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Novel Approach to Well-Defined Synthesis of a Polyester Bearing Phenol Moiety: Anionic Alternating Copolymerization of Ethylphenylketene with 4-(*tert*-Butyldimethylsilyloxy)benzaldehyde

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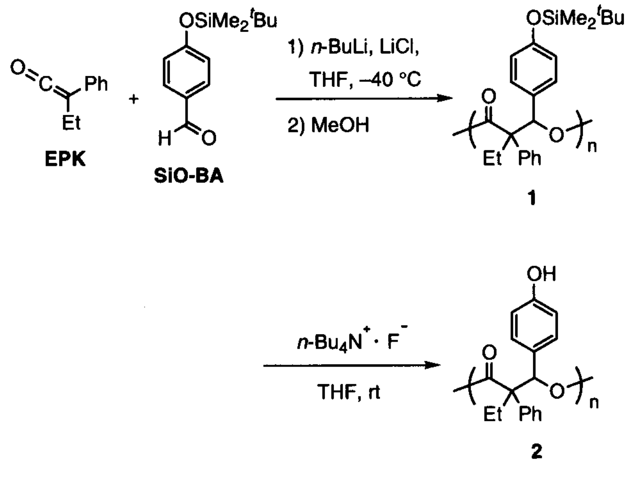
ABSTRACT: Anionic copolymerization of ethylphenylketene (**EPK**) with 4-(*tert*-butyldimethylsilyloxy)-benzaldehyde (**SiO−BA**) was carried out using butyllithium as an initiator in THF at −40 °C. The copolymerization proceeded via 1:1 alternation, generating the corresponding polyester having silyl protected phenol moiety in the side chain quantitatively. By addition of lithium chloride to the polymerization system, the polymerization proceeded in a living fashion to afford the corresponding polyester having narrow molecular weight distribution ($M_w/M_n < 1.2$). Treatment of the obtained polymer with tetrabutylammonium fluoride in the presence of acetic acid resulted in complete removal of the silyl group without main chain degradation to afford polyester having phenol moiety, which was soluble in methanol. Thermal degradability of the polyester with phenol moiety was considerably higher than that of the silyl-protected polymer, suggesting that the acidity of the phenol moiety would promote thermal dissociation of the polyester main chain.

Introduction

Polymers bearing hydroxyl group in their side chains have been widely applied as functional polymers such as resist materials,[1] biomedical materials,[2] and surfactants,[3] since the hydroxyl group makes the polymers reactive, hydrophilic, and biocompatible. Well-defined syntheses of these polymers has been one of the most important subjects in polymer science, because their functions can be modified or totally changed by controlling molecular weight and polymer shape (block copolymer, comblike polymer, starlike polymer). An established strategy is to protect the hydroxyl group of the monomer that is compatible with the polymerization conditions, and deprotect it after polymerization.[4] Another strategy involves living polymerization of monomer having extra vinyl group that can be converted into hydroxyl alkyl group by oxidation (osmylation, ozonolysis) or reduction (hydroboration, hydrosilylation).[5]

Previously, we developed a living anionic alternating copolymerization of ethylphenylketene (**EPK**) with 4-methoxybenzaldehyde (**MBA**), which afforded the corresponding polyester having alkoxy phenyl group in the side chain with predictable molecular weight and narrow molecular weight distribution.[6] This prompted us to use 4-silyloxybenzaldehyde as a monomer for the analogous copolymerization to afford the corresponding polyester **1**, whose silyl group can be removed to afford the polyester **2** having a phenol moiety (Scheme 1). The polyester **2** having a phenol moiety not only should be hydrophilic, but also should be applicable as a new resist polymer, whose main chain should be degradable into alkali-washable products.

Scheme 1



Experimental Section

Materials and Instruments. EPK[7] and 4-(*tert*-butyldimethylsilyloxy)benzaldehyde (**SiO−BA**)[8] were synthesized according to reported procedures and were distilled prior to use under reduced procedure. Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl prior to use. *n*-BuLi was purchased as a hexane solution (1.52 M) from Kanto Chemical, Co. LiCl (Kanto Chemical, Co., >99.95%) was dried with heating under vacuum in a polymerization vessel. Tetrabutylammonium fluoride was purchased as a THF solution (1.00 M) from Aldrich Chem. Co.

