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Block copolymerization of alkoxyallenes with phenylallene by the living coordination system with π-allylnickel catalyst

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Summary

The block copolymerization of alkoxyallenes (**2a**; *n*-octyloxyallene and **2b**; *n*-butoxyallene) with phenylallene (**3**) was carried out by $[(\pi\text{-allyl})NiOCOCF_3]_2$ (**1**) in toluene by the sequential addition of the two monomers. In spite of rather different polymerizability between **2** and **3** (i.e., **2** has ca. 70 times larger kinetic coefficient than **3**), block copolymers having narrow molecular weight distributions were obtained successfully by controlling the reactivity of the propagating end with the additives such as triphenylphosphine (PPh_3) and copper(I) iodide. In the case of the copolymerization of **3** with **2**, the addition of PPh_3 was effective for the control of the polymerization step of **2**. The block copolymers with controlled segment length and narrow molecular weight distributions ($M_w/M_n < 1.08$) were obtained almost quantitatively. Conversely, when the copolymerization was started from **2**, the control of the first stage required PPh_3 as a ligand of the initiator which interrupt the second polymerization of **3**. However, block copolymers with narrow molecular weight distributions ($M_w/M_n < 1.03$) were obtained simply by adding copper (I) iodide in the polymerization stage of **3**.

Introduction

Block copolymers often exhibit unique and useful properties both in solution and in solid states. Those composed of thermodynamically incompatible blocks are of importance for polymeric surfactants, and compatibilizers, etc. Though a variety of approaches have been attempted for the syntheses of block copolymers, only a few examples can provide block copolymers with controlled and well-defined structures. The method based on the living polymerizations is the most promising route for the syntheses of a varieties of block copolymers with well-defined structures, because the living polymerizations do not imply any termination or chain transfer processes. Block copolymers have been successfully prepared simply by the sequential addition of different monomers in cases of living anionic [1], cationic [2], group-transfer [3], and coordination [4] polymerizations. Recently, we have reported the living coordination polymerization of alkoxyallenes [5], arylallenes [6], and alkylallenes [7] by π-allylnickel systems to produce the polymers with predictable molecular weights and narrow molecular weight distributions ($M_w/M_n < 1.1$). Block copolymers from two kinds of alkoxyallenes have been also successfully obtained by the two-stage block copolymerization, because the propagating end in the polymerization is remarkably stable under nitrogen atmosphere [8]. Herein, we describe the block copolymerization of alkoxyallenes (**2a**; *n*-octyloxyallene and **2b**; *n*-butoxyallene) with phenylallene (**3**) by $[(\pi\text{-allyl})NiOCOCF_3]_2$ (**1**).

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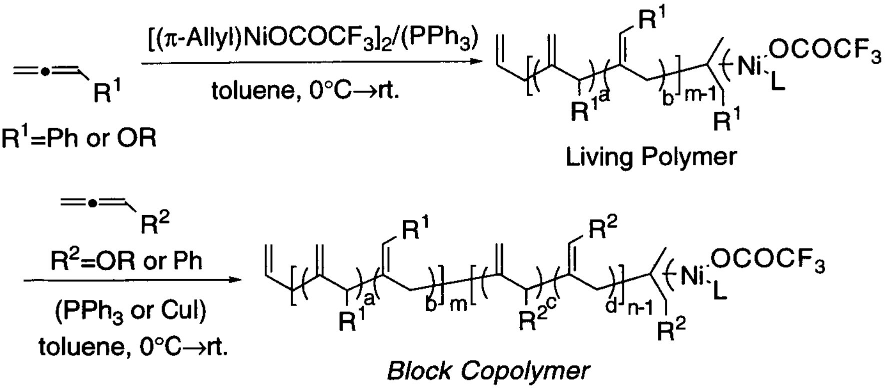
Scheme 1.



Results and discussions

Estimation of the polymerization rate of 2 and 3. In our previous papers, we have described independently the polymerization rate of alkoxyallenes [5b] and that of phenylallene [6]. However, they cannot be compared each other, because the catalyst systems used were different (i.e., the former was carried out in the presence of PPh_3, while the latter was performed without PPh_3). To estimate the polymerizabilities of these monomers under the same conditions, the polymerizations of *n*-octyloxyallene (**2a**) and phenylallene (**3**) were carried out independently by [(π-allyl)$NiOCOCF_3]_2$ (**1**) at 0 °C in toluene and their consumptions were monitored after designated reaction times (Figure 1). The time-conversion curves fitted well with the first order kinetic equations with respective to the monomers, in which the observed kinetic coefficients were evaluated to be $9.94\mathrm{x}10^3$ and $0.14\mathrm{x}10^3$ l•mol^{-1}•h^{-1} for **2a** and **3**, respectively. Accordingly, **2a** was confirmed to have higher polymerizability than **3** (by ca. 70 times in their kinetic coefficients).

