Protection and Polymerization of Functional Monomers. 13. Anionic Living Polymerization of *tert*-Butyl 4-Vinylbenzoate

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ABSTRACT: Anionic polymerization of *tert*-butyl 4-vinylbenzoate (**1e**) was initiated in tetrahydrofuran with oligo(α-methylstyryl)disodium, -dipotassium, and -dicesium as initiators to give poly(**1e**) in quantitative yield, whereas the lithium salts did not initiate the polymerization. At −78 and −40 °C, broadening of the molecular weight distribution (MWD) of poly(**1e**) resulted, which suggested that a termination reaction of the propagating end with the ester group of another polymer chain had occurred. At −95 °C, with the potassium salts, the side reaction was suppressed to afford poly(**1e**) of a narrow MWD and of a predictable molecular weight from the mole ratio of monomer to initiator, indicating that the anionic polymerization of **1e** at −95 °C gave a stable living polymer without chain transfer and termination reactions. New block copolymers, poly(MMA-*b*-**1e**-*b*-MMA) (MMA = methyl methacrylate), poly(**1e**-*b*-styrene-*b*-**1e**), and poly(**1e**-*b*-isoprene-*b*-**1e**) were prepared by means of this living system. The resulting poly(**1e**) was completely hydrolyzed with trimethylsilyl chloride/sodium iodide in a mixed solvent of acetonitrile and chloroform at ambient temperature for 10 min to give a corresponding poly(4-vinylbenzoic acid) with well-defined chain structure.

Introduction

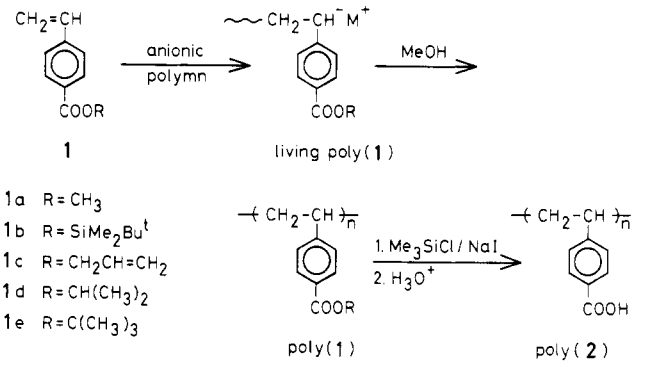
The pioneering discovery of Szwarc[1] in 1956 and the practical studies of Morton[2] in the 1960s on the anionic polymerizations of styrenes and dienes introduced the concept of living polymers. The utility of this method is derived from the absence of chain transfer and termination reactions, allowing the synthesis of polymers having predictable molecular weights and narrow molecular weight distributions. Anionic polymerizations of methacrylic acid esters such as methyl methacrylate (MMA) were also investigated under limited reaction conditions, avoiding the deactivation of the propagating chain end with a carbonyl group.[3]

Generally, a suitable choice of initiators, solvents, and reaction temperature is very important for the formation of living polymers from the monomers containing electron-withdrawing groups that might potentially be attacked by the nucleophilic propagating carbanions. By the selection of suitable protective groups and the control of reaction conditions, we have recently studied the strategy for the anionic polymerization of styrene derivatives such as *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *N*,*N*-diisopropyl(4-vinylbenzamide),[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline.[6] These polymerizations ideally proceeded in the 2,1-addition mode, and the propagating chain ends did not react with the functional groups, such as imine, amide, and oxazoline. The electron-withdrawing groups are thought to play an important role in the stabilization of living ends.

Here, we focus the study on the anionic polymerization of styrene derivatives containing ester groups. If the ester carbonyl group coexists with carbanions such as Grignard reagents and organolithium compounds, the anionic polymerization of the monomers containing ester groups will proceed to afford a living polymer.

Parham and co-workers demonstrated that stable aryllithium reagents were prepared by halogen–lithium exchange at very low temperature (−100 °C) with a variety of aryl bromides containing reactive functional groups (COO^-, COOR, CN, CH_2Cl, CH_2CH_2Br).[7] At such a low temperature, the halogen–lithium exchange reaction was still rapid, and undesirable side reaction of the organolithium reagent might be inhibited. An aryllithium reagent was typically prepared by the reaction of *tert*-butyl 4-bromobenzoate with *n*-BuLi at −100 °C, whereas less hindered methyl and isopropyl esters caused either self-condensation or reaction with unchanged bromoaryl ester.[8,9] The resulting aryllithium having a *tert*-butyl ester group is so susceptible to temperature that the undesirable self-condensation proceeds at −78 °C. Moreover, Beak and co-workers demonstrated that the direct ortho lithiation of alkyl benzoate occurred regioselectively and that the nucleophilic addition to ester moiety could be suppressed by using sterically hindered organolithium reagents and bulkier ester alkyl groups.[10] These observations indicate that reaction temperature and steric effects of reactants are of importance in the synthesis of organolithium compounds containing ester groups as models for living polymerizations.

Scheme I



In this report, we investigate the anionic polymerization of 4-vinylbenzoate (**1**) in detail to produce a living poly(**1**) and the hydrolysis of the resulting poly(**1**) to synthesize poly(4-vinylbenzoic acid), poly(**2**) (Scheme I).

Experimental Section

Materials. 4-Vinylbenzoic acid, kindly supplied from Hokko Chemical Industry Co., Ltd., was used without further purification. α-Methylstyrene, styrene, isoprene, and MMA were distilled over calcium hydride. 1,1-Diphenylethylene (DPE), prepared by a literature procedure,[11] was purified by fractional distillation and was finally distilled together with THF from benzylmagnesium chloride under vacuum. THF used as a solvent in all polymerization experiments was refluxed over sodium wire for 5 h and distilled from lithium aluminum hydride and finally through vacuum line from sodium naphthalenide solution.

Cumylpotassium was prepared by the reaction of cumyl methyl ether with a potassium–sodium alloy in THF at room temperature

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for 10 h followed by filtration of the reaction mixture. Metal naphthalenides were prepared by the reactions of a small excess of naphthalene with the corresponding alkali metal in THF. The oligo(α-methylstyryl)dilithium, -disodium, -dipotassium, and -dicesium were freshly prepared just prior to polymerization from the corresponding metal naphthalenides and a 2–4 M quantity of α-methylstyrene at 20 °C for 1 min and then at −78 °C for 10 min. Initiators were stored in ampules equipped with breakseals. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed tube under vacuum.

