*Macromolecules* **1999,** *32,* 1453−1462

# Protection and Polymerization of Functional Monomers. 29. Syntheses of Well-Defined Poly[(4-vinylphenyl)acetic acid], Poly[3-(4-vinylphenyl)propionic acid], and Poly(3-vinylbenzoic acid) by Means of Anionic Living Polymerizations of Protected Monomers Bearing Bicyclic Ortho Ester Moieties

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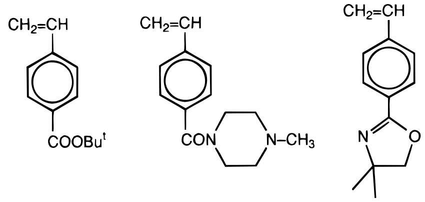
*Received September 21, 1998; Revised Manuscript Received December 22, 1998*

ABSTRACT: Anionic polymerizations of four styrenes protected with bicyclic ortho ester moieties, 1-(4-vinylphenyl)methyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**1**), 1-[2-(4-vinylphenyl)ethyl]-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**2**), 1-(3-vinylphenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**3**), and 1-(4-vinylphenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (**4**), were carried out in THF at −78 °C for 0.5 h with oligo(α-methylstyryl)lithium and -dipotassium and potassium naphthalenide. Poly(**1**)−(**3**) were quantitatively obtained, and the resulting polymers possessed the predicted molecular weights based on the molar ratios of monomers to initiators and narrow molecular weight distributions (MWDs, $M_w/M_n <$ 1.1). By contrast, polymerization of **4** did not go to completion and gave insoluble polymeric product in low yield due to the side reactions under the similar conditions. The substituent position in the monomer was very important for the success of the polymerization, although the bicyclic ortho ester was found to be stable under the polymerization conditions of **1**−**3**. Well-defined block copolymers of **1** and **2** with styrene were synthesized by the sequential block copolymerizations regardless of the order of addition of the monomers. Hydrolyses of bicyclic ortho ester moieties of the resulting polymers were performed at room temperature by treating with 6 N HCl in THF/MeOH for 1 h and subsequently with 10% NaOH(aq) in THF/MeOH for 12 h. Deprotections of poly(**1**), poly(**2**), and poly(**3**) quantitatively proceeded to afford poly[(4-vinylphenyl)acetic acid], poly[3-(4-vinylphenyl)propionic acid], and poly(3-vinylbenzoic acid) having tailored chain structures, respectively.

## Introduction

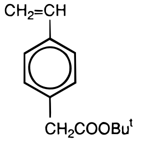
Protection of functional monomers and subsequent anionic living polymerization of the protected monomers have been proved as a valuable synthetic method for well-defined polymers.[1−3] This allows us to synthesize functional polymers having predicted chain lengths and narrow molecular weight distributions (MWDs), as well as block copolymers possessing well-defined chain structures and functional segments. In fact, we have succeeded in the tailored syntheses of a series of polystyrenes bearing reactive functional groups such as OH,[4] $NH_2$,[5] SH,[6] CHO,[7] $COCH_3$,[8] and C≡CH[9] groups. We also successfully demonstrated the synthesis of well-defined poly(4-vinylbenzoic acid) containing an aromatic COOH group in each monomer unit by using the above methodology. For this purpose, three protected monomers, *tert*-butyl 4-vinylbenzoate,[10] *N*-(4-vinylbenzoyl)-*N*′-methylpiperazine,[11] and 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline,[12] (Chart 1) were employed to protect the COOH function of 4-vinylbenzoic acid. In these polymerizations, we have observed that the nucleophilicity of the resulting living polymers is significantly lowered by the electron-withdrawing effect of three substituents through the extended π-conjugation systems.[13,14]

**Chart 1**



We herein try to develop a new synthetic route of polystyrenes bearing aliphatic carboxylic acids ($pK_a =$ 4.7), which show reactivities and acidities different from those of their aromatic counterparts ($pK_a = 4.2$). In this study, (4-vinylphenyl)acetic acid and 3-(4-vinylphenyl)propionic acid are the starting functional monomers. Although the COOH functions of (4-vinylphenyl)acetic acid and 3-(4-vinylphenyl)propionic acid can be similarly masked with ester, tertiary amide, and oxazoline protecting moieties, the protected structures of the monomers are considered to be problematic under the conditions of the anionic polymerization of styrene derivatives. The resulting active chain ends should be more reactive and basic because of the absence of the π conjugation, compared with those of 4-vinylbenzoic acid counterparts.

In fact, we prepared *tert*-butyl (4-vinylphenyl)acetate by protecting the COOH group of (4-vinylphenyl)acetic acid as its *tert*-butyl ester and attempted to polymerize it in THF at −95 °C for 2 h with oligo(α-methylstyryl)lithium or -dipotassium (see structure 1).



*tert*-butyl (4-vinylphenyl)acetate

However, the red color of initiator immediately disappeared in each case, when THF solution of the monomer

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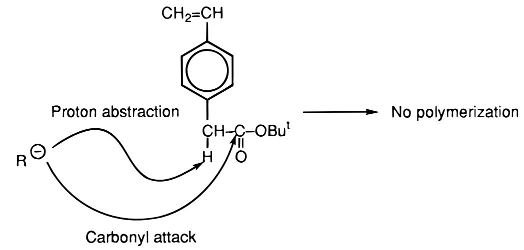
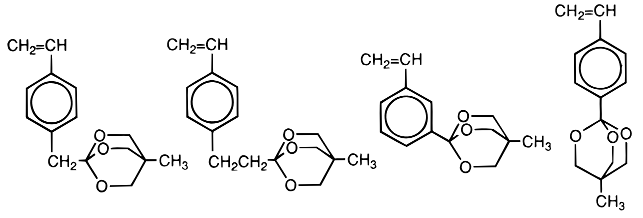
**Scheme 1**



was added to the initiator. After termination with methanol, no polymeric product was obtained, and the starting monomer was recovered quantitatively. No apparent polymerization was thus observed, because the inherent side reactions such as the nucleophilic carbonyl attack and/or the acidic proton abstraction ($pK_a = 23-25$)[15] of the initiator or the active chain end readily occurred at the initial stage of the polymerization, as shown in Scheme 1.

Hence, a new suitable protecting group is evidently required for the tailored syntheses of poly[(4-vinylphenyl)acetic acid] and poly[3-(4-vinylphenyl)propionic acid] via the anionic living polymerization of the protected monomers. We will protect the aliphatic COOH functions of (4-vinylphenyl)acetic acid and 3-(4-vinylphenyl)propionic acid by the formation of bicyclic ortho ester, 2,6,7-trioxabicyclo[2.2.2]octane, as shown in Chart 2 (**1** and **2**). The bicyclic ortho esters lack the labile acidic protons as well as the electrophilic carbonyl groups and are known to be stable even under highly basic conditions.[16−20] The aromatic COOH groups of 3- and 4-vinylbenzoic acid are also protected with the bicyclic ortho ester to examine the availability of this protecting group (Chart 2; **3** and **4**). In this study, the anionic polymerizations of four novel protected styrene monomers, **1**−**4**, are investigated to compare their polymerization behaviors.

