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Radical polymerization of butyl acrylate and random copolymerization of styrene and butyl acrylate and styrene and methyl methacrylate mediated by monospiro- and dispiropiperidinyl-*N*-oxyl radicals

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Abstract

Radical polymerization of butyl acrylate (BA) and random copolymerizations of styrene (St) and BA and St and methyl methacrylate (MMA) in the presence of 7-aza-15-hydroxydispiro[5.1.5.3]hexadecane-7-yloxyl (**1**) and 1-aza-2,2-dimethyl-4-hydroxyspiro[5.6]dodecane-1-yloxyl (**2**) were carried out. Radical polymerization of BA at 120 °C in the presence of **1** gave poly(BA) with $M_n = 20200$ and $M_w/M_n = 1.30$ at 23% conversion. The termination of polymerization observed around $\sim 20\%$ conversion was solved to a certain extent by an addition of small amounts of dicumyl peroxide, and poly(BA) with $M_n = 37400$ and $M_w/M_n = 1.33$ was obtained in 46% yield. Random copolymerizations of St and BA and St and MMA in the presence of **1** and **2** at 80 °C gave the corresponding random copolymers with narrow polydispersities of 1.12–1.38 at the molar fraction above 0.30 of St in feed. The kinetic study for the NO–C bond homolysis of the corresponding alkoxyamines prepared from **1** and **2** were carried out, and evaluation of the preexponential factors (A_{act}) and the activation parameters (E_{act}) showed that the steric factors of the nitroxides are reflected mainly on E_{act}.
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1. Introduction

'Living' free radical polymerization mediated by stable free radicals such as nitroxides has attracted much attention as a new method for syntheses of well-defined polymers with narrow polydispersities [1,2]. Since radical polymerization does not require highly purified monomers or strict polymerization conditions, the living radical method have many potentially important applications in the synthetic polymer chemistry. A wide variety of nitroxides including commercially available 2,2,6,6-tetramethylpiperidinyl-1-yloxyl (TEMPO) have been investigated to evaluate the abilities to control the radical polymerization [3,4], and three main problems to be solved, i.e. the narrow applicable monomers, the high temperature polymerization, and the extremely slow polymerization, were shown. Much effort has been paid to solve these problem, and *tert*-butyl 2-methy-1-phenylpropyl nitroxide (BMPN) [5] and *tert*-butyl

1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN) [6] solved these problems to a considerable extent. However, the nitroxide-mediated method still possesses problems to be improved compared with atom transfer radical polymerization (ATRP) [7,8] or reversible addition-fragmentation chain transfer (RAFT) [9].

We previously reported that the free radical polymerization of styrene (St) in the presence of **1** or **2** proceed in the living fashion even at 70 °C to give well controlled poly(St) with narrow polydispersities below 1.2 [10] (see Chart 1). Since **1** has two bulky cyclohexyl spiro-rings at the 2 and 6 positions of the piperidine ring and **2** has a bulky heptyl spiro-ring at the 2 position of the piperidine ring, large steric congestions around the N–O· moiety are expected for the two nitroxides. In this work we performed the radical homopolymerization of butyl acrylate (BA) and random copolymerization of St and BA and St and methyl methacrylate (MMA) in the presence of **1** and **2**. Although the nitroxide-mediated living radical polymerizations are successful for polymerization of St and St derivatives, the limited success has been shown for the polymerization of

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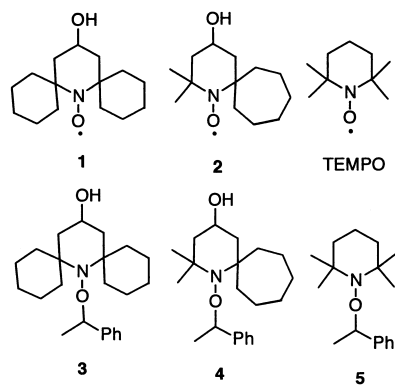*E-mail address:* miura@a-chem.eng.osaka-cu.ac.jp (Y. Miura).