4-Vinylbenzoyl Chloride. To a mixture of thionyl chloride (28 mL) and 4-*tert*-butylpyrocatecol (10 mg) under nitrogen in an ice bath was added 4-vinylbenzoic acid (13.1 g, 88.5 mmol) in small portions with stirring below 10 °C for 4 h and at 40 °C for 1 h to afford a homogeneous solution. After removal of unreacted thionyl chloride, distillation gave 13.3 g (79.9 mmol, 90%) of 4-vinylbenzoyl chloride as a colorless liquid at 79–83 °C (0.5 mmHg) (lit.[12] bp 69.5–70.0 °C (0.1 mmHg)): 90 MHz ^{1}H NMR ($CDCl_3$) δ 5.44 and 5.88 (2d, 2 H, J = 11 and 17 Hz, CH_2=), 6.72 (dd, 1 H, —CH=), 7.38–8.03 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 118.3 (vinyl, CH_2=), 126.5 (Ar, C3), 131.7 (Ar, C2), 132.1 (Ar, C1), 135.3 (vinyl, —CH=), 144.4 (Ar, C4), 167.5 (C=O).

Methyl 4-Vinylbenzoate (1a). To a mechanically stirred mixture of dry methanol (3.0 mL, 74 mmol) and triethylamine (10 mL) in dry ether (50 mL) under nitrogen, 4-vinylbenzoyl chloride (9.25 g, 55.6 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The precipitated salt was filtered off, and the filtrate was washed three times with 0.5 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL) and then dried over $MgSO_4$. After evaporation of ether, the residue was recrystallized from petroleum ether three times to yield a pure white crystal of **1a** (7.24 g; 44.7 mmol; 80%; mp 35–36 °C): 200 MHz ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3 H, —OCH_3), 5.39 and 5.86 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1 H, —CH=), 7.44–8.02 (m, 4 H, Ar); 50 MHz ^{13}C NMR ($CDCl_3$) δ 51.8 (—OCH_3), 116.2 (vinyl, CH_2=), 125.9 (Ar, C3), 129.1 (Ar, C1), 129.7 (Ar, C2), 135.9 (vinyl, —CH=), 141.7 (Ar, C4), 166.5 (C=O).

***tert*-Butyldimethylsilyl 4-Vinylbenzoate (1b).** To a stirred mixture of 4-vinylbenzoic acid (5.0 g, 34 mmol) and imidazole (6.0 g, 88 mmol) in dry *N,N*-dimethylformamide (DMF, 80 mL) under nitrogen, *tert*-butyldimethylsilyl chloride (6.7 g, 45 mmol) in dry DMF (20 mL) was added dropwise in an ice bath and then stirred overnight at room temperature. After removal of DMF under vacuum, distillation of the residue gave a liquid containing imidazole hydrochloride at 100–110 °C (1 mmHg). To remove the solid salt, hexane was added to the mixture, and the liquid layer was separated by decantation. After removal of hexane, distillation gave 2.6 g (9.9 mmol, 29%) of **1b** as a colorless liquid at 103–105 °C (1 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 0.36 (s, 6 H, Si—CH_3), 1.01 (s, 9 H, Si—C—CH_3), 5.36 and 5.83 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1 H, —CH=), 7.39–8.02 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ −4.6 (Si—CH_3), 18.0 (Si—C), 25.8 (—CH_3), 116.5 (vinyl, CH_2=), 126.2 (Ar, C3), 126.9 (Ar, C1), 130.5 (Ar, C2), 136.2 (vinyl, —CH=), 142.0 (Ar, C4), 166.4 (C=O).

Allyl 4-Vinylbenzoate (1c). The reaction was performed according to the procedure for **1a** using allyl alcohol (4.7 g, 81 mmol) in place of methanol and distillation gave 10.7 g (57.0 mmol, 77%) of **1c** as a colorless liquid at 96–106 °C (1 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 4.82 (br d, 2 H, —OCH_2—), 5.2–6.2 (overlapping m, 5 H, —OCH_2—C*H*=C*H*$_2$ and C*H*$_2$=), 6.75 (dd, 1 H, J = 11 and 18 Hz, —CH=), 7.41–8.07 (m, 4 H, Ar); 50 MHz ^{13}C NMR ($CDCl_3$) δ 65.4 (—OCH_2—), 116.3 (vinyl, CH_2=), 118.0 (allyl, CH_2=), 126.0 (Ar, C3), 129.7 (Ar, C1), 129.8 (Ar, C2), 132.2 (allyl, —CH=), 135.9 (vinyl, —CH=), 141.9 (Ar, C4), 165.7 (C=O).

Isopropyl 4-Vinylbenzoate (1d). The reaction was performed according to the procedure for **1a** using isopropanol (12.0 g, 200 mmol) in place of methanol and distillation gave 10.3 g (54.4 mmol, 79%) of **1d** as a colorless liquid at 69–70 °C (0.5 mmHg): 90 MHz ^{1}H NMR ($CDCl_3$) δ 1.38 (d, 6 H, J = 6 Hz, —CH_3), 5.25 (hepta, 1 H, J = 6 Hz, —C*H*—CH_3) 5.37 and 5.85 (2d, 2 H, J = 11 and 17 Hz, CH_2=), 6.76 (dd, 1 H, —CH=), 7.40–8.04 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 21.6 (—CH_3), 67.9 (—O—CH), 115.9 (vinyl, CH_2=), 125.8 (Ar, C3), 129.5 (Ar, C2), 129.9 (Ar, C1), 135.9 (vinyl, —CH=), 141.5 (Ar, C4), 165.3 (C=O).

***tert*-Butyl 4-Vinylbenzoate (1e).** To a mechanically stirred mixture of *tert*-butyl alcohol (100 mL), potassium *tert*-butoxide (180 mmol), and dry ether (50 mL) under nitrogen, 4-vinylbenzoyl chloride (13.3 g, 79.9 mmol) in dry ether (30 mL) was added dropwise with cooling in an ice bath and then stirred overnight at room temperature. The mixture was washed twice with 2 N HCl (100 mL) and twice with saturated $NaHCO_3$ solution (100 mL) and then dried over $MgSO_4$. After removal of ether, distillation gave 14.0 g (68.5 mmol, 86%) of **1e** as a colorless liquid at 82–84 °C (0.8 mmHg): 200 MHz ^{1}H NMR ($CDCl_3$) δ 1.60 (s, 9 H, C—CH_3), 5.36 and 5.84 (2d, 2 H, J = 11 and 18 Hz, CH_2=), 6.75 (dd, 1 H, —CH=), 7.41–7.96 (m, 4 H, Ar); 50 MHz ^{13}C NMR ($CDCl_3$) δ 28.3 (—CH_3), 80.8 (—O—*C*—CH_3), 116.0 (vinyl, CH_2=), 125.9 (Ar, C3), 129.6 (Ar, C2), 131.2 (Ar, C1), 136.1 (vinyl, —CH=), 141.4 (Ar, C4), 165.4 (C=O).