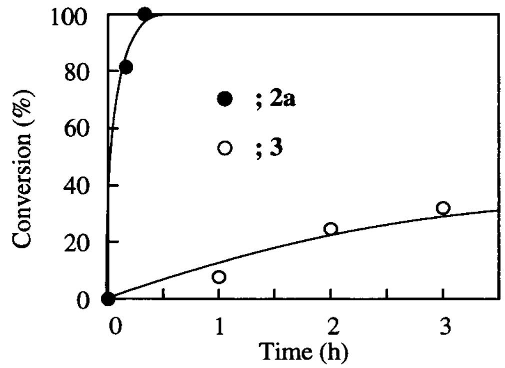
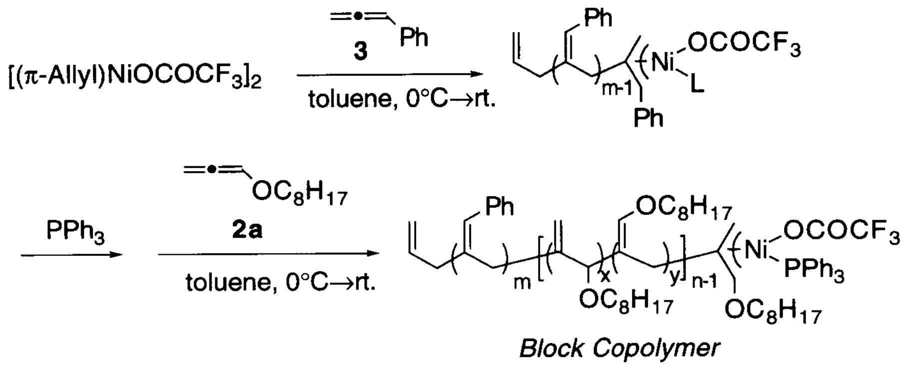


Figure 1. Time vs. conversion curves of **2a** and **3** in toluene at 0 °C using **1** as an initiator ([**2a**]$_0$=[**3**]$_0$=$5.0\mathrm{x}10^{-2}$ M, [**1**]=$1.0\mathrm{x}10^{-3}$ M).

Block copolymerization of 3 with 2. The block copolymerization of **3** with **2a** was performed in toluene by using **1** as an initiator (Scheme 2).

Scheme 2.



In the polymerization of **3** (30 equiv. relative to **1**) for 12 h, the complete consumption of **3** was monitored by GC and the number average molecular weight (M_n) and the molecular weight distributions (M_w/M_n) of the resulting polymer were estimated by GPC analysis by sampling a subtle amount of the polymer solution. Since the addition of phosphine ligand is effective to construct the living polymerization process of alkoxyallenes, a toluene solution of PPh_3 (2 equiv. relative to the nickel) was added to the polymerization mixture, and the following reaction of **2a** (30 equiv. relative to **1**) was conducted for 12 h. As is clearly observed from Figure 2, the elution peak in GPC shifted to the higher molecular weight region ((b); M_n=10,900, M_w/M_n=1.07) compared with that of the starting poly(**3**) ((a); M_n=4,820, M_w/M_n=1.04), keeping the narrow molecular weight distribution.

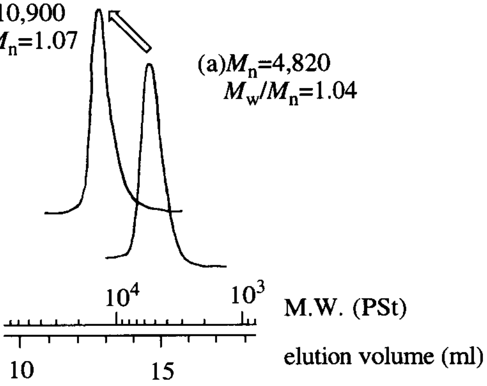


Figure 2. GPC traces of (a); poly(**3**) produced by the reaction of **3** (30 equiv.) by **1** and (b); obtained by the further polymerization of **2a** (30 equiv.).