Chart 1.

acrylates [11–13]. However, recently, BMPN [5] or DEPN [6] has proven to be effective for the polymerization of BA to give poly(acrylate)s with narrow polydispersities in high conversions. The living radical method is also useful for preparation of random copolymers with the same composition. However, the TEMPO-mediated random copolymerization of St and BA and St and MMA showed poor livingness. The successful living copolymerization was observed only at high St molar fraction in feed [14–21]. The purpose of this work is to evaluate to ability of **1** and **2** to control the radical polymerization of BA and the random copolymerization of St and BA and St and MMA.

2. Experimental section

2.1. General

^{1}H NMR (400 MHz) were recorded with a JEOL α-400 NMR spectrometer using CDCl$_3$ as the solvent and TMS as the standard. Size exclusion chromatography (SEC) was performed with a Tosoh 8020 series using TSK-gel G5000H$_{HR}$, MultiporeH$_{XL}$-M and GMH$_{HR}$-L columns calibrated with polystyrene standards, eluting with THF at 40 °C. Detection was made with a Tosoh refractive index detector RI8020.

FTNIR (FT near infrared) spectra were recorded on a JASCO FT/IR 410 spectrometer.

2.2. Materials

7-Aza-15-hydroxydispiro[5.1.5.3]hexadecane-7-yloxyl (**1**), 1-aza-2,2-dimethyl-4-hydroxyspiro[5.6]dodecane-1-yloxyl (**2**), N-(1-phenylethyloxy)-7-aza-15-hydroxydispiro [5.1.5.3]hexadecane (**3**), N-(1-phenylethyloxy)-1-aza-2,2-dimethyl-4-hydroxyspiro[5.6]dodecane (**4**), and N-(1-phenylethyloxy)-2,2,6,6-tetramethylpiperidine (**5**) were prepared as previously reported [10,21,22]. TEMPO and dicumyl peroxide (DCP) were commercially available. TEMPO was purified by sublimation and DCP was purified by recrystallization from MeOH.

2.3. Polymerization procedure

Polymerization was carried out in a sealed Pyrex tube. A typical procedure is as follows: 1.0 ml of BA (7.0 mmol) containing **3** (10 mmol l^{-1}) was placed in a Pyrex tube and the contents were degassed by three freeze-pump-thaw cycles using a high vacuum system. The Pyrex tube was then sealed off from the vacuum system and heated in an alumi thermo-bath (Iwaki Glass Co, Ltd.) for 1 to 10 h. The reaction mixture was poured into a large excess of 4:1 MeOH–H$_2$O, and the resultant viscous oil was collected by decantation. Purification by decantation were twice carried out. After drying at 50 °C in a vacuum oven, the polymer was weighed. M_n's and M_w/M_n's were determined by SEC.

3. Results and discussion

3.1. Homopolymerization of BA in the presence of **1** and **2**

The bulk polymerization of BA mediated by **1** and **2** was carried out at 100, 120, and 145 °C using **3** and **4** as initiator. The results of polymerization are summarized in Table 1. Although the polymerization at 100 °C initiated with **3** gave poly(BA) with a somewhat broad polydispersity of 1.48, those obtained by polymerization at 120 and 145 °C showed narrow polydispersities of 1.30–1.33 and the observed M_n's were in good agreement with the theoretical values calculated using Eq. (1). On the other hand, the polymerization of BA initiated with **4** gave poly(BA) with a polydispersity of 1.48 even at 120 °C, showing a somewhat poor livingness of polymerization. The above results were compared with the TEMPO-mediated radical polymerization of BA. In the TEMPO system, the copolymers showed a very broad polydispersity of 2.0 even in the polymerization at 120 °C [12], indicating that TEMPO is far less effective than **1** and **2**. To get more information with the polymerization of BA mediated by the spiro-piperidinyl-N-oxyls, we investigated the polymerization of BA in the presence of **1** in more detail.