Purification. To remove impurities in monomer, phenylmagnesium chloride (5 mL, 0.25 M solution in THF) was added to *tert*-butyl 4-vinylbenzoate (6.1 g, 30 mmol) at −78 °C under a degassed condition in an all-glass apparatus equipped with breakseals, and the mixture was stirred for 10 min. It was then degassed again and distilled on a vacuum line into the ampules fitted with breakseals. The other liquid monomers were also purified in a similar manner. The resulting monomer solutions, the concentrations of which were 0.4–0.6 M in THF, were stored at −30 °C until they were ready to use for anionic polymerization.

The purified crystalline methyl 4-vinylbenzoate was dried over P_2O_5 for 48 h in an apparatus equipped with a breakseal under vacuum (10^{-6} mmHg) and then diluted with THF to use for the anionic polymerization.

Polymerization Procedures. All the polymerizations were carried out at low temperatures with shaking under vacuum in the all-glass apparatus equipped with breakseals as previously reported.[13] Hexane–acetone (1:1) cooled with liquid nitrogen at −95 °C and dry ice–acetone at −40 and −78 °C were used as refrigerants. After the polymerization systems were kept at various temperatures for the required time, the reaction was terminated with methanol. The reaction mixture was concentrated by evaporation and poured into methanol to precipitate the polymers, and then the polymers were collected by filtration and freeze-dried from benzene. Poly(**1d**) and poly(**1e**) obtained were characterized by IR and ^{1}H and ^{13}C NMR spectroscopies. Poly(**1d**): IR 1710 (C=O), 1350, 1370 cm^{-1} (isopropyl, C—H deformation); 90 MHz ^{1}H NMR ($CDCl_3$) (Figure 1) δ 0.9–2.1 (m, 9 H, —CH_3 and —CH_2C*H*—), 5.2 (m, 1 H, —C*H*—CH_3), 6.2–7.8 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 22.0 (—CH_3), 40–42 (—CH_2CH—), 68.2 (—O—CH), 126—131 (Ar, C1, C2, C3), 149 (Ar, C4), 165.7 (C=O). Poly(**1e**): IR (Figure 6a) 1710 (C=O), 1360, 1390 cm^{-1} (*tert*-butyl, C—H deformation); 90 MHz ^{1}H NMR ($CDCl_3$) (Figure 7a) δ 1.0–2.1 (m, 12 H, —CH_3 and —CH_2CH—), 6.3–7.8 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 28.2 (—CH_3), 40–42 (—CH_2CH—), 80.7 (—O—*C*—CH_3), 126–131 (Ar, C1, C2, C3), 149 (Ar, C4), 165.5 (C=O). Anal. Calcd for poly(**1e**) $(C_{13}H_{16}O_2)_n$: C, 76.44; H, 7.90; N, 0.00. Found: C, 76.38; H, 7.89; N, 0.00.

Hydrolysis of Poly(1e). To a stirred mixture of poly(**1e**) (0.45 g, 2.2 mmol based on monomer unit) and sodium iodide (2.0 g, 14 mmol) in acetonitrile (10 mL) and chloroform (20 mL) was added 2.0 mL (15 mmol) of trimethylsilyl chloride at once at room temperature. The reaction mixture immediately turned yellow, and the white precipitate of sodium chloride appeared. After 10 min, the mixture was concentrated by evaporation, redissolved in THF, and poured into 0.1 N HCl containing $Na_2S_2O_3$ for decolorization to precipitate the polymer. The obtained polymer was purified by reprecipitation from THF–water and THF–hexane systems and then freeze-dried from benzene containing a small amount of methanol. A pure white powder (0.27 g, 82%, 1.8 mmol based on monomer unit) of poly(4-vinylbenzoic acid) was obtained: IR (Figure 6b) 3300–2500 (O—H), 1700 cm^{-1} (C=O); 90 MHz ^{1}H NMR (CD_3OD) (Figure 7b) δ 1.0–2.3 (m, 3 H, —CH_2CH—), 6.3–7.8 (m, 4 H, Ar); 23 MHz ^{13}C NMR (CD_3OD) δ 42–45 (—CH_2CH—), 128–133 (Ar, C1, C2, C3), 153 (Ar, C4), 170.6 (C=O). Anal. Calcd for $(C_9H_8O_2)_n$: C, 72.96; H, 5.44; N, 0.00. Found: C, 72.37; H, 5.98; N, 0.00.

Methylation of Poly(4-vinylbenzoic acid), Poly(2). To a suspension of poly(**2**) (0.18 g, 1.2 mmol based on monomer unit) in benzene (30 mL) was added diazomethane[14] (8.5 mmol) in ether (20 mL) by small portions at room temperature. As the meth-

Table I
Anionic Polymerization of 1a, 1b, 1c, and 1d with Various Initiators in THF

monomer		condition			polym	$10^{-4}\bar{M}_n$	$10^{-4}\bar{M}_n$	
type	mmol	temp, °C	time	initiator, mmol	yield, %	(calcd)[a]	(obsd)[b]	$\bar{M}_w/\bar{M}_n$
1a	3.06	−78	5 min	K-Naph,[c] 0.113/α-MeSt,[d] 0.322	0			
1a	3.06	−78	24 h	K-Naph, 0.117/DPE,[e] 0.286	0			
1b	2.75	−78	15 min	K-Naph, 0.166/α-MeSt, 0.380	0			
1b	3.13	−78	30 min	K-Naph, 0.139/DPE, 0.307	0			
1c	5.25	−78	5 min	K-Naph, 0.206/α-MeSt, 0.513	0			
1c	3.39	−78	2 h	K-Naph, 0.122/DPE, 0.360	0			
1c	6.03	−40	20 min	Na-Naph,[f] 0.195	0			
1d	3.22	−78	4 h	K-Naph, 0.138/α-MeSt, 0.364	43	0.44	0.74	1.32
1d	3.30	−78	20 h	K-Naph, 0.126/α-MeSt, 0.321	71	0.77	1.1	1.50
1d	3.59	−95	10 min	K-Naph, 0.115/α-MeSt, 0.298	25	0.36	0.46	1.13
1d	3.41	−95	4 h	K-Naph, 0.116/α-MeSt, 0.369	49	0.62	1.1	1.72

