 shows that the E_{act}s for **5** and **6** are smaller that of **9**, but higher than those for **7** and **8**. Although there may be considerable errors in determining A_{act} and E_{act}, the order of increasing E_{act}, **8** ≤ **7** < **6** < **5** < **9**, is in accordance with the order for the 'livingness' of polymerization evaluated by the poydispersity indexes, indicating that the steric factors for the nitroxides are reflected mainly on E_{act} in the piperidinyl-*N*-oxyl series.

Table 1
The values of k_{act} (s^{-1}) for the NO–C bond homolysis of **5** and **6** in toluene at 333–373 K

Temperature (K)	k_{act} (s^{-1}) × 10^5				
	5	**6**	**7**^{a}	**8**^{a}	**9**^{a}
323				0.16	
333		0.11	0.19	0.61	
343	0.087^b	0.27	0.74	2.4	0.098
353	0.33	1.2	2.5	6.8	0.41
363	0.96	4.6	7.7		1.4
373	3.3		18		4.1

[a] Taken from Ref. [10].

[b] The average of the two values is shown

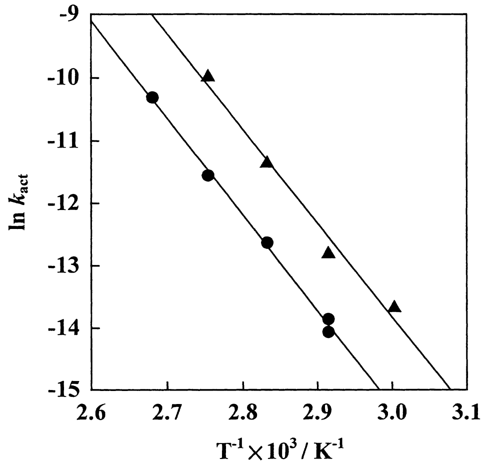


Fig. 8. Arrhenius plots of ln k_{act} vs T^{-1} for (●) **5**, (▲) **6**.

Fukuda et al. recently reported that the OH group of 4-hydroxy-TEMPO has a negligible effect on k_{act}, but a significant effect in decreasing k_{dec} [20]. The k_{dec} is the rate constant for the hydrogen abstraction from the propagating radicals by nitroxides. The presence of the HO group in **1**–**4** may therefore in part contribute to the 'livingness' of the polymerization mediated by **1**–**4**. The hydrogen abstraction from propagating radicals by nitroxides, leading to dead polymers, is an unavoidable side reactions in the nitroxide-mediated polymerization. In the polymerization of St, this side reaction is not so serious. However, in the polymerization of acrylates, particularly, in that of methacrylates, the reaction is a serious problem. However, the use of more sterically hindered nitroxides may solve the problem since the bulky substituents in nitroxides tend to suppress the hydrogen abstraction reaction [20]. In addition, sterically hindered nitroxides make the low temperature polymerization possible, which will suppress the side reaction to some extent.

3. Conclusion

The polymerization of St in the presence of **1** and **2** were carried out at 80–120 °C, and the ability to control the polymerization of St were evaluated. Radical **2** showed to be

Table 2
The Arrhenius parameters, A_{act} and E_{act}, for the NO–C bond homolysis of **5** and **6**

Alkoxyamine	A_{act} (s^{-1}) × 10^{-13}	E_{act} (kJ mol^{-1})
5	2.8	128
6	4.0	125
7^a	0.73	119
8^a	2.3	118
9^a	17	133

[a] Taken from Ref. [10].

effective as a mediator even at 80 °C, while the ability of **1** to control the polymerization of St was similar to that of TEMPO. The k_{act} for the corresponding alkoxyamines were measured, showing that the order of the decreasing k_{act}s, **8** > **7** > **6** > **9** ≥ **5**, agreed with the 'livingness' of the polymerization initiated by **5**–**9**. The A_{act} and E_{act} determined from the Arrhenious plots of k_{act} were compared with those for **7**–**9**, indicating that the steric effects of nitroxides are reflected mainly on E_{act}.

4. Experimental section

4.1. General

^{1}H NMR spectra were obtained with a JEOL α-400 NMR (400 MHz) spectrometer. Chemical shifts are expressed in ppm downfield from TMS as an internal standard. Mass spectra were recorded with a JEOL JMS-A × 500 spectrometer. Preparative HPLC purification was carried out on a Japan Analytical Industry LC-908 preparative recycling HPLC instrument, using $CHCl_3$ as the eluant. Size Exclusion Chromatography (SEC) measurements were performed with a Tosoh GPC 8020 series equipped with TSK_{gel} G5000H_{HR}, MultiporeH$_{XL}$-M, and GMH$_{HR}$-L columns with polystyrene standards, using THF as the eluant. Detection was made with Tosoh refractive-index detector RI8220. Silica gel column chromatography was performed with silica gel (Kanto Chemical, 60N).