**Chart 2**

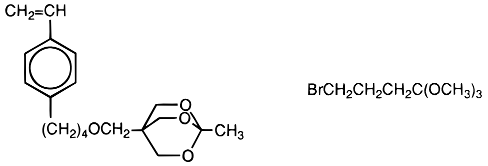


**1** **2** **3** **4**

## Results and Discussion

**Anionic Polymerization of 1 and 2.** In our previous paper, we synthesized a protected styrene, 4-{[4-(4-vinylphenyl)butoxy]methyl}-1-methyl-2,6,7-trioxabicyclo[2.2.2]octane, where a triol functionality of functional styrene was masked with bicyclic ortho ester (Chart 3).[21] The anionic polymerization of this monomer gave a stable living polymer without side reactions, and the bicyclic ortho ester moiety could be easily cleaved to regenerate the triol function under mild conditions. The stability of the ortho ester function and its usefulness as a protecting group for a COOH moiety through the reaction of anionic living polystyrene and 4,4,4-trimethoxy-1-bromobutane were demonstrated earlier (Chart 3).[22] The nucleophilic attack of terminal carbanion selectively occurred with the $CH_2Br$ bond but not with the ortho ester moiety. After the $S_N2$ functionalization and the hydrolysis of the ortho ester, the polystyrenes possessing the terminal $(CH_2)_3COOH$ group were produced in nearly quantitative yields. These previous findings strongly support the remarkable stability of the ortho ester-protecting groups toward the carbanionic species and the ease of deprotection.

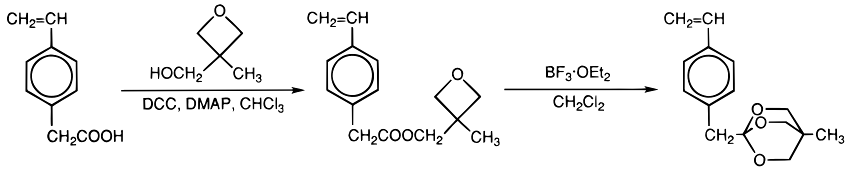
**Chart 3**



In this study, the bicyclic ortho ester, 2,6,7-trioxabicyclo[2.2.2]octane, was selected to mask the carboxyl group of (4-vinylphenyl)acetic acid. The new monomer **1** was prepared (Scheme 2) according to the reported procedure[16,17] and allowed to polymerize anionically in THF at −78 °C for 0.5 h with *sec*-butyllithium, lithium naphthalenide, potassium naphthalenide, and oligo(α-methylstyryl)lithium and -dipotassium. The polymerization system of **1** showed orange coloration in the presence of $Li^+$ or reddish brown coloration in the presence of $K^+$ over the course of polymerization. On the addition of a few drops of methanol, the coloration instantaneously disappeared, and polymers were obtained after precipitation into methanol. $^1H$ and $^{13}C$ NMR and IR spectroscopic analyses of the polymer confirmed that vinyl polymerization of **1** proceeded exclusively, and no cleavage of ortho ester moiety was observed.

Table 1 shows the polymerization results of **1** with various initiators at −78 °C in THF. The polymerizations of **1** were always complete within 0.5 h to afford the polymers quantitatively, regardless of the countercation of the initiator under the employed conditions. The size exclusion chromatography (SEC) curves of poly(**1**)s showed unimodal and narrow MWDs ($M_w/M_n = 1.04-1.12$). The number-average molecular weights of poly(**1**)s measured by vapor pressure osmometry (VPO) agreed well with the calculated values on the basis of the feed molar ratios of monomer to initiators. In one experiment (Table 1, run 4), the propagating carbanion derived from **1** was allowed to react with 1,1-bis(4′-trimethylsilylphenyl)ethylene[23] at −78 °C for 0.5 h to introduce a trimethylsilyl-substituted 1,1-diphenylethylene unit at the terminal of polymer. The $M_n$ value of the resulting poly(**1**) was then determined by $^1H$ NMR

**Scheme 2**



**1**

**Table 1. Anionic Polymerization of 1 and 2 in THF for 0.5 h[a]**

| run | monomer, mmol | initiator, mmol | α-MeSt[b] (mmol) | temp (°C) | $10^{-3}$ $M_n$ calcd[c] | $10^{-3}$ $M_n$ obsd[d] | $M_w/M_n$ |
|---|---|---|---|---|---|---|---|
| 1 | **1**, 2.80 | *s*-BuLi, 0.0648 | | −78 | 11 | 9.7 | 1.07 |
| 2 | **1**, 2.23 | Li-naph,[e] 0.107 | | −78 | 10 | 9.5 | 1.09 |
| 3 | **1**, 2.76 | *s*-BuLi, 0.0717 | 0.425 | −78 | 10 | 11 | 1.08 |
| 4 | **1**, 2.65 | *s*-BuLi, 0.0320 | 0.220 | −78 | 21 | 24[f] | 1.12 |
| 5 | **1**, 3.55 | *s*-BuLi, 0.0240 | 0.200 | −78 | 37 | 44 | 1.06 |
| 6 | **1**, 2.14 | K-naph,[g] 0.101 | | −78 | 10 | 8.2 | 1.04 |
| 7 | **1**, 1.81 | K-naph, 0.0987 | 0.425 | −78 | 10 | 8.7 | 1.06 |
| 8 | **1**, 2.79 | K-naph, 0.0918 | 0.348 | −78 | 14 | 12 | 1.09 |
| 9 | **2**, 1.68 | *s*-BuLi, 0.0557 | 0.230 | −78 | 8.4 | 24[h] | 2.29 |
| 10 | **2**, 2.05 | K-naph, 0.0903 | | −78 | 12 | 13[h] | 1.32 |
| 11 | **2**, 2.03 | Li-naph, 0.108 | | −40 | 10 | 11[i] | 1.04 |
| 12 | **2**, 2.56 | Li-naph, 0.0690 | | −40 | 19 | 20[i] | 1.04 |
| 13 | **2**, 1.99 | K-naph, 0.160 | | −40 | 6.4 | 7.0[i] | 1.03 |
| 14 | **2**, 2.43 | cumyl-K,[j] 0.0698 | | −40 | 9.2 | 10[i] | 1.05 |
| 15 | **2**, 2.61 | K-naph, 0.0813 | | −40 | 16 | 15[i] | 1.06 |

[a] Yields of polymers were quantitative in all cases. [b] α-Methylstyrene. [c] $M_n$ (calcd) = [monomer] × (MW of monomer) × $f$/[initiator] + MW of initiator; $f$ = 1 or 2, corresponding to the functionality of the initiators. [d] $M_n$ (obsd) was obtained by VPO in benzene. [e] Lithium naphthalenide. [f] $M_n$ was independently estimated to be 24 000 from the end-group analysis using $^1$H NMR. [g] Potassium naphthlenide. [h] From the SEC calibration using polystyrene standards. [i] From the end-group analysis using $^1$H NMR. [j] Cumylpotassium.