[a] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × 2 × (yield of polymer)/(100)[initiator] + MW of initiator. [b] $\bar{M}_n$(obsd) was obtained by GPC calibration using a standard polystyrene. [c] Potassium naphthalenide. [d] α-Methylstyrene. [e] 1,1-Diphenylethylene. [f] Sodium naphthalenide.

ylation proceeded, the polymer dissolved into the solution, yielding bubbles of nitrogen. The homogeneous yellow reaction mixture was kept in a well-ventilated hood overnight at room temperature. After the addition of acetic acid to quench unreacted diazomethane, the reaction mixture was concentrated by evaporation and poured into methanol. The polymer was recovered by filtration, redissolved in THF, and reprecipitated into methanol. The yield of polymer was fairly good (0.18 g, 90%). The polymer was identified as poly(methyl 4-vinylbenzoate) by IR and ^1H and ^{13}C NMR spectroscopic measurements: IR 1720 cm^{-1} (C=O); 90 MHz ^1H NMR ($CDCl_3$) δ 0.8–2.2 (m, 3 H, $-CH_2CH-$), 3.9 (br s, 3 H, $-OCH_3$), 6.8–7.9 (m, 4 H, Ar); 23 MHz ^{13}C NMR ($CDCl_3$) δ 40–42 ($-CH_2CH-$), 52.1 ($-OCH_3$), 126–131 (Ar, C1, C2, C3), 149 (Ar, C4), 166.8 (C=O).

Measurements. Infrared spectra (KBr disk) were recorded on a Jasco IR-G spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz ^1H, 22.53 MHz ^{13}C), a JEOL FX-200 (199.56 MHz ^1H, 50.18 MHz ^{13}C), and a JEOL GSX-270 (67.80 MHz ^{13}C) in $CDCl_3$ or CD_3OD. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^1H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Gel permeation chromatograms (GPC) for molecular weight distribution determination were obtained at 40 °C with a Toyo Soda HLC-802 instrument with ultraviolet or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL min^{-1}. Vapor pressure osmometry (VPO) measurements for number-average molecular weight determination were made with a Corona 117 instrument in benzene solution with a highly sensitive thermoelectric couple and equipment of very exact temperature control.

Results and Discussion

Polymerization of Methyl (1a), *tert*-Butyldimethylsilyl (1b), and Allyl (1c) 4-Vinylbenzoates. Anionic polymerizations of 4-vinylbenzoates, such as allyl, vinyl, and 2-butyn-1-yl esters, were investigated by D'Alelio and Hoffend to afford the linear soluble polymers in tetrahydrofuran (THF) at −40 °C with sodium naphthalenide as an initiator.[15] However, they did not mention the quantitative discussion of the molecular weight and the molecular weight distribution of the polymers produced. We have, here, examined the anionic polymerizations of several 4-vinylbenzoates in detail and explored the possibility of anionic living polymerization of the monomers.

Anionic polymerizations of **1a**, **1b**, and **1c** were performed with various initiators, such as oligo(α-methylstyryl)dipotassium and sodium naphthalenide, in THF. As shown in Table I, no polymer was obtained in each case. Steric hindrance of the methyl group of **1a** seems to be insufficient to protect the carbonyl moiety from nucleophilic attack at the initiation step of the polymerization. Anionic polymerization of **1b** with the bulky *tert*-butyldimethylsilyl group was not initiated and presumably terminated by nucleophilic attack of the initiator carbanion on the silicon atom. When **1c** was allowed to react with sodium naphthalenide in THF at −40 °C, no polymer was obtained. This was contrary to the results obtained by Hoffend and D'Alelio. Under more preferable conditions, including high initiator level, low reaction temperature, and long reaction time, the polymerization of **1c** also did not proceed and the monomer was quantitatively recovered. These contrasting results will not be here further discussed in this paper.

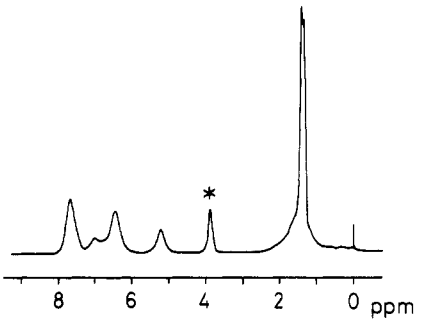

Figure 1. ^1H NMR spectrum of poly(**1d**). The peak attributable to methyl ester is marked with an asterisk.

Anionic Polymerization of Isopropyl 4-Vinylbenzoate (1d). Anionic polymerization of an alternative monomer, **1d**, an ester of a secondary alcohol, was initiated with oligo(α-methylstyryl)dipotassium in THF. In contrast to the results of **1a**, **1b**, and **1c**, poly(**1d**) was produced in 25–70% yield. During the polymerization at −78 °C, the characteristic dark red color of the reaction mixture was maintained and immediately disappeared by adding a few drops of methanol to quench the polymerization. Pouring the reaction mixture into an excess of methanol precipitated a white powder of poly(**1d**), which was purified by reprecipitation twice with a THF–methanol system. A typical ^1H NMR spectrum of poly(**1d**) is shown in Figure 1, where it is found that a considerable amount of pendant isopropyl ester groups are converted to methyl ester moiety by transesterification during the workup of polymer isolation. The ester exchange reaction, which presumably catalyzed with potassium methoxide formed by the termination reaction, was similarly observed in the recovered monomer. The corrected yields of poly(**1d**)s are not quantitative even after prolonged reaction time (20 h), and the molecular weight distributions are rather broad as shown in Table I. These results reveal that anionic polymerization of **1d** unequivocally takes place contrary to the cases of **1a**, **1b**, and **1c**. The bulky isopropyl ester may to some extent prevent the propagating chain end from deactivation. However, occasional termination and