By pouring the reaction mixture into H_2O/MeOH (v/v=1/1), the block copolymer (poly(**3**-**2a**)) was isolated in 95 % yield. In the ^1H NMR spectrum of poly(**3**-**2a**), peaks assignable both to poly(**2a**) and poly(**3**) segments could be observed, where the poly(**2a**) segment was composed of 1,2- and 2,3-polymerized units in the ratio of 26:74 (determined by the integral ratio of the peaks around 5.0 and 5.9 ppm, respectively), while poly(**3**) segment was exclusively composed of 2,3-polymerized unit (Figure 3). The copolymer composition (**3**:**2a**= 52:48) of the obtained poly(**3**-**2a**), which was determined by the integral ratio of the peaks at 7.2 (-C_6H_5) and 0.9 (-CH_3) ppm in the ^{1}H NMR spectrum, was agreed well with the feed ratio (**3**:**2a**=50:50) of the monomers. The double bonds in the block copolymer were also confirmed to remain quantitatively.

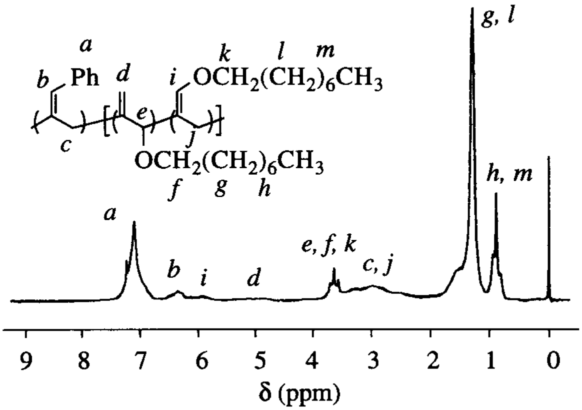


Figure 3. ^{1}H NMR spectrum of poly(**3**-**2a**) (Table 1, run 1).

Accordingly, the block copolymerization of **3** with **2a** by **1** proceeded successfully by the two-stage polymerization of **3** followed by **2a** (i.e., the polymerization of the monomer with lower polymerizability and then one with higher polymerizability). The block copolymerization of **3** with **2a** or with *n*-butoxyallene (**2b**) was carried out under the various feed ratio (Table 1, runs 1-6). In all cases, block copolymers with narrow molecular weight distributions were obtained in high yields, where the length of each segments in block copolymers could be controlled by the monomer feed ratio. Without the addition of PPh_3 to the polymerization system before feeding the second monomer (**2a**), however, the molecular weight distributions of the obtained block copolymer became a little broader ($M_w/M_n \cong 1.2$) (run 7) [9].

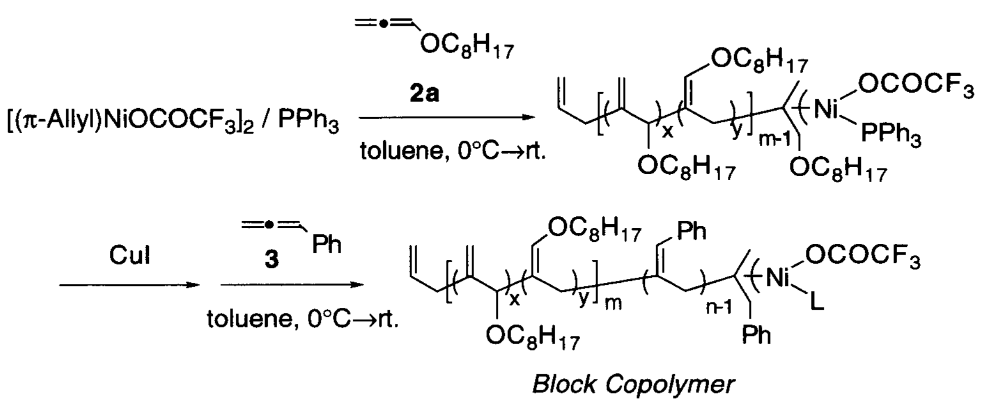
Table 1. The block copolymerization of **3** with **2a** or **2b** under various feed ratio.