**Table 2. Anionic Polymerization of 3 and 4 in THF at −78 °C**

| run | monomer, mmol | initiator, mmol | α-MeSt[b] (mmol) | time (h) | yield (%) | $10^{-3}$ $M_n$ calcd | $10^{-3}$ $M_n$ obsd[a] | $M_w/M_n$[a] |
|---|---|---|---|---|---|---|---|---|
| 16 | **3**, 1.46 | *s*-BuLi, 0.0587 | | 0.5 | 100 | 5.8 | 9.2 | 1.06 |
| 17 | **3**, 3.34 | cumyl-K, 0.109 | | 0.5 | 100 | 7.2 | 12 | 1.05 |
| 18 | **3**, 2.68 | K-naph, 0.137 | | 0.5 | 100 | 9.1 | 14 | 1.10 |
| 19 | **4**, 2.18 | *s*-BuLi, 0.0625 | 0.257 | 3 | 11 | 8.6 | 230 | 2.10 |
| 20 | **4**, 1.95 | Li-naph, 0.154 | 0.391 | 2 | 6[b] | 6.5 | *b* | *b* |
| 21 | **4**, 2.52 | K-naph, 0.126 | 0.373 | 2 | 31[b] | 10 | *b* | *b* |
| 22 | **4**, 2.00 | K-naph, 0.168 | 0.638 | 2 | 43[b] | 6.4 | *b* | *b* |

[a] $M_n$(obsd) and $M_w/M_n$ were estimated from the SEC calibration using polystyrene standards in DMF. [b] Insoluble polymeric products.

spectroscopy via end-group analysis using the integral intensity of the introduced trimethylsilyl protons. The observed $M_n$(NMR) value of 24 000 thus obtained was consistent with a $M_n$(VPO) of 24 000 and the calculated value ($M_n$ calcd = 21 000). This also supports the stability of the propagating carbanion derived from **1** even after the completion of polymerization.

The polymerization of **2**, with one more methylene side chain than **1**, was similarly performed in order to check the reliability of bicyclic ortho ester as a protecting group for the aliphatic COOH function of 3-(vinylphenyl)propionic acid. In the case of **2**, however, the resulting polymer precipitated out at −78 °C as the polymerization proceeded. As can be seen in Table 1, the poly(**2**)s produced at −78 °C possessed quite broad MWDs, probably because of the heterogeneity of the reaction system, although the polymerizations were complete within 0.5 h. Then, we raised the polymerization temperature from −78 to −40 °C. At −40 °C, polymerization proceeded homogeneously, and the MWD of resulting poly(**2**) was satisfactorily narrow ($M_w/M_n$ < 1.1). Consequently, the poly(**2**)s produced at −40 °C had the predicted $M_n$ values and the narrow MWDs as well as the poly(**1**)s. This clearly substantiates the living character of the anionic polymerizations of **1** and **2**, novel styrenes bearing a trioxabicyclo[2.2.2]octane moiety. Therefore, the introduction of the bicyclic ortho ester successfully eliminates the problems associated with the acidic $CH_2$ protons adjacent to the C=O linkages as well as the electrophilic C=O group.

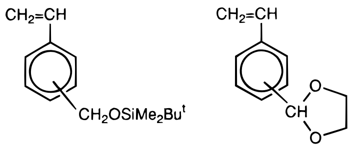
**Anionic Polymerization of 3 and 4.** To examine the generality of the ortho ester for protecting COOH functions, the aromatic carboxylic acids, 3- and 4-vinylbenzoic acid, were also protected with the ortho ester moiety, and we attempted to polymerize them anionically. The anionic polymerization of the *meta*-substituted monomer, **3**, proceeded heterogeneously in THF at −78 °C, and quantitative conversion of **3** was achieved within 0.5 h, as shown in Table 2. It was found that the SEC curves of poly(**3**)s thus obtained were unimodal and narrow, the polydispersity indices, $M_w/M_n$, being within 1.1. The $M_n$ values of poly(**3**)s estimated from the SEC calibration using polystyrene standards in DMF were always higher than the calculated values, and about 1.6 times larger than the calculated ones. The deviation between the observed $M_n$ values and the calculated ones is accounted for by the difference in the hydrodynamic volume of the poly(**3**) and polystyrene standards in DMF. We considered that the $M_n$ values of poly(**3**) might be overestimated in DMF. Thus, the polymerization of **3** is also found to proceed in a living manner, although the precise determination of $M_n$ values is necessary for the reliable conclusion.

In contrast to the polymerization results of **1**−**3**, we have found it difficult to anionically polymerize **4**, which is a *para* isomer of **3**. For example, the anionic polymerization of **4** was performed in THF at −78 °C for 3 h with oligo(α-methylstyryl)lithium. Upon addition of **4** in THF to the initiator solution, the red color of initiator immediately disappeared. After 3 h, a methanol-insoluble polymer was obtained in only 11% yield, and most of the unreacted **4** was recovered. The resulting polymer possessed a very broad MWD and molecular weight much higher than the expected value. The chemical structure of the polymeric product was confirmed by $^1$H NMR analysis to be a poly(α-methylstyrene) containing several units of **4**. The initiation of difunctional oligo(α-methylstyryl)dilithium or -dipotassium only gave the insoluble products in very low yields (6−43%). The insoluble product might be a cross-linked polymer of **4**. The polymerization behavior of **4** is thus a sharp contrast to the polymerization results of **3**, the *meta*-substituted monomer.

To study the polymerization mechanism further, living polystyrene was employed as a macroinitiator of **4**. The addition of **4** to the monofunctional living polystyrene ($M_n = 3900$, $M_w/M_n = 1.06$) prepared with *s*-BuLi gave soluble polymeric material in THF at −78 °C for 2 h, although most of the starting monomer was recovered from the polymerization system. The SEC curve of the product showed multimodal and very broad MWD. The $^1$H NMR spectrum indicated that the resulting polymer included a small amount of repeating units derived from **4** in addition to the polystyrene segment. On the other hand, when we used difunctional living polystyrenes, all of the resulting polymers became insoluble, and most of **4** (70%) was recovered. Thus, the initiation with difunctional living polystyrene afforded only the insoluble polymeric product in rather low yield.