$$M_n = MW_{BA} \times \text{conversion} \times [BA]/[\text{alkoxyamine}] \qquad (1)$$

The polymerization of BA at 120 °C was measured by following the relative intensity of the overtone absorption of ν C=C–H (6150 cm^{-1}) by the established FTNIR spectroscopic method (for the details for this method: see Ref. [23]). The ln([M]$_0$/[M]$_t$) vs time plots (Fig. 1) shows that a termination of polymerization of BA occurs after ca 7 h of polymerization. Such a termination has often observed in the nitroxide-mediated living radical polymerization of acrylates [11–13]. A most plausible explanation for the termination is the β-hydrogen abstraction from the propagating radical by nitroxide to yield N-hydroxyamine and poly(BA) with a double bond at the polymer chain end. To clarify whether such a side reaction takes place in the present polymerization system or not, the ^{1}H NMR spectra

Table 1
Results of the bulk polymerization of butyl acrylate initiated with **3** and **4** at various temperatures[a]

Run	Alkoxyamine	Concentration (mmol l^{-1})	DCP (mol l^{-1})	Time (h)	Temperature (°C)	Conversion[b] (%)	M_n[c,d]	Calcd. M_n[e]	M_w/M_n[c]
1	**3**	10	0	1	145	19	18,800	17,000	1.26
2	**3**	10	0	8	145	27	21,400	24,100	1.33
3	**3**	10	0	2	120	10	10,100	8930	1.38
4	**3**	10	0	10	120	23	20,200	20,500	1.30
5	**3**	10	0.67	7	120	46	37,400	41,100	1.33
6	**3**	20	1.33	3	120	40	17,200	17,900	1.32
7	**3**	20	1.33	8	120	50	20,300	22,300	1.29
8	**3**	20	0	4	100	8	6130	3570	1.48
9	**4**	20	0	1	120	14	20,200	6250	1.52
10	**4**	20	0	2	120	17	24,300	7590	1.48

[a] BA 1.0 ml (6.98 mmol).
[b] The conversions were determined by the weights of poly(BA) obtained.
[c] Determined by SEC.
[d] Poly(St) equivalent values.
[e] Calculated by Eq. (1).

of the resultant poly(BA)s were examined. In the ^{1}H NMR spectra the peaks due to the terminal C=C double bond were unequivocally observed at 5.8 and 6.7 ppm, indicating that such a termination reaction certainly occurs in our system.

In order to enhance the polymerization rate of BA, an appropriate amount of DCP was added to the polymerization system. An addition of DCP was previously reported by Fukuda and Goto [12]. The thermal homolysis of DCP compensates the loss of propagating radical by the disproportionation reaction between the propagating radical and nitroxide. As shown by Fig. 1, an addition of 0.067 equiv of DCP for **3** enhanced the polymerization rate by ca 3 times relative to the DCP-unadded system, and the conversion reaches 46% yield. In Fig. 2a, the number average molecular weight (M_n) vs conversion plots for the polymerization of BA at 120 °C are depicted, indicating that the M_n increases linearly with conversion and all the plots are almost on the same straight line, regardless of the presence or absence of DCP. This means that the influence of an addition of DCP on M_n is negligible. Although the polydispersity indexes (M_w/M_n,s) are high in the initial stage of polymerization,
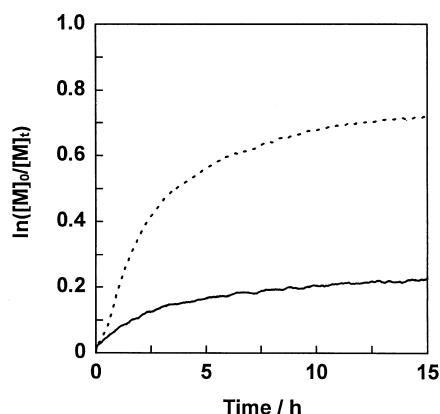
they decrease with conversion, reaching 1.29–1.33 at 46–50% conversions (Fig. 2b). Accordingly, it is obvious that DCP-added homopolymerization of BA mediated by **1** at 120 °C enhanced the polymerization rates, without causing appreciable broadening of the molecular weight distribution of the resultant polymers.