Table II
Anionic Polymerization of 1e with Various Initiators in THF

run	1e, mmol	condition: temp, °C	condition: time	initiator, mmol	polym yield, %	$10^{-4}\bar{M}_n$ (calcd)[a]	$10^{-4}\bar{M}_n$ (obsd)[b]	$\bar{M}_w/\bar{M}_n$
1	3.74	−78	30 min	*n*-BuLi, 0.0653/α-MeSt,[c] 0.651	0			
2	3.76	−78	10 min	Li–Naph,[d] 0.142/α-MeSt, 0.305	0			
3	3.12	−95	4 h	Li–Naph, 0.137/DPE,[e] 0.187	0			
4	3.74	−78	10 min	Na–Naph,[f] 0.125/α-MeSt, 0.305	80	1.0	1.4	1.18
5	2.87	−40	10 min	K–Naph,[g] 0.116/α-MeSt, 0.244	100	1.1	1.6	1.59
6	4.77	−78	5 min	K–Naph, 0.173/α-MeSt, 0.563	66	0.82	0.94	1.11
7	3.51	−78	40 min	K–Naph, 0.138/α-MeSt, 0.339	100	1.1	1.0	1.18
8	2.19	−78	4 h	K–Naph, 0.113/α-MeSt, 0.334	100	0.86	0.97	1.26
9	2.65	−78	20 h	K–Naph, 0.0921/α-MeSt, 0.373	100	1.3	1.8	1.55
10	3.32	−95	8 h	K–Naph, 0.204/α-MeSt, 0.378	100	0.71	0.65	1.10
11	3.29	−95	8 h	K–Naph, 0.145/α-MeSt, 0.348	100	0.98	0.98	1.11
12	2.48	−95	4 h	K–Naph, 0.0944/α-MeSt, 0.335	100	1.2	1.2	1.15
13	6.08	−95	8 h	K–Naph, 0.163/α-MeSt, 0.302	100	1.6	1.3	1.12
14	5.69	−95	4 h	Cumyl K,[h] 0.0375/α-MeSt, 0.350	61	2.0	1.9	1.09
15	8.35	−95	8 h	Cumyl K, 0.0404/α-MeSt, 0.269	94	4.3	5.0	1.14
16	7.80	−95	12 h	Cumyl K, 0.0256/DPE, 0.0333	100	6.3	5.9	1.18
17	2.87	−78	10 min	Cs–Naph,[i] 0.0909/α-MeSt, 0.314	51	0.74	0.73	1.08
18	4.26	−78	90 min	Cs–Naph, 0.164/α-MeSt, 0.320	100	1.1	1.4	1.25

[a] $\bar{M}_n$(calcd) = [monomer] × (MW of monomer) × f × (yield of polymer)/(100)[initiator] + MW of initiator, f = 1 or 2 corresponding to the functionality of the initiators. [b] $\bar{M}_n$(obsd) was obtained by VPO in benzene solution. [c] α-Methylstyrene. [d] Lithium naphthalenide. [e] 1,1-Diphenylethylene. [f] Sodium naphthalenide. [g] Potassium naphthalenide. [h] Cumylpotassium. [i] Cesium naphthalenide.

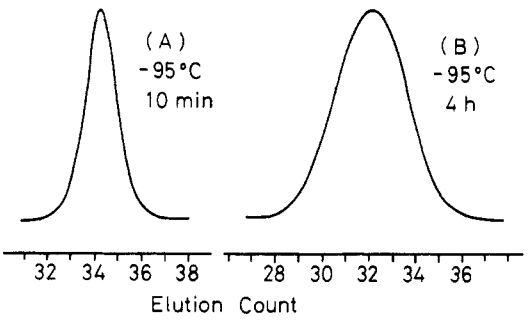

Figure 2. GPC curves of poly(**1d**)s obtained with the potassium salt: (A) $\bar{M}_n$(obsd, GPC) = 0.46 × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.13; (B) $\bar{M}_n$(obsd, GPC) = 1.1 × 10^4, $\bar{M}_w/\bar{M}_n$ = 1.72.

transfer reactions still occur in the course of the polymerization.

At −95 °C for 10 min, nearly monodispersed poly(**1d**) was obtained. However, the molecular weight distribution (MWD) of the polymer broadened after 4 h as shown in Figure 2. The deactivation of propagating chain end could not be suppressed by lowering the reaction temperature. Furthermore, in the case using lithium salts as initiators, poly(**1d**) was not virtually produced.

Anionic Polymerization of *tert*-Butyl 4-Vinylbenzoate (1e). Anionic polymerization of **1e**, where the ester carbonyl moiety was protected with a bulkier alkyl group than that of **1d**, was carried out in THF with various initiators at −40 to −95 °C. The initiators included oligo(α-methylstyryl)dilithium, -disodium, -dipotassium, and -dicesium and cumylpotassium. The reaction mixture showed a characteristic dark red color similar to that of living polystyrene during the course of the polymerization. The coloration remained unchanged at −78 °C even after 20 h and disappeared immediately with a small amount of methanol as expected. The reaction mixture was poured into a large amount of methanol for precipitation. The yielding polymer was purified by reprecipitation twice with a THF–methanol system and then freeze-dried from benzene. No transesterification of the pendant *tert*-butyl ester group of poly(**1e**) was observed during the polymer isolation process by ^{1}H and ^{13}C NMR spectroscopies, although the isopropyl ester group of poly(**1d**) was considerably converted into methyl ester by precipitation with methanol. Figures 6a and 7a show typical IR and ^{1}H NMR spectra of poly(**1e**), respectively.

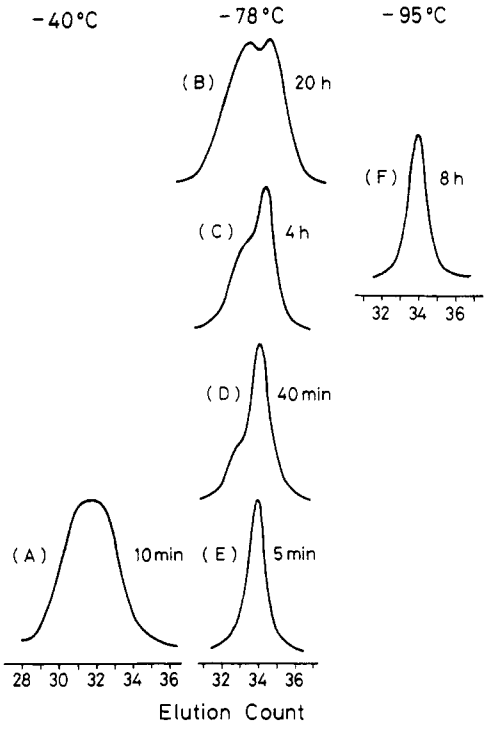

Figure 3. Effects of polymerization temperature and time on the MWD of poly(**1e**). Detailed data were shown in Table II: (A) run 5, $\bar{M}_w/\bar{M}_n$ = 1.59; (B) run 9, $\bar{M}_w/\bar{M}_n$ = 1.55; (C) run 8, $\bar{M}_w/\bar{M}_n$ = 1.26; (D) run 7, $\bar{M}_w/\bar{M}_n$ = 1.18; (E) run 6, $\bar{M}_w/\bar{M}_n$ = 1.11; (F) run 11, $\bar{M}_w/\bar{M}_n$ = 1.11.