The polymerization results of **3** versus **4** are consistent with our previous observations in the polymerizations of styrenes bearing (trialkylsilyloxy)methyl groups,[4b] and 1,3-dioxolane rings,[7b] as shown in Chart 4. The anionic polymerizations of the *meta* isomers bearing these substituents proceed in a controlled fashion to produce living polymers. In contrast, the polymerization of the corresponding *para* isomer involves serious side reactions after the initiation reaction.[4b,7b] The proposed mechanism of the side reaction is that the propagating carbanion of poly(**4**) readily induces intramolecular 1,6-elimination of the ortho ester moiety through the phenylene ring to form the highly reactive *p*-xylylene intermediate along with the formation of alkoxide, as shown in Scheme 3.[4b,7b] Then, either the resulting xylylene moiety or the isomeric biradical is nucleophilically attacked by the carbanionic species or undergoes the radical combination leading to the cross-linked polymer.

**Chart 4**



We have thus realized that the monomer structure and the substituent position in the styrene monomer is essentially important for the success of the polymerization, even though the bicyclic ortho ester is stable under the conditions of the anionic polymerization of styrene derivatives.

**Block Copolymerization of 1 and 2 with Styrene.** We carried out the sequential copolymerizations of **1** and **2** with styrene to synthesize tailored block copolymers having well-defined chain structures under the similar conditions (Table 3).

First of all, sequential copolymerization of **1** (first monomer) and styrene (second monomer) was initiated with oligo(α-methylstyryl)lithium, which was prepared from *s*-BuLi and 5-fold α-methylstyrene in THF at −78 °C. The first-stage polymerization of **1** was completed in THF at −78 °C within 0.5 h, and then styrene was added to the reaction system and allowed to react further for 10 min. The copolymer was obtained quantitatively after the termination with MeOH. The SEC curve of copolymer is unimodal and narrow ($M_w/M_n = 1.12$) and shifts toward the higher molecular weight region after the addition of styrene, as shown in Figure 1. It was confirmed by $^1$H NMR spectroscopy that the composition of each polymer segment was in good accordance with the feed molar ratio of **1** and styrene. The $M_n$ value of the copolymer agreed well with the calculated value based on the $[M]/[I]$ ratios. Thus, it is substantiated that the resulting diblock copolymer, poly(**1**-*b*-styrene), possesses the predicted composition and molecular weight in addition to the narrow MWD. This also strongly indicates that the propagating carbanion of poly(**1**) is completely stable at -78 °C and can initiate the polymerization of styrene quantitatively. Similarly, well-defined block copolymers of **1** or **2** and styrene could be synthesized by initiation with potassium naphthalenide at −78 °C. The resulting triblock copolymers, poly(styrene-*b*-**1**-*b*-styrene) and poly(styrene-*b*-**2**-*b*-styrene), had relatively narrow MWDs ($M_w/M_n = 1.15$ and

**Scheme 3**

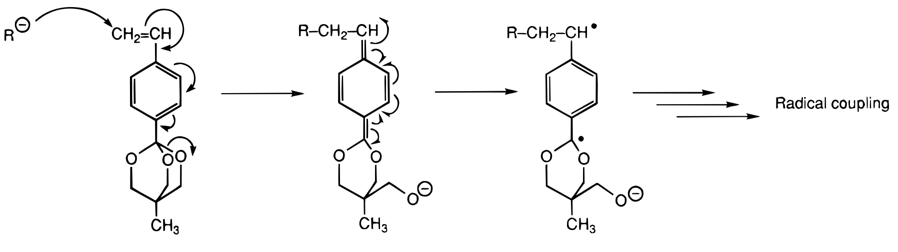


**Table 3. Anionic Block Copolymerization of 1 and 2 in THF at −78 °C[a]**

| | | | | | block copolymer (homopolymer[b]) | | |
|---|---|---|---|---|---|---|---|
| | | | | | $10^{-3}$ $M_n$ | | |
| run | initiator | block sequence | A monomer | B monomer | calcd | obsd[c] | $M_w/M_n$ |
| 23 | *s*-BuLi/α-MeSt | A−B | **1** | styrene | 35 (8.5) | 38 (10) | 1.12 (1.07) |
| 24 | K-naph | B−A−B | **1** | styrene | 18 (7.0) | 15 (5.5) | 1.15 (1.04) |
| 25 | K-naph | B−A−B | styrene | **1** | 13 (5.3) | 12 (5.5) | 1.07 (1.06) |
| 26[d] | K-naph | B−A−B | **2** | styrene | 17 (5.4) | 19 (5.3) | 1.13 (1.04) |
| 27 | K-naph | B−A−B | styrene | **2** | 14 (6.3) | 14 (6.0) | 1.04 (1.05) |

[a] Yields of polymers were nearly quantitative in each case. [b] Homopolymers were obtained at the first-stage polymerization of A monomer. [c] $M_n$'s of the block copolymers were determined by using the $M_n$'s of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by $^1$H NMR. [d] Carried out at −40 °C.

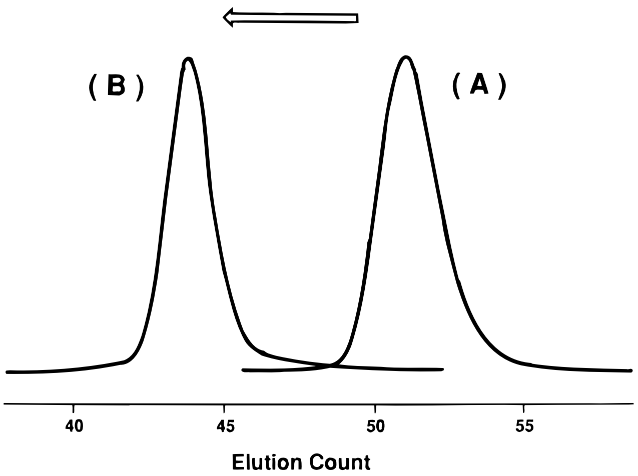


**Figure 1.** SEC curves of poly(**1**) (peak A, $M_w/M_n = 1.07$) and poly(**1**-*b*-styrene) (peak B, $M_w/M_n = 1.12$) produced at −78 °C in THF (the second feed of monomer was added 0.5 h after the first-stage polymerization).

1.13, respectively) and controlled $M_n$ values. The stability of the active chain end derived from **2** is also clarified under the conditions employed here.

We changed the order of addition of the comonomers in the sequential block copolymerization; styrene was used as the first monomer, and **1** or **2** was used for a second monomer. First-stage polymerization of styrene was performed with potassium naphthalenide to prepare the difunctional living polystyrene. The second monomer, **1** or **2**, was then added to the polymerization system and allowed to react for 0.5 h to achieve the quantitative conversion. The triblock copolymers with controlled primary structures in terms of $M_n$'s and compositions were produced in quantitative yields, as expected. The block copolymers maintained narrow MWDs ($M_w/M_n < 1.1$). It is clear that the anionic living polystyrene is an excellent macroinitiator for the sequential copolymerization of **1** or **2** to afford the tailored block copolymers.