3.2. Random copolymerization of St and BA and St and MMA in the presence of 1 and 2

Random copolymerizations of St and BA and St and MMA in the presence of **1** and **2** were carried out at 80 °C. The polymerization temperature, 80 °C, is much lower than those (120–130 °C) for the previously reported random copolymerizations [14–20]. The reason why the random

Fig. 1. The ln([M]$_0$/[M]$_t$) vs time plots for the polymerization of BA at 120 °C initiated by **3**. BA 1.0 ml, **3** 10.0 mmol l^{-1}; (—) DCP 0 mmol l^{-1}; (- - -) DCP 0.67 mmol l^{-1}.
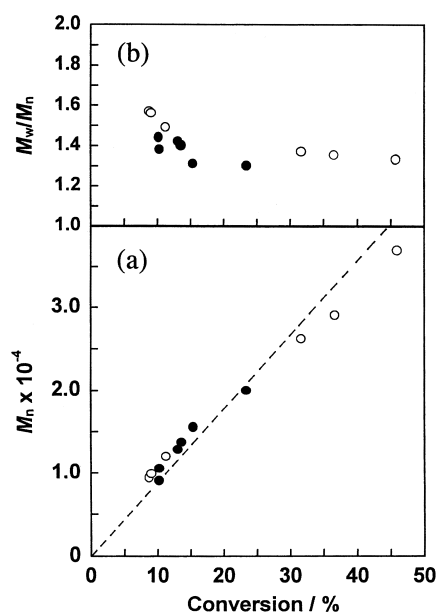

Fig. 2. (a) The M_n vs conversion plots and (b) the M_w/M_n vs conversion plots for the polymerization of BA at 120 °C initiated by **3**. BA 1.0 ml, **3** 10.0 mmol l^{-1}; (●) DCP 0 mmol l^{-1}; (○) DCP 0.67 mmol l^{-1}.

copolymerizations were carried at such a low temperature is to suppress side reactions such hydrogen abstraction. The compositions of the copolymers obtained were determined by the ^{1}H NMR method. For the copolymers from St and BA the molar fractions were determined by comparing the intensity ratio of the peaks due to the aromatic protons with the peak due to $-C(=O)OCH_2-$, and for the copolymers from St and MMA those were determined by comparing the intensity ratios of the peaks due to the aromatic protons with the peak due to $-OCH_3$. In Table 2, some results of the copolymerizations are summarized.

The random copolymerizations of St (m_1) and BA (m_2) mediated by **1** and **2** were carried out at 0.10–0.80 for f_1. When f_1 was more than 0.50, the resultant copolymers showed narrow polydispersities of 1.20–1.23, and when f_1 was 0.30, the polydispersity indexes, 1.33–1.38, were somewhat broader. In comparison with the previously reported TEMPO-mediated random copolymerization of St and BA at 125 °C [16], the TEMPO-system showed a fairly broad polydispersity of 1.45 at f_1 of 0.50, indicating that TEMPO is less effective than **1** or **2** for the living copolymerization of St and BA.

The random copolymerizations of St (m_1) and MMA (m_2) were carried out at 0.10–0.88 for f_1. When f_1 was more than 0.30, the resultant copolymers showed narrow poly-dispersites of 1.11–1.29, indicating that the copolymerization proceeds in a satisfactory living fashion. However, when f_1 was 0.10, the M_w/M_n was 1.59, showing a somewhat poor livingness. For comparison, the TEMPO-mediated random copolymerization of St and MMA was carried out at 80 °C. When f_1 was 0.50, the resultant copolymer showed a polydispersity index of 1.47 at 48% conversion, indicating a fairly poor livingness of the TEMPO-mediated copolymerization of St and MMA compared with that mediated by **2**.