^{1}H NMR spectra were recorded with a JEOL Lambda-300 spectrometer with tetramethylsilane (TMS) as an internal

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standard; the δ and J values were given in ppm and Hz, respectively. IR spectra were recorded with a Jasco FT-IR-5300 spectrometer and the values were given in cm^{-1}. Number-average molecular weights (M_n) and molecular weight distributions (M_w/M_n) were estimated by size exclusion chromatography (SEC) on a Tosoh HLC 8120 system equipped with two consecutive polystyrene gel columns (Tosoh TSK gels G4000HXL and G-2500HXL), ultraviolet, reflactive index, viscometer, and light scattering (Viscotek model T60, 670 nm) detectors using tetrahydrofuran (THF) as an eluent, with a flow rate of 1.0 mL/min by polystyrene calibration at 40 °C. Thermogravimetric (TG) analysis was carried out on a Seiko Instrument TG/DTA 6200 at a heating rate of 10 °C/min under a nitrogen atmosphere.

Copolymerization of EPK with SiO−BA. Typical procedure: **EPK** (440 mg, 3.00 mmol), **SiO−BA** (760 mg, 3.20 mmol), and *n*-BuLi (33 μL of 1.52 M in hexane, 0.05 mmol) were added to a THF solution (10 mL) of LiCl (63.6 mg, 1.50 mmol) at −40 °C, and the mixture was stirred for 10 min at the same temperature. The reaction was quenched by addition of MeOH (1 mL). SEC analysis of the crude mixture was carried out to estimate the molecular weight (M_n) and the molecular weight distribution (M_w/M_n) of the formed polymer ($M_n = 10\,600$, $M_w/M_n = 1.16$). The mixture was poured into MeOH (100 mL), and the resulting precipitates were collected by filtration with suction and dried under vacuum to obtain **1** (1.11 g, 96% yield) as white powder. Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.21; H, 7.90. Found: C, 71.82; H, 8.27. T_{d5} (temperature at 5% weight loss) = 213 °C; T_{d95} (temperature at 95% weight loss) = 323 °C.

Deprotection of Polymer 1. Acetic acid (90 μL, 1.59 mmol) and tetrabutylammonium fluoride (0.78 mL of 1.00 M THF solution, 0.78 mmol) were added dropwise to a THF solution of the polymer **1** (200 mg, 0.52 mmol of silyloxy group) at 0 °C. The reaction mixture was stirred for 1 h at room temperature. The mixture was poured into 1 M aqueous HCl (30 mL), and the resulting precipitate was collected by filtration with suction, dissolved in THF, and reprecipitated with hexane. Reprecipitation was repeated once, and the resulting precipitate was collected by filtration with suction and dried under vacuum to obtain **2** (145 mg, quantitative yield) as white powder. Anal. Calcd for $C_{17}H_{16}O_3$: C, 76.10; H, 6.01. Found: C, 75.68; H, 6.71. T_{d5} = 158 °C; T_{d95} = 253 °C.

Results and Discussion

Anionic Copolymerization of EPK with SiO−BA. The optimum conditions for the anionic copolymerization of **EPK** with 4-methoxybenzaldehyde (**MBA**) were applied to that of **EPK** with 4-(*tert*-butyldimethylsilyloxy)benzaldehyde (**SiO−BA**):[6] Using *n*-BuLi as an initiator, **EPK** (*n* equiv to *n*-BuLi) was copolymerized with **SiO−BA** (1.1*n* equiv to *n*-BuLi) in the presence of LiCl (30 equiv to *n*-BuLi) in THF at −40 °C. When the feed ratio of $[\textbf{EPK}]_0/[n\text{-BuLi}]_0$ was 60, the polymerization proceeded rapidly, and the characteristic yellow color of **EPK** disappeared within 5 min to indicate its complete consumption. SEC analysis of the resulting mixture indicated formation of the corresponding polymer having a narrow unimodal profile, which was isolated quantitatively by precipitation with MeOH. The elemental analysis of the obtained polymer supported the incorporation of **EPK** and **SiO−BA** units into the polymer in 1:1 ratio, which was further confirmed by the ^{1}H NMR spectrum of the polymer, in which the signals corresponding to *tert*-butyldimethylsilyl group and those corresponding to the aromatic protons were observed with the expected integration ratio (Figure 1a). A strong absorption peak was observed at 1738 cm^{-1} in the IR spectrum of the obtained polymer, which is attributable to ester linkage but not to the polyester obtained by the homopolymerization of **EPK** (IR-absorption at 1745 cm^{-1}).[6,9] From these results, the structure of the polymer was determined as **1**, which was formed by alternating copolymerization of **EPK** with **SiO−BA**.