As shown in Table II, the remarkable effect of the countercation on the polymerization is observed. By three initiators with lithium cation, poly(**1e**) is not formed as well as the polymerization of **1d**. Contrary to the case of lithium salt, sodium, potassium, and cesium salts give poly(**1e**)s in good to quantitative yields. In most cases, the polymerization produces nearly monodispersed poly(**1e**) whose molecular weight observed agrees well with that calculated on the basis of the mole ratio of monomer to initiator. The rate of the polymerization seems to be significantly slow compared with that of anionic polymerization of styrene; the complete conversion requires about 40 min at −78 °C.

Table III
Block Copolymerization of 1e with Methyl Methacrylate, Isoprene, and Styrene at -95 °C in THF

run	type of block copolym	A monomer	B monomer	block copolym[a] (homopolym)[b] $10^{-4}\bar{M}_n$(calcd)	$10^{-4}\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$
1	B-A-B	1e	MMA	2.5 (0.71)	2.2 (0.68)	1.27 (1.10)
2	A-B-A	1e	styrene	2.5 (1.4)	2.5 (1.4)	1.13 (1.06)
3	A-B-A	1e	isoprene	2.7 (1.5)	2.5 (1.2)	1.13 (1.07)

[a] Yields of polymers were nearly quantitative in each case. [b] Homopolymers were obtained at the first-stage polymerization.

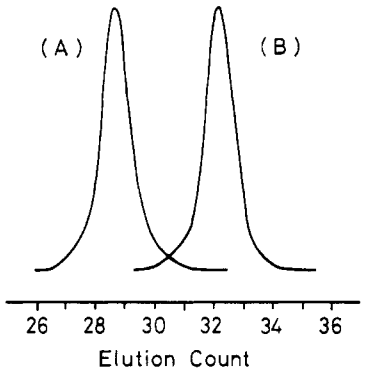

Figure 4. GPC curves of poly(1e)s obtained at -95 °C. Detailed data were shown in Table II: (A) run 16, $\bar{M}_n$(obsd) = 5.9 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.18; (B) run 14, $\bar{M}_n$(obsd) = 1.9 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.09.

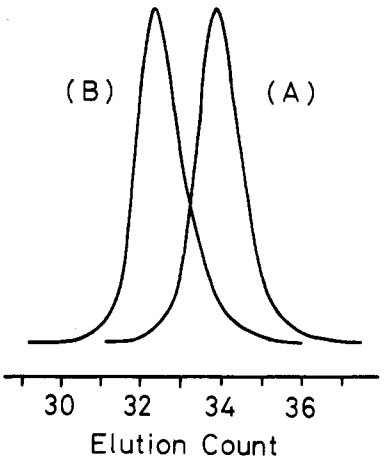

Figure 5. GPC curves of poly(1e)s obtained at -95 °C: first polymerization (A), $\bar{M}_n$(obsd) = 0.65 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.10; second polymerization (B), $\bar{M}_n$(obsd) = 1.3 × 10⁴, $\bar{M}_w/\bar{M}_n$ = 1.12 (the second monomer was added 4 h after the first addition).

At -78 °C, the prolonged polymerization time leads to broadening of the GPC curves of poly(1e) obtained under similar conditions as shown in Figure 3. A shoulder appears at the higher molecular weight side after 40 min and results in a bimodal peak after 20 h, where the summit of the higher molecular weight side corresponds to about a 2-fold higher molecular weight than the original one. This phenomenon suggests that the propagating chain end attacks the pendant ester group of another polymer chain. The polymerization system at -78 °C affords a long-lived propagating species but is not completely stable. At -40 °C, the MWD of the polymer is already broad in 10 min with an increase in the termination reaction. In contrast, at -95 °C, 1e is completely transformed to the polymer which has a very narrow MWD even after 8 h. Hence, the side reaction seemed to be suppressed at -95 °C for a long time. The stability of the carbanion is similar to that of aromatic organolithium reagents bearing electrophilic groups developed by Parham; *tert*-butyl 4-lithiobenzoate reacts with benzophenone to give a triarylcarbinol in good yield without self-condensation at -100 °C but attacks itself to form condensates when it is warmed to -78 °C.[8,9] At -95 °C, the anionic polymerization produces poly(1e) with molecular weights in the range 6500–59 000, which agree fairly well with those calculated from the mole ratios of monomer to initiator. The $\bar{M}_w/\bar{M}_n$ values of the resulting polymers are in the range 1.09–1.18, indicating that the MWDs of the polymers are very narrow. The representative GPC curves of poly(1e) obtained at -95 °C are shown in Figure 4. These facts suggest that the termination reaction is completely suppressed at -95 °C to give a living end stabilized by an electron-withdrawing ester group.

Furthermore, to prove the living nature of the polymerization system of 1e, the postpolymerization was carried out as follows. The first-stage polymerization was initiated with oligo(α-methylstyryl)dipotassium at -95 °C. After complete consumption of the monomer, the resulting polymerization mixture was divided into two portions. One was terminated with methanol, while monomer was again added to the other to propagate the second-stage polymerization at -95 °C. In both cases, the poly(1e)s are obtained quantitatively, the GPC curves of which are very narrow as shown in Figure 5. The GPC curve of the postpolymer shifts toward higher molecular weights without a shoulder at the elution count of the prepoly(1e). The observed molecular weights of the pre- and postpolymers agree fairly well with the predicted ones. These results substantiate that a stable living polymer of *tert*-butyl 4-vinylbenzoate forms at -95 °C, which is able to further propagate with quantitative efficiency.

We have already confirmed that the anionic polymerizations of *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *N*,*N*-diisopropyl(4-vinylbenzamide),[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline[6] proceeded to afford stable living polymers at -78 °C. Their propagating chain ends do not react with the functional groups, such as imine, amide, and oxazoline, at -78 °C. This can be explained by stabilization of the carbanions with electron-withdrawing groups. However, the reaction of the propagating end of poly(1e) with pendant ester group partially occurs at -78 °C. The different stabilities of their crucial propagating ends to the functional groups are of interest.