In Fig. 3, the $\ln[M]_0/[M]_t$ vs time plots for the random copolymerization of St and BA mediated by **3** are shown. The monomer concentrations refer to the total monomer concentrations. When f_1s are 0.70 and 0.50, the copolymer-izations obey the first-order dependence on the total monomer concentration. However, when f_1s are 0.30 and 0.10, the polymerizations do not obey the first-order kinetics and the polymerization rates decreases with a decrease in f_1. This is in contrast to the conventional random copolymer-ization of St and BA, where the polymerization rates increase with a decrease in f_1. For this opposite results the following two explanations are plausible: one is the permanent deactivation of the propagating radicals by hydrogen abstraction from the propagating radicals by nitroxides which occurs more frequently with an increase in f_2 and the other is a shift of the equilibrium to the dormant side since the dormant species from the BA-end propagating chains has a stronger NO–C bond than the dormant species from the St-end propagating chain. However, as shown in Figs. 4a and b, the M_n,s increase linearly along with the same straight line with the conversion at any f_1, and the polydispersity indexes keep the value below the theoretical limit of 1.5, In particular, when f_1,s are more than 0.50, the resultant copolymers showed very narrow polydispersities of 1.20–1.23.

Table 2
Polydispersity indexes, M_w/M_n, and poly(St) equivalent molecular weights, M_n, for the syrene (St) and butyl acrylate (BA) and St and methyl methacrylate (MMA) random copolymerization initiated with **3** and **4** at 80 °C

Comonomer	Ratio of St/comonomer[a]	Alkoxyamine[b]	Time (h)	Conversion[c] (%)	M_n[d,e]	M_w/M_n[d]	St molar percent in copolymer[f]
BA	70/30	**3**	144	56	39,800	1.20	68
	50/50	**3**	189	63	56,500	1.23	56
	30/70	**3**	216	49	39,100	1.38	37
	10/90	**3**	408	37	28,900	1.45	22
	80/20	**4**	97	42	27,600	1.20	81
	70/30	**4**	72	26	22,000	1.22	72
	60/40	**4**	120	41	33,400	1.21	67
	30/70	**4**	194	36	29,400	1.33	33
	10/90	**4**	171	18	37,500	1.34	24
MMA	88/12	**4**	169	64	48,400	1.11	81
	80/20	**4**	144	60	49,700	1.12	74
	70/30	**4**	144	62	51,200	1.15	63
	50/50	**4**	145	59	46,200	1.18	47
	30/70	**4**	168	43	17,700	1.29	33
	10/90	**4**	142	15	13,000	1.59	16
	50/50	**5**	161	40	35,900	1.47	48

[a] The initial molar ratio of monomers in the feed.
[b] Alkoxyamine 10.0 mM.
[c] Calculated based on the total molar amount.
[d] Determined by SEC using standard poly(St)s as the reference.
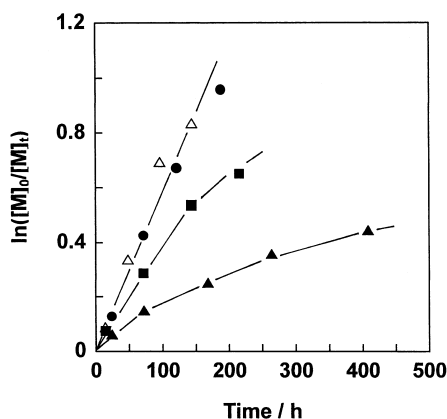[e] Poly(St) equivalent molecular weight.
[f] Determined by ^{1}H NMR (400 MHz).

Fig. 3. The $\ln([M]_0/[M]_t)$ vs time plots for the random copolymerization of St (m_1) and BA (m_2) at 80 °C initiated by **3**. **3** 10.0 mmol l^{-1}; (▲) $f_1 = 0.10$; (■) $f_1 = 0.30$; (●) $f_1 = 0.50$; (△) $f_1 = 0.70$.