	Homopolymer			Block Copolymer					
run	[**3**]/[**1**]	M_n a)	M_w/M_n a)	**2**	[**2**]/[**1**]	M_n a)	M_w/M_n a)	yield (%) b)	m:n c)
1	30	4,820	1.04	**2a**	30	10,900	1.07	95	52:48
2		4,370	1.04		50	12,500	1.04	97	38:62
3		5,050	1.05		70	14,800	1.05	99	31:69
4	30	4,260	1.04	**2b**	30	8,730	1.08	94	53:47
5		4,290	1.04		50	11,000	1.05	93	38:62
6		4,120	1.04		70	13,300	1.05	99	33:67
7 d)	30	4,890	1.04	**2a**	30	10,700	1.17	96	53:47

a) Estimated by GPC (THF, PSt Std). b) The isolated yield after precipitation with H_2O/MeOH (v/v=1/1).
c) The length of each segment was determined by ^{1}H NMR of the block copolymer.
d) The polymerization of the second monomer (**2a**) was carried out in the absence of PPh_3 ligand.

Block copolymerization of 2 with 3 (In reverse monomer feeding). The block copolymerization was also demonstrated by the another order of the monomer addition (i.e., the polymerization of **2a** followed by that of 3) (Scheme 3).

Scheme 3.



The polymerization of **2a** (30 equiv. relative to **1**) by **1** was carried out in the presence of PPh_3 for 12 h. After checking the complete consumption of **2a**, a subtle amount of the polymerization mixture was sampled up for the GPC measurement. The block copolymerization with **3** did not proceed when the monomer (**3**) was added directly to the polymerization solution, because the polymerization of **3** does not proceed in the presence of PPh_3 (run 5). Though the block copolymer with predicated segment length could be obtained successfully when the polymerization of both **2a** and **3** was carried out without PPh_3, the molecular weight distribution of the resulting block copolymer became a little bloader ($M_w/M_n \cong 1.2$) (run 6) [9]. To carry out the polymerization of **2** in the presence of PPh_3 and to obtain a moderate reactivity of the living end for the polymerization of **3**, modification of the propagating end was examined. In the case of the Stille coupling reaction (i.e., the Pd-catalyzed cross-coupling reaction of organotins with aromatic halides), the addition of a Cu (I) salt has been reported to be effective to enhance the catalytic activity, where the Cu salt is proposed to be a excellent scavenger of PPh_3 from the palladium. As the copper salt or the combination of the copper salt and the phosphine ligand was confirmed not to react with the monomer (**3**) or the polymer under the polymerization conditions, CuI (1 equiv. relative to PPh_3) was added to the polymerization system followed by the addition of **3** (30 equiv. relative to **1**). As a result, the polymerization of **3** took place to reach its complete conversion within 2 days at ambient temperature. The elution peak in GPC shifted to the higher molecular weight region ((b); M_n=10,900, M_w/M_n=1.03) compared with the starting poly(**2a**) ((a); M_n=6,690, M_w/M_n=1.05), keeping the narrow molecular weight distribution (Figure 4). The block copolymer (poly(**2a**-**3**)) was isolated in 97 % yield by pouring the reaction mixture into H_2O/MeOH (v/v=1/1). From the ^1H NMR spectrum of the block copolymer, the length of each segments (poly(**2a**):poly(**3**)=49:51) agreed well with the value predicted from the monomer feed ratio (**2a**:**3**=50:50). Likewise, the block copolymerization of **2a** (or **2b**) with **3** was performed under various monomer feed ratio to yield the block copolymers with predictable segment ratios and narrow molecular weight distributions (Table 2, runs 1-4). Generally, the order of the monomer addition is quite important factor to obtain well-defined block copolymers if the monomers have much different polymerizability. Namely, it is preferable to polymerize less reactive monomer followed by more reactive one, because the propagating species generated from less reactive monomer generally has higher reactivity which can effectively re-initiate the polymerization of the second monomer. Conversely, less reactive propagating species is produced by the reverse order of the monomer feeding, which does not re-initiate effectively the polymerization of less reactive second monomer. Although the polymerizability of **2** is considerably higher than that of **3** (by ca. 70 times based on their k_{obs}s), the present living system could afford block copolymers with controlled length of each segments and narrow molecular weight distributions irrespective of the order of the monomer addition. In the present living system, control of the reactivity of the propagating end could be available simply by adding PPh_3 or CuI after the polymerization of the first monomer, which might be a part of reasons for the smooth re-initiation of the second monomer.