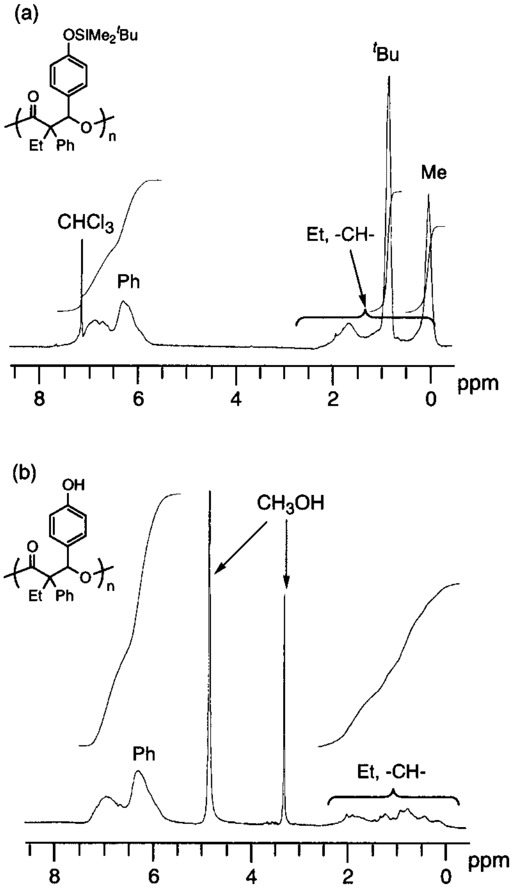


Figure 1. ^{1}H NMR spectra of the polymers (300 MHz, at room temperature): (a) polymer **1** (in $CDCl_3$); (b) polymer **2** (in CD_3OD).

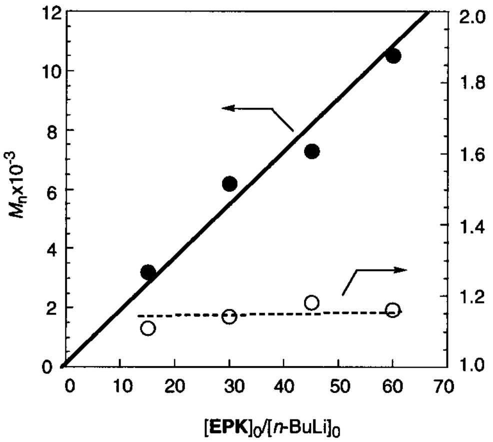


Figure 2. M_n and M_w/M_n vs $[\textbf{EPK}]_0/[n\text{-BuLi}]_0$ in the copolymerization of **EPK** with **SiO−BA**.

The number-average molecular weight (M_n) of **1** could be controlled by the monomer-initiator feed ratio. As shown in Figure 2, SEC-estimated M_n increased in direct proportion to the monomer feed ratio maintaining narrow molecular weight distribution (M_w/M_n, MWD < 1.18) to indicate that chain transfer can be neglected in the present polymerization.