Fig. 5. The $\ln([M]_0/[M]_t)$ vs time plots for the random copolymerization of St (m_1) and MMA (m_2) at 80 °C initiated by **4** and **5**. **4** 10.0 mmol l^{-1}; (▲) $f_1 = 0.10$; (■) $f_1 = 0.30$; (○) $f_1 = 0.50$; (△) $f_1 = 0.70$; (□) $f_1 = 0.80$; (○) $f_1 = 0.88$; (×) **5** 10.0 mmol l^{-1}, $f_1 = 0.50$.

In the copolymerization of St and MMA initiated with **4**, the polymerizations obey the first-order dependence on the total monomer concentration at f_1,s above 0.50, and the M_n,s increase linearly along with the same straight line with conversion, keeping the narrow polydispersities below 1.20 (Figs. 5 and 6). However, when f_1s are 0.30 and 0.10, the polymerizations do not obey the first-order kinetics and the polymerization rates decrease with a decrease in f_1, similar to the copolymerization of St and BA. This can be again explained by the permanent deactivation of the propagating radicals by hydrogen abstraction by nitroxide from the propagating radicals and a shift of the equilibrium to the dormant side. Although, at 0.30 of f_1 the M_n vs conversion plots show a large downward deviation from the above straight line, the M_w/M_n still keeps the value below 1.3. When f_1 is 0.10, an obvious termination of polymerization is
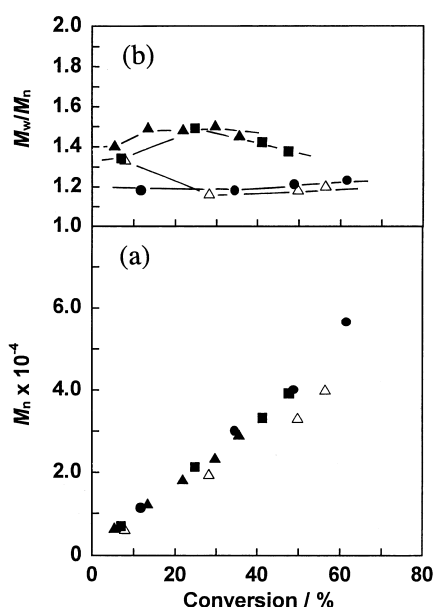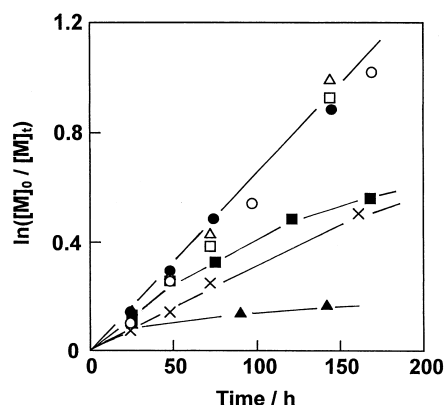
observed and the resultant copolymer shows a considerably broad polydispersity of 1.6 (Fig. 5).

3.3. Kinetic study for the NO–C bond homolysis of akoxyamines 3 and 4

One of the basic requirements for attaining low polydispersities is a large activation rate constants for dormant species, which is largely depends on the structures of the nitroxide moieties, and k_{act}'s were determined by many groups using the SEC [6,24–26], nitroxide exchange [27,28], oxygen-present radical trapping [29], and pre-fluoresent nitroxide switch methods [30]. In a previous paper [10] we reported that the equilibrium constants (K) for
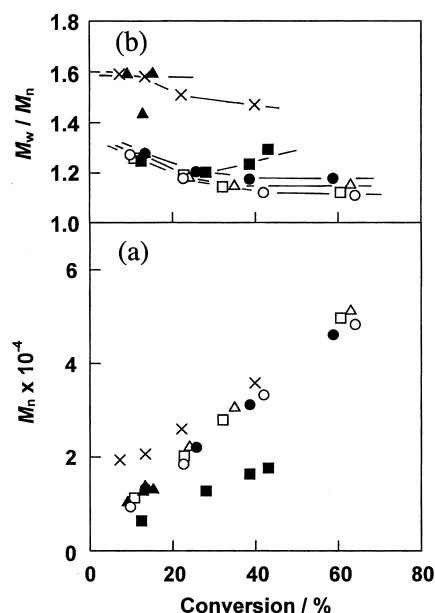