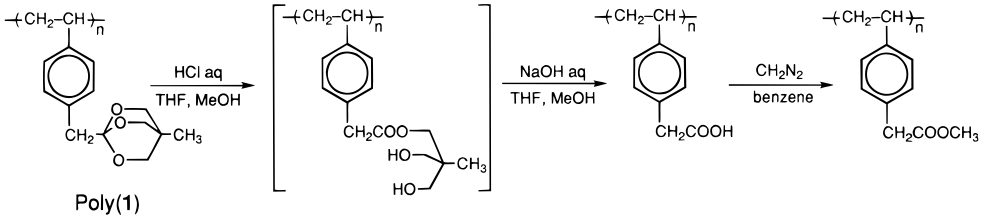
These results support that the anionic polymerizabilities of **1** and **2** are comparable to that of styrene, because the "reversible" block copolymerization between **1** or **2** and styrene is possible in quantitative efficiencies. By contrast, such sequential block copolymerization between the living polymers of *tert*-butyl ester,[10] *N*,*N*-dialkylamide,[11,13] and oxazoline derivatives[12] and styrene have failed to result in the recovery of homopolymers or the formation of a mixture of homopolymer and block copolymer having ill-controlled chain structure. These propagating carbanions stabilized by the electron-withdrawing substituents could not initiate the styrene polymerization at all or could react with styrene only in very low efficiencies, although the reversed sequential addition of comonomers readily provided the tailored block copolymers.[13] Thus, the anionic polymerizability comparable to styrene is an apparent synthetic advantage for **1** and **2** to prepare the well-defined amphiphilic block copolymers having the COOH segment in the expected sequence.

**Deprotection of Poly(1)−(3).** We previously succeeded in the complete removal of bicyclic ortho ester moieties to afford the polystyrene bearing triol functionality in each monomer unit.[21] The hydrolyses of the ortho ester moieties of poly(**1**)−(**3**) are similarly carried out to regenerate the COOH functionalities via the two-step reaction, as shown in Scheme 4.

For example, poly(**1**) was treated with 6 N HCl in THF/MeOH for 1 h and subsequently with 10% NaOH aqueous solution in THF/MeOH overnight at room temperature.[24] Both reactions proceeded homogeneously. In the $^1$H NMR of the resulting polymer after the two-step reaction, signals due to $CH_3$ (0.75 ppm) and $C(CH_2O)_3C$ (3.9 ppm) completely disappeared, and the signal of benzylic protons shifted from 2.7 to 3.6 ppm. The change of the spectrum of the polymer is also observed in the $^{13}$C NMR, as shown in Figure 2. The $^{13}$C NMR signals at 14.7 ($CH_3$), 30.5 ($CH_3$-*C*), 72.7 ($CH_2O$), and 108.8 ppm [$(CH_2O)_3C$] are no longer present after the hydrolysis, whereas the typical signal derived from the carbonyl carbon of the COOH function newly appears at 176 ppm. The IR absorptions due to the C−O linkage of the ortho ester at 990, 1011, and 1056 cm$^{-1}$ and due to the $CH_3$ group at 1346 and 1368 cm$^{-1}$ disappeared after the reaction, and alternatively, new absorptions corresponding to the C=O and OH groups of the carboxylic acid at 1711 and 2500−3700 cm$^{-1}$ were observed. These spectroscopic observations strongly support that the complete deprotection of ortho ester is achieved to give a poly[(4-vinylphenyl)acetic acid] through the acid hydrolysis and the following basic saponification. Similar deprotections of ortho ester moieties of poly(**2**) and -(**3**) proceeded quantitatively under mild conditions to afford poly[3-(4-vinylphenyl)propionic acid] and poly(3-vinylbenzoic acid), respectively.[24] The resulting polymers have polar carboxylic acid groups and are difficult to analyze by the SEC measurement in THF, probably because of the strong adsorption of COOH functionalities on the polystyrene gel columns.

The resulting deprotected polymers were then converted into their methyl esters to examine their MWDs by SEC measurement by treating with diazomethane in benzene, as shown in Scheme 4. The quantitative transformation of COOH groups into the $COOCH_3$ groups was confirmed by the spectroscopic information of the resulting polymers (see Experimental Section). The SEC curves of the poly[methyl (4-vinylphenyl)acetate], poly[methyl 3-(4-vinylphenyl)propionate], and poly(methyl 3-vinylbenzoate) maintained their unimodal and narrow shapes and shifted slightly from those of poly(**1**)−(**3**) toward the lower molecular weight regions, respectively. The typical SEC curves of polymers before deprotection and after esterification are shown in Figure 3. The SEC curve of poly[methyl 3-(4-vinylphenyl)-

**Scheme 4**



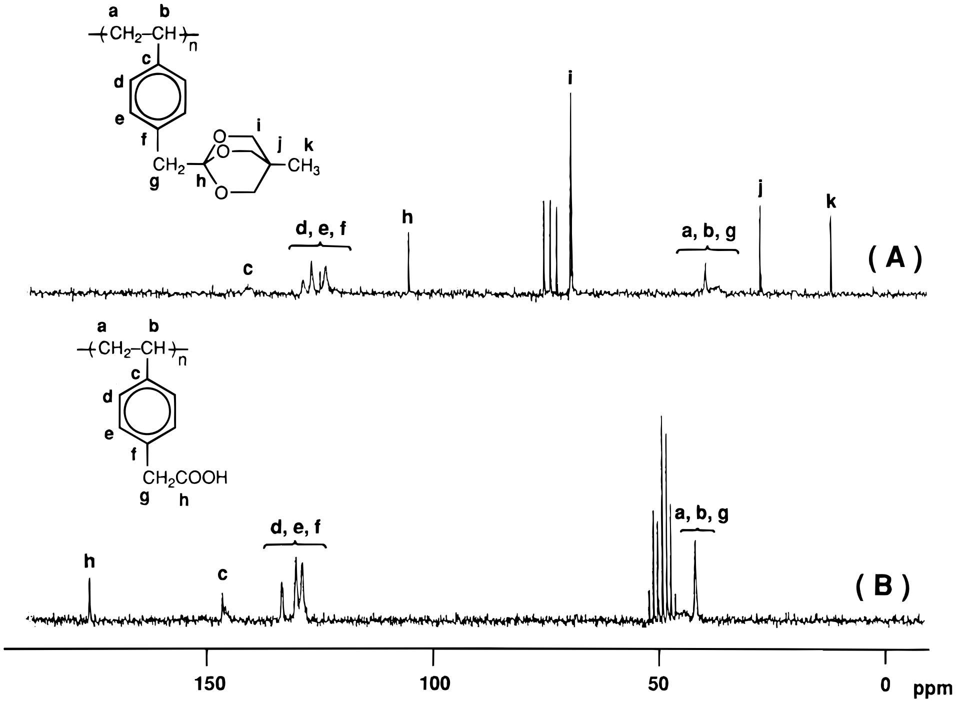


**Figure 2.** $^{13}$C NMR spectra of poly(**1**) (A) in $CDCl_3$ and poly[(4-vinylphenyl)acetic acid] after deprotection (B) in $CD_3OD$.