We also confirmed that termination is negligible in the present polymerization by a two-stage polymeriza-

Table 1. Desilylation of Polymer 1 with Tetrabutylammonium Fluoride (TBAF)

entry	amount of TBAF/equiv	amount of AcOH/equiv	M_n (M_w/M_n)[a] of **1**	M_n (M_w/M_n)[a] of **2**	M_n(calcd)[b] of **2**	degree of desilylation[c]	yield/%[d]
1	6	0	5300 (1.21)	200 (2.19)	3700	>0.95	70
2	3	0	5100 (1.23)	800 (1.89)	3600	>0.95	81
3	1.5	0	5300 (1.21)	1600 (1.41)	3700	>0.95	90
4	1.5	1.7	6100 (1.19)	2700 (1.21)	4300	>0.95	92
5	1.5	3.0	6400 (1.15)	3400 (1.14)	4500	>0.95	quant
6	1.5	6.0	5500 (1.16)	3000 (1.16)	3900	>0.95	87

[a] Estimated by SEC-analysis (THF, PSt-standards). [b] Calculated M_n of **2** from **1**. [c] Determined by ^{1}H NMR. [d] Hexane-insoluble parts.

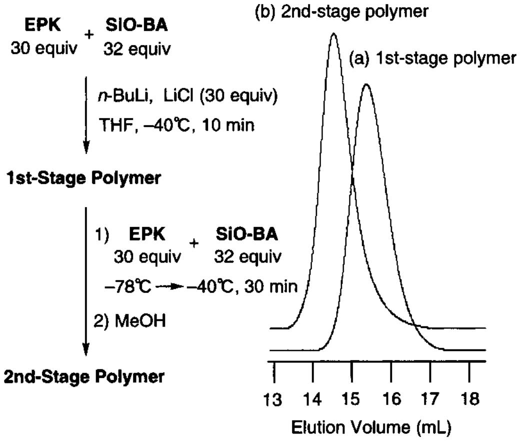


Figure 3. SEC profiles obtained by the copolymerization of **EPK** with **SiO−BA** in the presence of 30 equiv of LiCl to *n*-BuLi in THF at −40 °C: (a) polymer obtained after the first-stage polymerization for 10 min, M_n = 5700, M_w/M_n = 1.13; (b) polymer obtained after the second-stage polymerization for 30 min, M_n = 11 300, M_w/M_n = 1.18. [*n*-BuLi]$_0$ = 0.005 M; [**SiO−BA**]$_0$/[**EPK**]$_0$ = 1.1.

tion experiment. As shown in Figure 3, SEC analysis showed that the unimodal peak of the second-stage polymer shifted from that of the first-stage polymer toward higher molecular weight, maintaining narrow MWD, to support the living mechanism of the present polymerization.

Removal of the Silyl Group from the Obtained Polymer. The *tert*-butyldimethylsilyl (TBDMS) group is widely applied to protect the hydroxyl group in organic synthesis, since it has the virtue of being stable under basic conditions and weakly acidic conditions. Among various conditions for its removal, treatment with fluoride anion is the most widely used method, because other functional groups are not affected. As a fluoride source, tetrabutylammonium fluoride (TBAF) is most widely used for this purpose. Living anionic polymerization of 4-(*tert*-butyldimethylsilyloxy)styrene, followed by desilylation of the resulting polymer with TBAF, is a reliable method to synthesize well-defined poly(4-vinylphenol).[4c]

Thus, TBAF was used as the reagent for desilylation of polymer **1**. The conditions and results of desilylation are shown in Table 1. When **1** was treated with TBAF (6 equiv relative to the TBDMS group) in THF at room temperature, the TBDMS group was completely removed within 1 h. However, the polymer main chain degraded to afford a mixture of oligomers (Table 1, entry 1). Although the main chain degradation was slightly suppressed by decreasing the amount of TBAF, the results were not satisfactory (entries 2 and 3). The scission of the ester main chain is presumably caused by nucleophilic attack by phenoxide anion, which is formed by nucleophilic substitution at the silicon atom by fluoride anion. The formed phenoxide anion is a "naked anion", whose nucleophilicity and basity are quite high due to weak interaction with tetrabutylammonium countercation. Thus, to promote protonation of the formed phenoxide anion and neutralize the reaction conditions, acetic acid was added to the system (Scheme 2). As shown in entries 4−6 in Table 1, the main chain degradation was remarkably suppressed maintaining high efficiency in the desilylation to afford polymer **2** having narrow MWD in good yields. Figure 1b shows the ^{1}H NMR spectrum of the polymer **2** obtained in entry 5, in which the signals corresponding to TBDMS group completely disappeared. The resulting desilylated polymer **2** has polar phenol moiety and its molecular weight would be smaller than expected one from that of protected polymer **1** (Table 1), because of the strong absorption of OH functionalities on the polystyrene gel columns. Thus, the change of M_n through the desilylation was also evaluated by viscometer light scattering (VLS) analysis of the polymers.[10] The M_n of **1**, used in entry 5, was estimated to be 8300, from which the M_n of **2** was calculated to be 5800 on assumption that the desilylation proceeded quantitatively. The M_n of **2**, obtained in entry 5, was estimated to be 5200 by VLS analysis, which agreed with the calculated one to indicate that no main chain degraded.