Block Copolymerization of 1e. In a manner similar to that of postpolymerization, we attempted to synthesize block copolymers by addition of the second monomer to the living poly(1e) prepared at -95 °C. However, the living poly(1e) did not initiate the polymerizations of isoprene and styrene to recover homopoly(1e) without isoprene and styrene units in the polymer chain, whereas MMA, a more reactive monomer in anionic mechanism, reacted with living poly(1e) to yield the poly(MMA-*b*-1e-*b*-MMA) with regulated block length and narrow MWD as shown in Table III. The reactivity of the carbanion derived from 1e is supposed to be lowered on account of the electron-withdrawing ester group. Similar behavior was observed in the series of our study on the anionic polymerization of styrene derivatives bearing electron-withdrawing groups at the para position, *N*-(4-vinylbenzylidene)cyclohexylamine,[4] *N*,*N*-diisopropyl(4-vinylbenzamide),[5] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline.[6] The carbanions derived from these monomers are able to initiate the po-

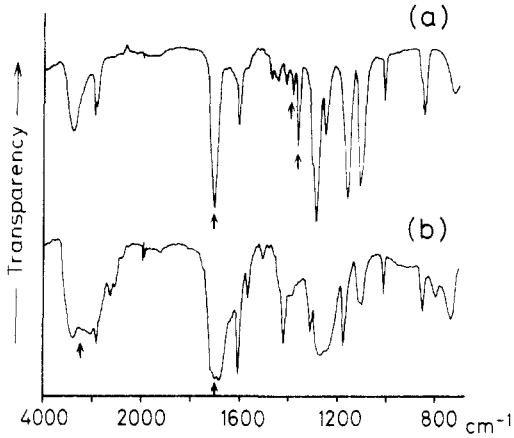

Figure 6. IR spectra of poly(**1e**) (a) and poly(**2**) (b). The full elaboration on the absorption bands indicated by arrows is described in the Results and Discussion.

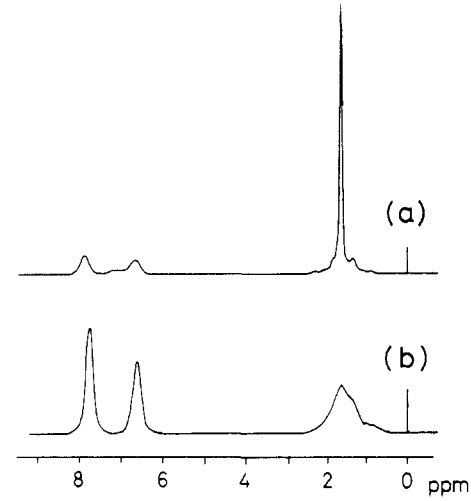

Figure 7. ^{1}H NMR spectra of poly(**1e**) (a) and poly(**2**) (b).

lymerization of MMA but are virtually ineffective for initiating styrene and isoprene. Living poly(**1e**) also has a reactivity of this class.

On the other hand, the block copolymers with reversed block sequences having regulated molecular weights and very narrow MWDs can be prepared by addition of **1e** to the living polymers of styrene and isoprene at −95 °C (Table III).

Hydrolysis of the Ester Group. In the hydrolyses of polymers with ester groups under acidic and basic conditions, some difficulties are occasionally encountered due to insolubility of the polymers in the reaction media. Recently, trimethylsilyl iodide (TMSI) has been proposed as an effective reagent for dealkylation of esters under neutral and mild conditions.[16] Bugner demonstrated the utility of TMSI in the hydrolysis of poly[(MMA)-*b*-(*tert*-butyl methacrylate)], where the *tert*-butyl ester moiety completely cleaved at ambient temperature, but the methyl ester was unreactive, resulting in poly[(MMA)-*b*-(methacrylic acid)].[17] The stability of leaving carbocation in the ester group may be responsible for this chemoselectivity.

The hydrolysis of poly(**1e**) was carried out by modifying Bugner's method. In place of TMSI, we conveniently employed trimethylsilyl chloride (TMSCl) and sodium iodide, which yielded TMSI in situ in the reaction mixture.[18] Poly(**1e**) was treated with TMSCl and NaI at ambient temperature for 10 min in a mixture of acetonitrile and chloroform. The product was isolated by precipitation in aqueous 0.1 N HCl solution and freeze-dried from benzene containing a small amount of methanol. Elemental analysis and IR and ^{1}H and ^{13}C NMR spectra of the polymer produced are identical with those of poly(4-vinylbenzoic acid), poly(**2**), indicating that complete hydrolysis of *tert*-butyl ester of poly(**1e**) is achieved. As described previously,[6] the poly(4-vinylbenzoic acid) obtained by the hydrolysis of the oxazoline protective group contained $^7/_{10}$ mole of water per each monomer unit. However, it is revealed from the elemental analysis of poly(**2**) prepared here that most water molecules can be removed from the polymer by thorough freeze-drying followed by heating at 60 °C for 5 h. The characteristic C=O and O—H stretching absorptions of the carboxy group are observed at 1700 and 2500–3300 cm^{-1}, respectively, whereas the absorptions corresponding to the ester carbonyl at 1710 cm^{-1} and the *tert*-butyl group at 1360 and 1690 cm^{-1} disappear as shown in Figure 6b. The ^{1}H NMR spectrum of poly(**2**) shows the signals responsible for the poly(4-vinylbenzoic acid) and the resonance corresponding to *tert*-butyl group of starting poly(**1e**) no longer exists (Figure 7b). Moreover, the ^{13}C signals due to the *tert*-butyl ester group at 28.2 (—C—CH_3), 80.7 (—C—CH_3), and 165.5 ppm (C=O) thoroughly disappear and that of carboxy group (COOH) appears at 170.6 ppm. In contrast to the complete cleavage of the *tert*-butyl ester group, no hydrolysis of poly(**1d**) containing the isopropyl ester group occurred under similar conditions even after 20 h.

Because the carboxy group of the hydrolyzed polymer was adsorbed on the cross-linked polystyrene gel column, the GPC measurement of poly(**2**) could not be performed. Hence, poly(**2**) was furthermore converted into poly(methyl 4-vinylbenzoate) by diazomethane as described in the Experimental Section, to evaluate the degree of polymerization (DP) and $\bar{M}_w/\bar{M}_n$ of poly(**2**), which were found almost unchanged compared with those of the poly(**1e**) before hydrolysis; DP and $\bar{M}_w/\bar{M}_n$ of poly(**2**) and the corresponding poly(1e) (Table II, run 12) are 59, 1.15 and 55, 1.18, respectively. These results lead us to conclude that the quantitative hydrolysis of poly(**1e**) proceeds without any detectable degradation and cross-linking of the main chain to afford the poly(4-vinylbenzoic acid) with a predictable molecular weight and a very narrow MWD.