4.2. Materials

2,2,4,4,6-Pentamethyl-2,3,4,5-tetrahydropyrimidine (acetonin) monohydrate (**9**·H_2O) [11] and di-*tert*-butyl diperoxyoxalate (DBDPX) [22] were prepared by the reported procedures.

4.3. Synthesis of nitroxide **1** (Scheme 1)

4.3.1. 6-Aza-7,7-dimethyl-9-oxospiro[4.5]decane(**11**)

A mixture of **10**·H_2O (30 g, 0.17 mol), cyclopentanone (73 g, 0.87 mol) and NH_4Cl (9.3 g) was stirred at 60 °C for 10 h. After cooling to 0 °C, 10% HCl (360 cm^3) was added and the unreacted cyclopentanone was removed by extraction with ether. Then, the aqueous layer was made alkaline by adding 20% aqueous NaOH (ca 360 cm^3), and the resultant aqueous layer was extracted with ether. The combined ether extracts were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was then distilled under 5 mmHg, and the fraction at 118–122 °C was collected. The fraction on standing became semisolid, which was purified by sublimation. Colorless needles; yield 6.2%; Mp 48–49 °C; MS (EI, 70 eV): *m/z* 181 (M$^+$, 19). ^{1}H NMR ($CDCl_3$): δ 1.22 (s, CH_3, 6H), 1.57–1.73 (m, spirocyclopentyl, 10H), 2.29 (s, –**CH$_2$**C(=O)**CH$_2$**–, 4H).

4.3.2. 6-Aza-7,7-dimethyl-9-hydroxyspiro[4.5]decane (**12**)

To a stirred solution of **11** (2.0 g, 11 mmol) in MeOH (100 cm^3), $NaBH_4$ (1.9 g) was added, and the mixture was stirred at room temperature for 4 h, concentrated, and extracted with ethyl acetate. The combined extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was then chromatographed on silica gel with 1:1 EtOH-ethyl acetate. Crystallization of the residue from hexane gave **12** as colorless plates in 65% yield. Mp 110–112 °C, MS (EI, 70 eV): *m/z* 183 (M$^+$, 30); ^{1}H NMR ($CDCl_3$): δ 1.01 and 1.08 (each dd, both $J = 12$ Hz, –CH**H**CH(OH)CH**H**–, 2H), 1.15 (s, CH_3, 6H), 1.40–1.89 (m, spirocyclopentyl, 8H), 1.92 and 2.02 (each ddd, $J =$ 12, 4.2 and 1.7 Hz, –C**H**HCH(OH)C**H**H–, 2H), 1.43 (m, –CH(O**H**)–, 1H), 3.99 (tt, $J =$ 12, 4.2 Hz, –C**H**(OH)–, 1H).

4.3.3. 6-Aza-7,7-dimethyl-9-hydroxyspiro[4.5]decane-6-yloxyl(**1**)

A mixture of **12** (1.0 g, 5.5 mmol), H_2O_2 (35%) (0.12 g, 1.3 mmol), Triton B (benzyltrimethylammonium hydroxide) (0.75 cm^3), and $Na_2WO_4 2H_2O$ (0.40 g) in MeOH (15 cm^3) was stirred at room temperature for 24 h. After the mixture was made alkaline with 10% K_2CO_3, the mixture extracted with ethyl acetate. The combined ethyl acetate extracts were washed with brine and dried over anhydrous Na_2SO_4. Evaporation of the solvent and recrystallization from hexane gave red needles of **1** in 78% yield. Mp 93–94 °C; MS (EI, 70 eV): *m/z* 198 (M$^+$, 100). Anal. Calcd for $C_{11}H_{20}NO_2$: C, 66.63; H, 10.17; N, 7.06. Found: C, 66.89; H, 10.36; N, 7.09.

4.4. Synthesis of nitroxide **2** (Scheme 2)

4.4.1. 1-Aza-2,2-dimethyl-4-oxospiro[5.5]undecane (**13**)

A mixture of **10**·H_2O (30 g, 0.17 mol), cyclohexanone (85 g, 0.87 mol), and NH_4Cl (9.3 g) was stirred at 60 °C for 10 h. After cooling to 0 °C, 10% HCl (360 cm^3) was added. After the precipitated solid (the HCl salt of 7-aza-15-oxodispiro[5.1.5.3]hexadecane) was removed by filtration, the unreacted cyclohexanone was removed by extraction with ether. After the aqueous layer was made alkaline by adding 20% aqueous NaOH (360 cm^3), the mixture extracted with ether, and the combined ether extracts were washed with brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residue was chromatographed on silica gel with 1:1 hexane–ethyl acetate and then distilled under 0.5 mmHg. The fraction at 84–87 °C was collected as a viscous oil. Yield 14%; MS (EI, 70 eV): *m/z* 195 (M$^+$, 17); ^{1}H NMR ($CDCl_3$): δ 1.23 (s, CH_3, 6H), 1.40–1.76 (m, spirocyclohexyl, 10H), 2.29 (s, –**CH$_2$**C(=O)**CH$_2$**–, 4H).