Scheme 2

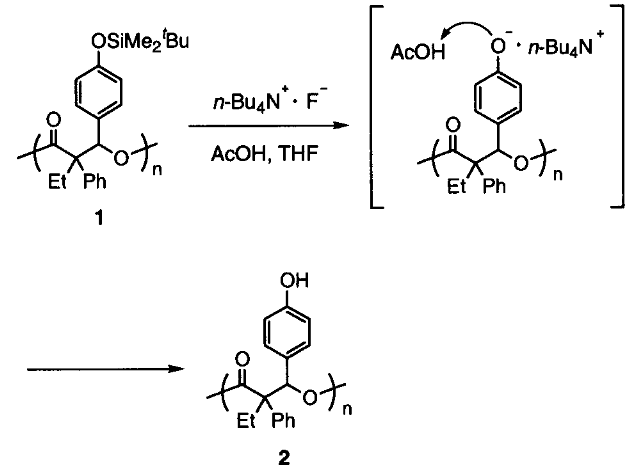


Table 2. Solubility of Polymers 1 and 2[a]

polymer	hexane	benzene	CHCl$_3$	THF	DMF	EtOH	MeOH	H$_2$O
1	○	○	○	○	×	×	×	×
2	×	×	×	○	○	○	○	×

[a] 100 mg of the polymer was added to 1.0 mL of solvent: (○) soluble; (×) insoluble.

Properties of the Obtained Polymers. Table 2 summarizes the solubilities of the obtained polymers. The solubilities of the protected polymer **1** and the deprotected one **2** were very different: **1** is soluble in

Table 3. Degradation of Polymers 2 and 3 under Acidic and Basic Conditions[a]

				M_n (M_w/M_n) of **2**		M_n (M_w/M_n) of **3**	
entry	reagent (M)	solvent	time	before degradation	after degradation	before degradation	after degradation
1	TFA (0.1)[b]	CH_2Cl_2	5 min	3000 (1.16)	600 (1.12)	3600 (1.16)	600 (1.19)
2	pyridine (1)[c]	THF	24 h	3700 (1.14)	3700 (1.14)	3200 (1.15)	3200 (1.15)
3	triethylamine (1)[c]	THF	24 h	3700 (1.14)	3700 (1.14)	3200 (1.15)	3200 (1.15)
4	DMAP (1)[c]	THF	24 h	3700 (1.14)	1500 (1.65)	3200 (1.15)	3200 (1.15)

[a] All experiments were carried out at room temperature. [b] 14 equiv to repeating unit of the polymers **2** and **3**. [c] 6 equiv to repeating unit of **2** and **3**. [d] Estimated by SEC analysis (THF, PSt standards).