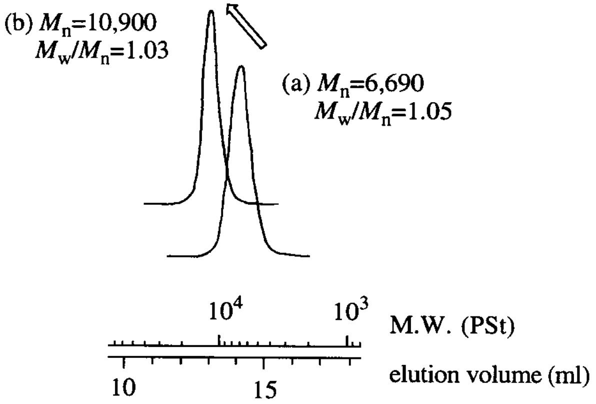


Figure 4. GPC traces of (a); poly(**2a**) produced by the reaction of **2a** (30 equiv.) by **1** and (b); obtained by the further polymerization of **3** (30 equiv.).

Table 2. The block copolymerization **2a** or **2b** with **3** under various feed ratio.

	Homopolymer				Block Copolymer				
run	2	[2]/[1]	M_n [a]	M_w/M_n [a]	[3]/[1]	M_n [a]	M_w/M_n [a]	yield (%) [b]	m:n [c]
1	**2a**	30	6,690	1.05	30	10,900	1.03	97	49:51
2			6,540	1.05	50	12,100	1.03	98	37:63
3	**2b**	30	4,470	1.07	30	9,050	1.03	96	48:52
4			4,680	1.06	50	10,900	1.03	96	34:66
5 [d]	**2a**	30	5,700	1.06	30	-	-	- [e]	-
6 [f]			8,090	1.26		11,700	1.15	98	47:53

a) Estimated by GPC (THF, PSt Std). b) The isolated yield after precipitation in H_2O/MeOH (v/v=1/1).
c) The length of each segment was determined by ^1H NMR of the block copolymer.
d) The polymerization of the second monomer (**3**) was carried out without CuI.
e) The block copolymer was not obtained.
f) The polymerization of both **2a** and **3** was performed without PPh_3 ligand.

Experimental section

Materials and instruments. Alkoxyallenes (**2a** and **2b**) [10] and phenylallene (**3**) [11] were synthesized as described previously and distilled before use. Toluene was dried over sodium and distilled under nitrogen. All the polymerizations were carried out under nitrogen.

^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a JEOL EX-90 or a JEOL EX-400 instrument (tetramethylsilane as an internal standard). IR spectra were obtained on a JASCO FT/IR-5300 spectrometer. Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G2500H$_{XL}$ + G3000H$_{XL}$ or G4000H$_{XL}$ + G5000H$_{XL}$, THF as an eluent) on the basis of standard polystyrene samples. Gas chromatographic (GC) analyses were performed on a Shimadzu GC-4A equipped with a FID detector using *n*-tetradecane as an internal standard (SE-30, 1 m, gradient temperature of 100 to 230 °C, 10 °C/min).

Block copolymerization of 3 with 2a (Typical procedure). To a flask containing a magnetic stir bar, were added a toluene solution of **1** (2.0×10^{-2} mmol) and **3** (0.070 g, 0.60 mmol, 30 equiv. relative to **1**) at 0 °C, and the polymerization was conducted for 12 h at ambient temperature. After checking the complete conversion of **3** by GC, a small portion of the polymer solution (ca. 20 µl) was subjected to the GPC measurement. To the polymer solution, were added a toluene solution of PPh_3 (4.0×10^{-2} mmol) and then **2a** (0.101 g, 0.60 mmol, 30 equiv. relative to **1**) at 0 °C and the further polymerization was performed for 12 h. After monitoring the complete consumption of **2a** by GC, the solvent was removed under reduced pressure and the resulting viscous product was dissolved into THF (2 ml) and was precipitated into H_2O/MeOH (v/v=1/1) (100 ml) to give poly(**3**-**2a**) in 95 % yield (0.160 g); ^{1}H NMR ($CDCl_3$, δ, ppm) 0.55-1.10 ($-CH_3$, 3nH), 1.10-1.85 ($-(CH_2)_6-$, 12nH), 2.20-3.55 ($=C-CH_2-C=$, 2nHx0.74+2mH), 3.55-4.30 ($=C-OCH_2-$, $>C-OCH_2-$, $>CH-O$, 1nHx0.26+2nH), 4.60-5.60 ($=CH_2$, 2nHx0.26), 5.60-6.20 ($=CH-O-$, 1nHx0.74), 6.20-6.70 ($=CH-Ph$, 1mH), 6.70-7.60 ($-C_6H_5$, 5mH), m:n=52:48. Similarly, block copolymers were obtained as follows:

Poly(**3**-**2b**) (from **3** (30 equiv.) and **2b** (30 equiv.)): 94 % yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 0.55-1.10 ($-CH_3$, 3nH), 1.10-1.85 ($-(CH_2)_2-$, 4nH), 2.20-3.55 ($=C-CH_2-C=$, 2nHx0.74+2mH), 3.55-4.30 ($=C-OCH_2-$, $>C-OCH_2-$, $>CH-O$, 1nHx0.26+2nH), 4.60-5.60 ($=CH_2$, 2nHx0.26), 5.60-6.20 ($=CH-O-$, 1nHx0.74), 6.20-6.70 ($=CH-Ph$, 1mH), 6.70-7.60 ($-C_6H_5$, 5mH), m:n=53:47.

Block copolymerization of 2a with 3 (Typical procedure). To a flask containing a magnetic stir bar, a toluene solution of **1** (2.0×10^{-2} mmol) and PPh_3 (4.0×10^{-2} mmol), was added **2a** (0.101 g, 0.60 mmol, 30 equiv. relative to **1**) at 0 °C and the polymerization was conducted for 12 h at ambient temperature. After checking the complete conversion of **2a** by GC, a small portion of the polymer solution (ca. 20 µl) was subjected to the GPC measurement. To the polymer solution, were added CuI (8.0×10^{-3} g, 4.0×10^{-2} mmol) and then **3** (0.070 g, 0.60 mmol, 30 equiv. relative to **1**) at 0 °C and the further polymerization was performed for 2 days. After monitoring the complete consumption of **3** by GC, the solvent was removed under the reduced pressure and the resulting viscous product was dissolved into THF (2 ml) and was precipitated into H_2O/MeOH (v/v=1/1) (100 ml) to give poly(**2a**-**3**) in 97 % yield (0.166 g); ^{1}H NMR ($CDCl_3$, δ, ppm) 0.55-1.10 ($-CH_3$, 3mH), 1.10-1.85 ($-(CH_2)_6-$, 12mH), 2.20-3.55 ($=C-CH_2-C=$, 2mHx0.74+2nH), 3.55-4.30 ($=C-OCH_2-$, $>C-OCH_2-$, $>CH-O$, 2mH+1mHx0.26), 4.60-5.60 ($=CH_2$, 2mHx0.26), 5.60-6.20 ($=CH-O-$, 1mHx0.74), 6.20-6.70 ($=CH-Ph$, 1nH), 6.70-7.60 ($-C_6H_5$, 5nH), m:n=49:51.

Poly(**2b**-**3**) (from **2b** (30 equiv.) and **3** (30 equiv.)): 96 % yield; ^{1}H NMR ($CDCl_3$, δ, ppm) 0.55-1.10 ($-CH_3$, 3mH), 1.10-1.85 ($-(CH_2)_2-$, 4mH), 2.20-3.55 ($=C-CH_2-C=$, 2mHx0.74+2nH), 3.55-4.30 ($=C-OCH_2-$, $>C-OCH_2-$, $>CH-O$, 1mHx0.26+2mH), 4.60-

5.60 (=CH_2, 2mHx0.26), 5.60-6.20 (=CH-O-, 1mHx0.74), 6.20-6.70 (=CH-Ph, 1nH), 6.70-7.60 (-C_6H_5, 5nH), m:n=48:52.

Estimation of the kinetic coefficient (Typical procedure). The polymerization of **2a** ($[\mathbf{2a}]_0/[\mathbf{1}]=50$, $[\mathbf{2a}]_0=5.0\times10^{-2}$ M) was performed in toluene containing *n*-tetradecane (2.0×10^{-3} M) as an internal standard at 0 °C similar to the above mentioned procedure. After the designated reaction period at 0 °C, a small portion of the reaction mixture was sampled by the syringe (ca. 10 μl) and the conversion of **2a** was estimated by GC analyses.

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