4.4.2. 1-Aza-2,2-dimethyl-4-hydroxyspiro[5.5]undecane (**15**)

To a stirred solution of **13** (5.0 g, 26 mmol) in MeOH (150 cm^3), $NaBH_4$ (4.8 g, 0.13 mol) was added and the mixture was stirred at room temperature for 4 h. The mixture was then concentrated and extracted with ethyl acetate. The combined ethyl acetate extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated. The residue was then chromatographed on silica gel with EtOH to give **15** as a colorless viscous oil in 44% yield. MS (EI, 70 eV): *m/z* 197 (M^+, 23); ^{1}H NMR ($CDCl_3$): δ 0.83 and 1.05 (each dd, both *J* = 12 Hz, −CH**H**CH(OH)CH**H**−, 2H), 1.18 (s, CH_3, 6H), 1.26–1.71 (m, spirocyclohexyl, 10H), 1.92 and 2.16 (each ddd, *J* = 12, 4.2 and 1.7 Hz, −CH**H**CH(OH)CH**H**−, 2H), 4.00 (tt, *J* = 12 and 4.2 Hz, C**H**(OH), 1H).

*4.4.3. 1-Aza-2,2-dimethyl-4-hydroxyspiro[5,5]undecane-1-yl-oxyl (**2**)*

A mixture of **15** (1.0 g, 5.1 mmol), H_2O_2 (35%) (0.11 g, 1.2 mmol), Triton B (0.70 cm^3), and $Na_2WO_4.2H_2O$ (0.37 g) in MeOH (11 cm^3) was stirred at room temperature for 24 h. After the mixture was made alkaline with 10% K2CO3, the resultant mixture was extracted with ethyl acetate and the combined ethyl acetates extracts were washed with brine and dried over Na_2SO_4. Evaporation of the solvent and recrystallization from hexane gave light red needles of **2** in 84% yield. Mp 100–101 °C; MS (EI, 70 eV): *m/z* 212 (M^+, 100). Anal. Calcd for $C_{12}H_{22}NO_2$: C, 67.89; H, 10.44; N, 6.60. Found: C, 67.77; H, 10.34; N, 6.59.

*4.5. Synthesis of alkoxyamines **5** and **6***

*4.5.1. N-(1-phenylethyloxy)-6-aza-7,7-dimethyl-9-hydroxyspiro[4.5]decane (**5**)*

A solution of **2** (0.50 g, 2.5 mmol) and DBDPX (ca. 0.89 g, ca. 3.8 mmol) in ethylbenzene (30 cm^3) was stirred at 38 °C for 3 h under a nitrogen stream. The mixture was then concentrated to 2–3 cm^3 under reduced pressure, and the resulting residue was chromatographed on silica gel with 1:1 hexane–ethyl acetate to give **5** as a viscous oil. Further purification with a preparative recycling HPLC instrument with $CHCl_3$ as the eluant gave pure **5** in 30% yield. FABMS (matrix *m*-NBA-d_4): *m/z* 304 ($[M + 1]^+$); on addition of aq KI, *m/z* 342 ($[M + K]^+$); ^{1}H NMR ($CDCl_3$): δ 0.70, 1.10, 1.24, 1.35 (each s, CH_3, 6H), 0.76–2.3 (m, spirocyclopentyl and −C**H**$_2$CH(OH)C**H**$_2$−, 12H), 1.49 and 1.50 (each d, *J* = 6.8 Hz, PhCH(C**H**$_3$)−, 3H), 3.88 (m, −C**H**(OH)−, 1H), 4.82 and 4.84 (q, *J* = 6.8 Hz, PhC**H**(Me)−, 1H), 7.24–7.32 (m, aromatic, 5H). Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62. Found: C, 74.36; H, 9.58; N, 4.57.