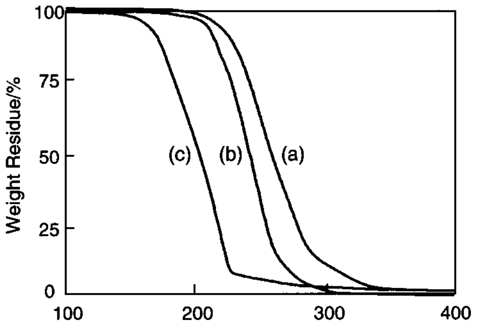
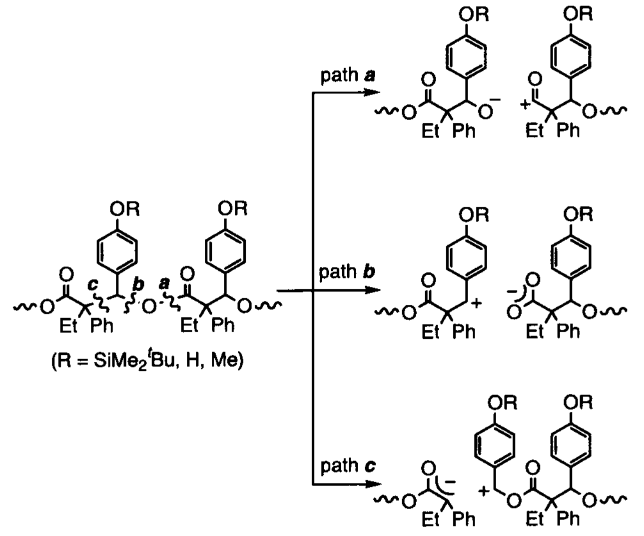


Figure 4. TG curves of the polymers: (a) polymer **1** (M_n = 5700, M_w/M_n = 1.13); (b) polymer **3** (M_n = 4600, M_w/M_n = 1.13) obtained by the copolymerization of **EPK** with 4-methoxybenzaldehyde (**MBA**); (c) polymer **2** (M_n = 3700, M_w/M_n = 1.14).

Scheme 3



nonpolar solvents such as hexane and benzene and insoluble in polar solvents such as *N*,*N*-dimethylformamide (DMF), ethanol, methanol, and water. In contrast, as expected from the high polarity of the phenol moiety, **2** is insoluble in hexane and benzene and soluble in DMF, ethanol, and methanol.

Figure 4 shows the TG curves of the polymers **1** and **2**, and that of the polymer **3** obtained by the copolymerization of **EPK** with 4-methoxybenzaldehyde (**MBA**). Polymer **2** was more thermally degradable than **1** and **3**, suggesting that the phenol moiety enhances the main chain scission. Scheme 3 depicts the plausible pathways for degradation of the polymer. In all cases, the acidity of the phenol moiety should promote the main chain scission through activation of the carbonyl group by its protonation. Paths b and c involve the formation of a benzyl cation, which is more feasible for polymer **2** (R = H) than for **1** (R = TBDMS) and **3** (R = Me), because the benzyl cation can be more strongly stabilized by a hydroxyl group at the para position than by silyloxy and methoxy groups, and the corresponding counteranion can be immediately trapped by proton migration from phenol. These results were in contrast to the previous work by Nakahama and co-workers, in which poly(4-vinylphenol) was more thermally stable than polystyrene presumably due to the associative hydrogen bonding between polymer chains. [11]

Next, we examined the degradability of **2** under acidic and basic conditions. To clarify the effect of the phenol moiety on the degradability, it was compared with that of polymer **3** having methoxyphenyl moiety. Treatment of **2** and **3** with trifluoroacetic acid (TFA) in CH_2Cl_2 at room temperature resulted in remarkably rapid main chain degradation of the both polymers to give oligomers within 5 min (Table 3, entry 1). On the other hand, treatment with weak bases such as pyridine and triethylamine in THF for 24 h resulted in no degradation of the both polymers (entries 2 and 3). When the polymers were treated with more basic 4-(dimethylamino)pyridine (DMAP), **2** degraded but **3** did not (entry 4). These results suggest that the formation of phenoxide anion under basic conditions enhances the degradability of **2** through its nucleophilic attack on the ester main chain.

Summary

Anionic alternating copolymerization of ethylphenylketene (**EPK**) with 4-(*tert*-butyldimethylsilyloxy)benzaldehyde (**SiO−BA**) proceeded in a living manner to afford the corresponding polyester with silyl-protected phenol moieties in its side chain. The polymer was successfully desilylated using a tetrabutylammonium fluoride−acetic acid system without significant main chain degradation. The obtained polyester with phenol moiety was hydrophilic and degradable thermally, and also under both acidic and basic conditions, which might be applicable to resist materials.

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(10) SEC data in Table 1 were estimated by reflactive index detector and are the relative M_n values after calibration with polystyrene standards, while VLS data were estimated by viscometer light scattering detector and are the inherent values.

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