Fig. 4. (a) The M_n vs conversion and (b) M_w/M_n vs conversion plots for the random copolymerization of St (m_1) and BA (m_2) at 80 °C initiated by **3**. **3** 10.0 mmol l^{-1}; (▲) $f_1 = 0.10$; (■) $f_1 = 0.30$; (●) $f_1 = 0.50$; (△) $f_1 = 0.70$.

Fig. 6. (a) The M_n vs conversion and M_w/M_n vs conversion plots plots for the random polymerization of St (m_1) and MMA (m_2) at 80 °C initiated by **4** and TEMPO. **4** 10.0 mmol l^{-1}; (▲) $f_1 = 0.10$; (■) $f_1 = 0.30$; (●) $f_1 = 0.50$; (△) $f_1 = 0.70$; (□) $f_1 = 0.80$; (○) $f_1 = 0.88$. (×) **5** 10.0 mmol l^{-1}, $f_1 = 0.50$.

the dormant species were in the order $K(\mathbf{3}) > K(\mathbf{4}) \gg K(\mathbf{5})$. Interestingly, this order was in good agreement with that for the NO–C bond dissociation energies of the alkoxyamines calculated by the DFT Becke 3LYP method using the STO 6-31G basis set. In the present work we determined k_{act}'s for the NO–C bond homolysis of **3**, **4**, and **5** using the method of Bon, et al. (oxygen-present radical trapping method) [29].

$$\text{PhCH(Me)ONR} \underset{k_{deact}}{\overset{k_{act}}{\rightleftarrows}} \text{PhĊH(Me)} + \text{RNO·} \qquad (2)$$
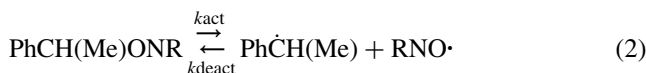
In this method the NO–C bond homolysis are conducted under the atmospheric conditions. Since the atmospheric oxygen serves as a scavenger for the carbon-centered radicals, the pseudo-first-order kinetics with the nitroxide concentrations can be established. The kinetic studies for **3–5** were carried out at 323–373 K using toluene as the solvent, and the concentrations of the nitroxides generated were determined by ESR using TEMPO as the reference. The pseudo-first-order plots at 80 °C are drawn in Fig. 7. The linear relationships between the nitroxide concentration and time are observed in the initial step of the reactions for all the alkoxyamines, and k_{act}'s were determined from the slopes. The results are summarized in Table 3. In Fig. 8, the Arrhenious plots for k_{act}'s are depicted, and the preexponential factors (A_{act}) and the activation parameters (E_{act}) were determined from the intercept and slope. In Table 4, the A_{act} and E_{act} are summarized, along with the literature values for **5** [27,28,30]. In comparison with those, both the A_{act} and E_{act} parameters for **5** in this work are in the range of the literature values.

Since the deactivation processes generally show only a small activation energy, the activation energy for the NO–C bond homolysis must be close to the NO–C bond dissociation energy. The E_{act}s for **3** and **4** are similar to each other, but they are substantially lower than that of **5**. This is in good agreement with the results of the MO calculations mentioned above. On the other hand, the A_{act} of **5** is much larger than those of **3** and **4**, but the contribution to the NO–C bond homolysis is of second inportance because

Table 3
The rate constants (k_{act}) for the NO–C bond homolysis of **3–5** in toluene at 323–363 K under the atmospheric conditions