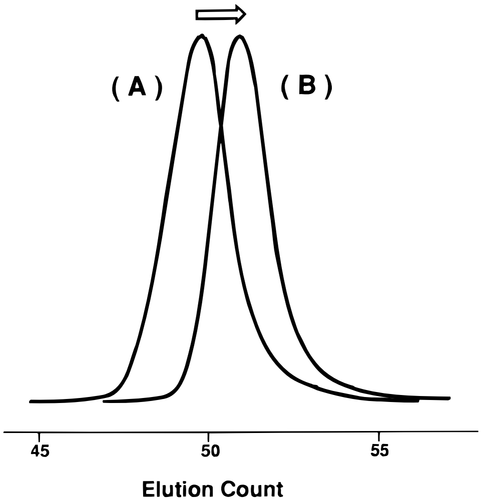


**Figure 3.** SEC curves of poly(**2**) (peak A, $M_w/M_n = 1.06$) and poly[methyl 3-(4-vinylphenyl)propionate] after deprotection and methylation (peak B, $M_w/M_n = 1.07$).

propionate] shifts from that of poly(**2**) toward the lower molecular weight region and keeps the narrow MWD. This strongly indicates that three-step polymer reactions (acid hydrolysis, basic saponification, and methylation) ideally proceed without side reactions such as cross-linking and chain degradation of the polymer. Thus, we have succeeded in the syntheses of well-defined poly[(4-vinylphenyl)acetic acid], poly[3-(4-vinylphenyl)propionic acid], and poly(3-vinylbenzoic acid) possessing narrow MWDs and predicted $M_n$ values via the anionic living polymerizations of **1**−**3** and the following complete deprotections of the bicyclic ortho ester moieties. The dual protecting potentials of bicyclic ortho ester moiety are clearly shown for the protection of styrene derivatives bearing carboxylic acid functions (this work) or triol functions (previous work).[21]

**Solubilities and Glass-Transition Temperatures of the Polymers.** The solubilities of the resulting polymers are summarized in Table 4 with those of poly(4-vinylbenzoic acid)[10−12] and polystyrene as the references. Poly(**1**) and -(**2**) were soluble in a variety of organic solvents and showed good solubility similar to polystyrene except for in $Et_2O$. On the other hand, poly(**3**) showed a quite limited solubility and was soluble only in $CHCl_3$, DMF, and DMSO. The methylene spacers between the polystyrene backbone and the bicyclic ortho ester moiety seemed to enhance the solubilities of poly(**1**) and -(**2**).

The drastic change in solubility of the polymers before and after deprotection was observed during the transformation of the bicyclic ortho ester into carboxylic acid, as expected. The resulting poly(3-vinylbenzoic acid) became insoluble in $CHCl_3$ but soluble in THF, pyridine, ethanol, and methanol. These solubilities resembled those of the *para* substituted counterpart, poly(4-vinylbenzoic acid). Poly[(4-vinylphenyl)acetic acid] and poly[3-(4-vinylphenyl)propionic acid] after deprotection were insoluble in benzene and $CHCl_3$, and soluble in polar solvents such as ethanol and methanol. The solubilities of the deprotected polymers clearly reflected the high polarity and hydrophilic nature of the COOH functionalities.

The glass transition temperatures ($T_g$'s) of the polymers were measured by differential scanning calorimetry (DSC). Poly(**1**) showed an endothermic peak at 160−170 °C, probably derived from the glass transition behavior, but also showed a large exothermic peak at 180−190 °C. This latter exotherm might account for the thermal ring-opening polymerization of the bicyclic ortho ester moieties in poly(**1**). Because the $T_g$ measurement of the polymers before deprotection seemed difficult because of the thermally labile pendant ortho ester moieties, we analyzed the $T_g$ values of the deprotected carboxylic acid polymers. Poly[4-vinylphenyl)acetic acid], poly[3-(4-vinylphenyl)propionic acid], and poly(3-vinylbenzoic acid) presented $T_g$ values of 151, 119, and 190,°C, respectively, which were higher than that of the parent polystyrene ($T_g$ = 100 °C). These higher $T_g$

**Table 4. Solubility of Polymers**

| solvent | poly(**1**) | poly(**2**) | poly(**3**) | poly(4VPAA)[a] | poly(4VPPA)[b] | poly(3VBA)[c] | poly(4VBA)[d] | PSt |
|---|---|---|---|---|---|---|---|---|
| hexane | I | I | I | I | I | I | I | I |
| benzene | S | S | I | I | I | I | I | S |
| $CHCl_3$ | S | S | S | I | I | I | I | S |
| $Et_2O$ | I | I | I | I | I | I | I | S |
| acetone | S | S | I | S | S | I | I | S |
| ethyl acetate | S | S | I | S | S | I | I | S |
| 1,4-dioxane | S | S | I | S | S | Sw | Sw | S |
| THF | S | S | I | S | S | S | S | S |
| DMF | S | S | S | S | S | S | S | S |
| DMSO | S | S | S | S | S | S | S | S |
| EtOH | I | I | I | S | S | S | S | I |
| MeOH | I | I | I | S | S | S | S | I |
| water | I | I | I | I | I | I | I | I |

[a] Poly(4-vinylphenylacetic acid). [b] Poly[3-(4-vinylphenyl)propionic acid]. [c] Poly(3-vinylbenzoic acid). [d] Poly(4-vinylbenzoic acid). [e] I: insoluble. Sw: swelling. S: soluble.

values might be derived from the intramolecular and intermolecular hydrogen bonding of the COOH groups in the repeating units.

In conclusion, we have successfully demonstrated the anionic living polymerizations of novel styrene monomers, **1**−**3**, bearing COOH functions protected with bicyclic ortho ester functionalities. Poly(**1**)−(**3**) of controlled molecular weights and narrow MWDs were prepared. The living character of the propagating carbanion derived from **1** and **2** was also proved by the tailored syntheses of block copolymers by the sequential copolymerization of **1** or **2** and styrene, respectively. Quantitative acid hydrolysis and the subsequent saponification of poly(**1**)−(**3**) readily provided poly[(4-vinylphenyl)acetic acid], poly[3-(4-vinylphenyl)propionic acid], and poly(3-vinylbenzoic acid) having well-defined chain structures. These indicate the availability of the bicyclic ortho ester protecting group for the anionic living polymerization of styrene derivatives containing an aliphatic or an aromatic carboxylic acid function.