*4.5.2. N-(1-phenylethyloxy)-1-aza-2,2-dimethyl-4-hydroxyspiro[5,5]undecane (**6**)*

A solution of **2** (0.50 g, 2.4 mmol) and DBDPX (ca. 0.83 g, ca. 3.5 mmol) in ethylbenzene (30 cm^3) was stirred at 38 °C for 3 h under a nitrogen stream. The mixture was then concentrated to 2–3 cm^3 under reduced pressure, and the resulting residue was chromatographed on silica gel with 1:1 hexane-ethyl acetate to give **6** as a viscous oil. Further purification with a preparative recycling HPLC instrument with $CHCl_3$ as eluant gave pure **6** in 36% yield. FABMS (matrix *m*-NBA-d_4): *m/z* 318 ($[M + 1]^+$); on addition of aq KI, *m/z* 356 ($[M + K]^+$); ^{1}H NMR ($CDCl_3$): δ 0.70, 1.10, 1.24, 1.35 (each s, CH_3, 6H), 0.79–2.10 (m, spirocyclohexyl, 10H), 0.94 and 1.07 (each dd, *J* = 12and 3.4 Hz, −C**H**HCH(OH)C**H**H−, 2H),), 1.50 and 1.51 (d, *J* = 6.8 Hz, PhCH(C**H**$_3$, 3H), 2.35 and 2.48 (each dt, *J* = 12 and 3.4 Hz, −CH**H**CH(OH)C**H**H−, 2H), 3.87 (m, −C**H**(OH)−, 1H), 4.74 and 4.77 (each q, *J* = 6.8 Hz, PhC**H**(Me)−, 1H), 7.23–7.32 (m, aromatic, 5H). Anal. Calcd for $C_{20}H_{31}NO_2$: C, 75.67; H, 9.84; N, 4.41. Found: C, 75.51; H, 9.73; N, 4.42.

4.6. Polymerization

All polymerizations were carried out in Pyrex glass tubes. A typical procedure is as follows: an alkoxyamine solution (10.0 mmol dm^{-3}) of St was placed in a Pyrex glass tube, the content was degassed by three freeze-pump-thaw cycles, using a high vacuum system, and tube was sealed off from the high vacuum system. After the tube was heated for the prescribed time in an alumi thermo-bath (Iwaki Glass Co., Ltd), the mixture was poured into a large amount of MeOH. After the resultant poly(St) was once purified by decantation (toluene/MeOH), it was dried at 50 °C in a vacuum oven. The conversion was calculated from the weight of the poly(St), and M_n and M_w/M_n were determined by SEC.

Acknowledgements

This work was financially supported in part by a Grant-in-Aid for Scientific Research (No. 12450376) from the Ministry of Education, Science, Sports, and Culture, Japan.

References

[1] Hawker CJ, Bosman AW, Harth E. Chem Rev 2001;101:3661.
[2] Matyjaszewski K, editor. Controlled/living radical polymerization. ACS symposium series 768, Washington, DC: American Chemical Society; 2000.
[3] Kamigaito M, Ando T, Sawamoto M. Chem Rev 2001;101:3689.
[4] Mayadunne RTA, Rizzardo E, Chiefari J, Chong YK, Moad G, Thang S. Macromolecules 1999;32:6977.
[5] Georges MK, Veregin RPN, Kazmaier PM, Hamer GK. Macromolecules 1993;26:2987.
[6] Benoit D, Chaplinski V, Braslau R, Hawker CJ. J Am Chem Soc 1999;121:3904.
[7] Benoit D, Grimaldi S, Robin S, Finet J-P, Tordo P, Gnanou Y. Am Chem Soc 2000;122:5929.
[8] Miura Y, Mibae S, Moto H, Nakamura N, Yamada B. Polym Bull 1999;42:17.
[9] Miura Y, Nakamura N, Taniguchi I. Macromolecules 2001;34:447.
[10] Miura Y, Nakamura N, Taniguchi I, Ichikawa A. Polymer 2003;40:3461.
[11] Ma Z, Huang Q, Bobbitt JM. J Org Chem 1993;58:4837.

[12] Miura Y, Hirota K, Moto H, Yamada B. Macromolecules 1998;(31): 4659.

[13] Miura Y, Hirota K, Moto H, Yamada B. Macromolecules 1999;(32): 8356.

[14] Lacroix-Desmazes P, Lutz J-F, Boutevin B. Macromol Chem Phys 2000;201:662.

[15] Goto A, Fukuda T. Macromol Chem Phys 2000;201:2138.

[16] Skene WG, Belt ST, Connolly TJ, Hahn P, Scaiano JC. Macromolecules 1998;31:9103.

[17] Bon SAF, Chambard G, German AL. Macromolecules 1999;32:8269.

[18] Marque S, Mercier CL, Tordo R, Fisher H. Macromolecules 2000;33: 4403.

[19] Ballesteros OG, Maretti L, Sastre R, Scaiano JC. Macromolecules 2001;34:6184.

[20] Goto A, Kwak Y, Yoshikawa C, Tsujii Y, Sugiura Y, Fukuda T. Macromolecules 2002;35:3520.

[21] Dervan P, Aldabbagh F, Zetterlund PB, Yamada B. J Polym Chem Polym Chem Ed 2003;41:327.

[22] Bartlett PD, Benzing EP, Pincock RE. J Am Chem Soc 1960;82:1762.