Temperature (K)	k_{act} (s^{-1}) × 10^5		
	3	**4**	**5**
323	0.16		
333	0.61[a]	0.19	
343	2.4[a]	0.74[a]	0.098[a]
353	6.8[a]	2.5	0.41
363		7.7	1.4[a]

[a] The average values of two experiments are shown.

the difference between A_{act}s are not so large in magnitude as in E_{act}. This means that the steric factors of the nitroxides are reflected mainly on E_{act}, which is in contrast to a previous paper [26] in which the contribution of A_{act} is emphasized for the NO–C bond homolysis of the DEPN or di-*tert*-butyl nitroxide end-capped poly(St)s. This means that the relative importance of E_{act} and A_{act} for the NO–C bond homolysis depends on the structures of nitroxides.

4. Conclusions

The bulk polymerizations of BA mediated by **1** and **2** at 100–145 °C indicated that the polymerizations mediated by **1** at 120 and 145 °C gave well-controlled poly(BA)s with narrow polydispersities. The termination of the polymerization taking place around 20% conversion was overcome to a certain extent by adding DCP to the polymerization system. Radical **1** is obviously superior to TEMPO in the ability to control the polymerization of BA, but inferior to BMPN or DEPN in that the polymerization does not proceed to high conversions. To solve this problem, we plan to modify the nitroxide to a more sterically crowding structure. The random copolymerization of St and BA and St and MMA mediated by **1** and **2** at 80 °C gave well-controlled random copolymers with narrow polydispersities except the case of 0.10 for f_1. The kinetic ESR studies for the NO–C
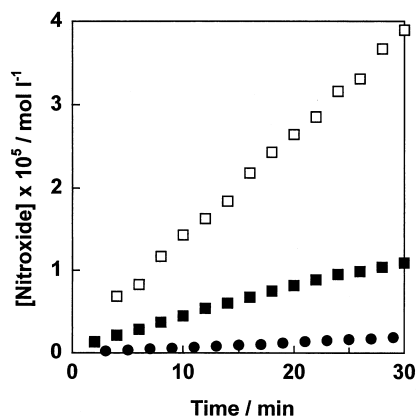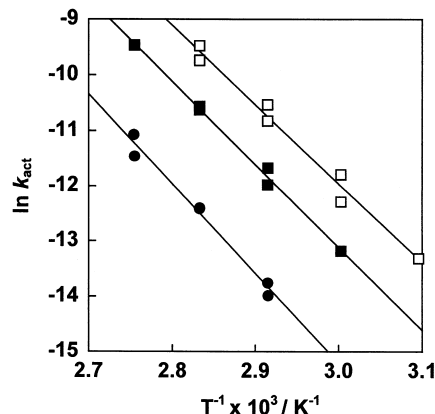

Fig. 7. First-order plots for the NO–C bond homolyses of the alkoxyamines **3**,**4** and **5** in toluene at 70 °C under the atmospheric conditions. [Akoxyamine] 10.0 mmol l^{-1}; (□) **3**; (■) **4** (●) **5**.

Fig. 8. Arrhenius plots of ln k_{act} vs T^{-1} for (□) **3**, (■) **4** (●) and **5**.

Table 4
The arrhenius parameters, A_{act} and E_{act}, for the C–O bond homolysis of of **3**–**5**

Run	Alkoxyamine	A_{act} $(s^{-1}) \times 10^{13}$	E_{act} $(kJ\ mol^{-1})$	Reference
1	**3**	2.3	118	This work
2	**4**	0.73	119	This work
3	**5**	17	133	This work
4	**5**[a]	5.0	128.3	27
5	**5**[a]	25	133	28
6	**5**[b]	2.0	126	30

[a] The values determined by the nitroxide exchange method.
[b] The value determined by the prefluoresent nitroxide switch method.

bond homolysis of alkoxyamines **3**–**5** showed that the steric effects of **1** and **2** were reflected mainly on E_{act}, rather than A_{act}.

Acknowledgements

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