In our previous work, linear poly(4-vinylbenzoic acid) with controlled chain structure was successfully synthesized by the anionic living polymerization of 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline and removal of the oxazoline moiety from the resulting polymer.[6] The complete hydrolysis of oxazoline group required a two-step reaction including acid hydrolysis at 80–90 °C for 10 h and subsequent saponification at 80–90 °C for 6 h. Compared with this process, deprotection of poly(**1e**) advantageously proceeds under very mild conditions.

Furthermore, the hydrolysis of the block copolymers, poly(**1e**-*b*-styrene-*b*-**1e**) and poly(MMA-*b*-**1e**-*b*-MMA) was also carried out under similar conditions. In both cases, the analyses by IR and ^{1}H and ^{13}C NMR spectroscopies showed quantitative cleavage of *tert*-butyl ester of poly(**1e**) block. ^{13}C NMR spectra (Figure 8) clearly show that the highly chemoselective hydrolysis of the block copolymer with MMA occurs similarly to the result of Bugner.[17] The signals due to the *tert*-butyl ester of poly(**1e**) segment in the block copolymer are no longer present, whereas those of poly(methyl methacrylate) segment are unchanged. These high reactivities and chemoselectivities to the ester function clearly demonstrate the utility of TMSI in the synthesis of amphiphilic block copolymer with controlled structure.

Solubility of the Polymers. Table IV summarizes the solubilities of polymers synthesized in this study. Poly(alkyl 4-vinylbenzoate)s have solubilities similar to that

Table IV
Solubilities of Poly(4-vinylbenzoic acid), Poly(4-vinylbenzoate)s, Block Copolymer, and Polystyrene[a]

solvent	polymer					
	poly(2)	poly(1a)	poly(1d)	poly(1e)	block copolym[b]	polystyrene
hexane	I	I	I	I	I	I
benzene	I	S	S	S	I	S
carbon tetrachloride	I	S	S	S	I	S
chloroform	I	S	S	S	Sw	S
diethyl ether	I	S	S	S	I	S
ethyl acetate	I	S	S	S	Sw	S
1,4-dioxane	Sw	S	S	S	S	S
tetrahydrofuran	S	S	S	S	S	S
N,N-dimethylformamide	S	S	S	S	S	S
ethanol	S	I	I	I	Sw	I
methanol	S	I	I	I	Sw	I
water (basic)	I	I	I	I	I	I
water (acidic)	Sw	I	I	I	I	I

[a] I, insoluble; S, soluble; Sw, swelling. [b] $(2)_{30}$–$(\text{styrene})_{130}$–$(2)_{30}$: obtained by the hydrolysis of block copolymer shown in Table III, run 2.

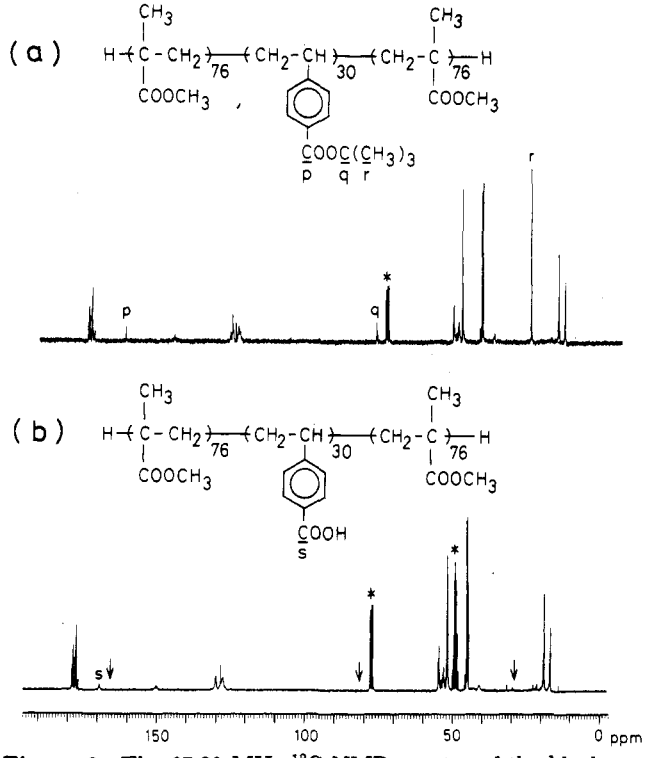

Figure 8. The 67.80 MHz ^{13}C NMR spectra of the block copolymer (Table III, run 1) before hydrolysis in $CDCl_3$ (a) and the hydrolyzed one in the mixed solvent of $CDCl_3$ and CD_3OD (b). After hydrolysis, peaks p, q, and r corresponding to the *tert*-butyl ester carbons disappear as indicated by arrows and new signal, s, due to carboxy carbon appears. Peaks attributable to solvent are marked with asterisks.

of polystyrene. In contrast, hydrophilic poly(**2**) is soluble in methanol, ethanol, THF, and *N,N*-dimethylformamide and insoluble in nonpolar solvents. The block copolymer of 4-vinylbenzoic acid and styrene shows the intermediate solubility and is particularly dissolved in mixtures of polar and nonpolar solvents: benzene/methanol, chloroform/methanol, and diethyl ether/methanol.

Conclusion

At −95 °C, the anionic polymerization of **1e** constructs a stable living polymer inhibiting the undesirable side reaction. The bulkiness of the ester alkyl group and the electron-withdrawing effect of ester group seem to play an important role in the stabilization of the living end. From this living polymerization system, poly(**1e**)s and the block copolymers with well-defined chain structures are synthesized. Finally, the resulting poly(**1e**) is completely hydrolyzed under mild condition to afford poly(**2**) with controlled chain length.

Registry No. **1a**, 1076-96-6; **1b**, 119212-19-0; **1c**, 16215-43-3; **1d**, 2715-40-4; poly(**1d**), 26776-36-3; **1e**, 84740-98-7; poly(**1e**), 91380-16-4; (**1e**)(MMA) (block copolymer), 120361-73-1; (**1e**)(styrene) (block copolymer), 120361-72-0; (**1e**)(isoprene) (block copolymer), 120361-74-2; poly(**2**) methyl ester, 26836-79-3; 4-vinylbenzoyl chloride, 1565-41-9; 4-vinylbenzoic acid, 1075-49-6; *tert*-butyldimethylsilyl chloride, 18162-48-6; dipotassiopoly(α-methylstyrene), 52219-57-5; disodiopoly(α-methylstyrene), 37244-89-6; dicesiopoly(α-methylstyrene), 117895-96-2; cumylpotassium, 3003-91-6.

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