## Experimental Section

**Materials.** 4-Vinylbenzoic acid and 4-(2-hydroxyethyl)styrene were kindly supplied from Hokko Chemical Industry Co., Ltd., and used for the monomer synthesis without further purification. 4-(Chloromethyl)styrene was similarly supplied from Seimi Chemical Co., Ltd. 3-Bromostyrene and 1,1-bis[4′-(trimethylsilyl)phenyl]ethylene ($TMS_2DPE$) were synthesized as previously reported.[23] 3-Methyl-3-hydroxymethyloxetane was prepared in 55% yield by the reaction of trimethylolethane and diethyl carbonate according to the reported procedure.[25] 4-(Dimethylamino)pyridine (DMAP), *N,N*′-dicyclohexylcarbodiimide (DCC), boron trifluoride etherate, and thionyl chloride were used for the monomer synthesis without purification. Styrene and α-methylstyrene were distilled in vacuo over $CaH_2$. These styrenes were further purified by distillation in the presence of phenylmagnesium chloride (THF solution) on a vacuum line. THF used as a polymerization solvent was refluxed over sodium wire, then distilled from $LiAlH_4$, and finally through a vacuum line from sodium naphthalenide solution.

**Initiators.** Commercially available *s*-BuLi as a 1.05 M solution in cyclohexane (Nakarai Tesque) was diluted with dry *n*-heptane. Lithium naphthalenide and potassium naphthalenide were prepared by the reactions of a small excess of naphthalene and the corresponding alkali metal in THF at room temperature. Cumylpotassium was prepared from cumyl methyl ether and a sodium−potassium alloy in THF. Initiators were stored at −30 °C in ampules equipped with breakseals. Monofunctional and difunctional living oligomers of α-methylstyrene were prepared in THF as previously reported.[21] The concentration of initiators was determined by colorimetric titration with standardized 1-octanol in a sealed reactor in vacuo.[26]

**3-Vinylbenzoic Acid.** A THF (150 mL) solution of 3-bromostyrene[23] (35.39 g, 193 mmol) was added dropwise at 0 °C to a suspension of magnesium turnings (6.02 g, 248 mmol) in THF (50 mL) under nitrogen. The mixture was stirred to complete the reaction at room temperature for 1 h and then added to a mixture of large excess of dry ice and $Et_2O$ (100 mL). The reaction mixture was allowed to stir for 1 h and quenched with 2 N HCl solution. The layers were separated, and the aqueous phase was extracted with $Et_2O$ three times. The combined organic phase was concentrated by rotary evaporator and extracted with 10% NaOH solution. The aqueous phase was washed with $Et_2O$ and poured into cold concentrated HCl to afford a white solid of carboxylic acid. The solid was collected by filtration and washed with cold water. Vacuum drying gave as a white solid 3-vinylbenzoic acid (17.94 g, 121 mmol, 63%): $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 5.33 and 5.82 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.77 (dd, 1H, $-CH{=}$), 7.3−8.7 (m, 4H, aromatic), 11.4 (bs, 1H, COOH); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 115.4 ($CH_2{=}$), 128. 2 (Ar, C2), 128.8 (Ar, C5), 129.6 (Ar, C4), 130.1 (Ar, C3), 131.4 (Ar, C6), 136.1 ($-CH{=}$), 138.4 (Ar, C1), 172.1 (C=O).

**3-Vinylbenzoyl chloride** was prepared by the reaction of 3-vinylbenzoic acid (17.76 g, 120 mmol) and thionyl chloride (27 mL, 370 mmol) in the presence of *tert*-butylcatecohol (10 mg) at 0 °C 4 h and then at 40 °C for 1 h under nitrogen. After excess thionyl chloride was removed in vacuo, vacuum distillation gave as a colorless liquid 3-vinylbenzoyl chloride (13.44 g, 80.7 mmol, 67%, bp 65−67 °C/1 mmHg): $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 5.39 and 5.84 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.76 (dd, 1H, $-CH{=}$), 7.3−8.2 (m, 4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 116.2 ($CH_2{=}$), 128. 6 (Ar, C2), 129.0 (Ar, C5), 130.2 (Ar, C4), 132.5 (Ar, C6), 133.8 (Ar, C3), 135.2 ($-CH{=}$), 138.7 (Ar, C1), 167.8 (C=O).

**(3-Methyloxetan-3-yl)methyl 3-Vinylbenzoate.** A solution of 3-vinylbenzoyl chloride (13.44 g, 80.7 mmol) in $Et_2O$ (40 mL) was added dropwise at 0 °C to a mixture of 3-methyl-3-hydroxymethyloxetane (8.30 g, 81.4 mmol), triethylamine (15 mL, 108 mmol), and $Et_2O$ (40 mL) under nitrogen. The reaction mixture was stirred overnight at room temperature and then poured into a saturated $NaHCO_3$ solution. The layers were separated, and the aqueous phase was extracted with $Et_2O$ three times. The combined ether solution was washed with both saturated $NaHCO_3$ solution and brine and dried over anhydrous $MgSO_4$. After the solvent was removed in vacuo, vacuum distillation gave as a colorless liquid (3-methyloxetan-3-yl)methyl 3-vinylbenzoate (14.96 g, 64.5 mmol, 80%, 110−112 °C/2 mmHg): $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 1.43 (s, 1H, $CH_3$), 4.41 (s, 2H, $COOCH_2$), 4.44 and 4.65 (2d, 4H, $J$ = 6 Hz, $CCH_2O$), 5.33 and 5.81 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.76 (dd, 1H, $-CH{=}$), 7.3−8.1 (m, 4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ = 21.2 ($CH_3$), 39.6 ($\mathit{C}CH_2O$), 69.1 ($C\mathit{C}H_2O$), 79.4 ($COO\mathit{C}H_2$), 115.0 ($CH_2{=}$), 127.3 (Ar, C2), 127.6 (Ar, C5), 128.7 (Ar, C4), 130.4 (Ar, C3), 130.6 (Ar, C6), 135.9 ($-CH{=}$), 138.2 (Ar, C1), 166.2 (C=O).

**1-(3-Vinylphenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]-octane (3).**[16] Boron trifluoride etherate (2 mL, 16.2 mmol) was added at −20 °C to a solution of (3-methyloxetan-3-yl)methyl 3-vinylbenzoate (14.66 g, 63.2 mmol) in $CH_2Cl_2$ (150 mL). The mixture was stirred at −20 °C for 12 h and then the reaction was quenched with triethylamine (10 mL). After $CH_2Cl_2$ was removed in vacuo, $Et_2O$ was added to precipitate the $BF_3$ amine complex. The solid was filtered off, and the filtrate was concentrated in vacuo to afford crude product (6.02 g). Column chromatography (silica gel pretreated with triethylamine; hexane/ethyl acetate = 9/1) and subsequent recrystallization from hexane gave as a white solid **3** (3.17 g, 13.7 mmol, 22%, mp 72−73 °C): $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 0.86 (s, 3H, $CH_3$), 4.07 (s, 6H, $CH_2O$), 5.23 and 5.73 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.72 (dd, 1H, $-CH{=}$), 7.2−7.7 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 14.5 ($CH_3$), 30.6 ($\mathit{C}CH_3$), 73.4 ($CH_2O$), 107.7 (ArCO), 113.9 ($CH_2{=}$), 124.0 (Ar, C2), 125.4 (Ar, C6), 126.9 (Ar, C5), 128.1 (Ar, C4), 137.0 ($-CH{=}$), 137.6 (Ar, C1), 138.1 (Ar, C3); IR (KBr, $cm^{-1}$) 805, 908, 997, 1006, 1027, 1054, 1397, 2878, 2957, 2965.

**1-(4-Vinylphenyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane** [**4**, mp 116−118 °C (dec)] was similarly synthesized as above via the acidic isomerization[16] of (3-methyloxetan-3-yl)methyl 4-vinylbenzoate in 22% yield: $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 0.86 (s, 3H, $CH_3$), 4.07 (s, 6H, $CH_2O$), 5.24 and 5.73 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.71 (dd, 1H, $-CH{=}$), 7.2−7.7 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 14.4 ($CH_3$), 30.4 ($\mathit{C}CH_3$), 73.2 ($CH_2O$), 107.7 (ArCO), 114.3 ($CH_2{=}$), 125.8 and 125.9 (Ar, C2 and C3), 136.5 ($-CH{=}$), 136.8 (Ar, C1), 138.2 (Ar, C4); IR (KBr, $cm^{-1}$) 844, 915, 980, 1000, 1020, 1053, 1339, 1630, 2878, 2933, 2960.

**(4-Vinylphenyl)acetic acid**[27] was synthesized in 79% yield by the Grignard reaction of 4-(chloromethyl)styrene and carbon dioxide in $Et_2O$: $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 3.63 (s, 2H, $ArCH_2$), 5.23 and 5.72 (2d, 2H, $J$ = 11 and 17 Hz, $CH_2{=}$), 6.71 (dd, 1H, $-CH{=}$), 7.2−7.4 (m, 4H, aromatic), 8.5 (bs, 1H, COOH); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 40.8 ($ArCH_2$), 113.9 ($CH_2{=}$), 126.5 (Ar, C3), 129.5 (Ar, C2), 132.9 (Ar, C4), 136.6 ($-CH{=}$), 137.0 (Ar, C1), 177.5 (C=O).

***tert*-Butyl (4-Vinylphenyl)acetate** (bp 82−83 °C/0.5 mmHg) was synthesized in 12% yield by the reaction of (4-vinylphenyl)acetic acid (11.60 g, 71.6 mmol) and *tert*-butyl alcohol (6.80 g, 82.2 mmol) in the presence of DMAP (4.27 g, 35.0 mmol) and DCC (19.04 g, 92.4 mmol) in $CHCl_3$ (150 mL): $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 1.43 (s, 9H, $CH_3$), 3.50 (s, 2H, $CH_2$), 5.21 and 5.71 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.70 (dd 1H, $-CH{=}$), 7.1−7.4 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 27.9 ($CH_3$), 42.3 ($CH_2$), 80.6 ($\mathit{C}(CH_3)_3$), 113.4 ($CH_2{=}$), 126.2 (Ar, C3), 129.2 (Ar, C2), 134.2 (Ar, C1), 136.1 (Ar, C4), 136.5 ($-CH{=}$), 170.5 (C=O); IR (KBr, $cm^{-1}$) 828, 907, 990, 1142, 1368, 1635 (C=C), 1734 (C=O), 2933, 2979, 3005.

**(3-Methyloxetan-3-yl)methyl (4-Vinylphenyl)acetate.** DCC (28.86 g, 140 mmol) was added in several portions at room temperature to a $CHCl_3$ (250 mL) solution of (4-vinylphenyl)acetic acid (17.54 g, 108 mmol), 3-methyl-3-hydroxymethyloxetane (10.60 g, 104 mmol), and DMAP (1.28 g, 10.5 mmol). The mixture was stirred overnight at room temperature and then concentrated in vacuo to remove $CHCl_3$. Hexane was added to the residue to precipitate the white solid, and the resulting solid was filtered off. The filtrate was washed with 0.5 N HCl, saturated $NaHCO_3$ solution, and brine and dried over anhydrous $MgSO_4$. After hexane was removed in vacuo, the residue was purified by column chromatography (silica gel; hexane/ethyl acetate = 9/1). Vacuum distillation gave as a colorless liquid (3-methyloxetan-3-yl)methyl (4-vinylphenyl)acetate (20.32 g, 82.6 mmol, 76%, 123−124 °C/0.5 mmHg). $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 1.27 (s, 3H, $CH_3$), 3.64 (s, 2H, $ArCH_2$), 4.16 (s, 2H, $COOCH_2$), 4.33 and 4.48 (2d, 4H, $J$ = 6 Hz, $CCH_2O$), 5.22 and 5.71 (2d, 2H, $J$ = 11 and 17 Hz, $CH_2{=}$), 6.70 (dd, 1H, $-CH{=}$), 7.2−7.4 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 20.7 ($CH_3$), 38.8 ($\mathit{C}CH_2O$), 40.7 ($ArCH_2$), 68.6 ($C\mathit{C}H_2O$), 79.0 ($COO\mathit{C}H_2$), 113.5 ($CH_2{=}$), 126.1 (Ar, C3), 129.1 (Ar, C2), 133.2 (Ar, C4), 136.1 ($-CH{=}$), 136.2 (Ar, C1), 180.0 (C=O).

**1-(4-Vinylphenyl)methyl-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (1)** was synthesized from (3-methyloxetan-3-yl)methyl (4-vinylphenyl)acetate (9.83 g, 40.0 mmol) by the acidic isomerization with boron trifluoride etherate (2.84 g, 20 mmol) in $CH_2Cl_2$ (50 mL) at −20 °C for 15 h. Column chromatography (silica gel pretreated with triethylamine; hexane/ethyl acetate = 9/1) and subsequent recrystallizations from a mixed solvent of hexane and benzene afforded **1** (6.12 g, 24.9 mmol, 62%, mp 103−105 °C): $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 0.76 (s, 3H, $CH_3$), 2.98 (s, 2H, $ArCH_2$), 3.87 (s, 6H, $CH_2O$), 5.18 and 5.69 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.69 (dd, 1H, $-CH{=}$), 7.2−7.4 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 14.4 ($CH_3$), 30.4 ($\mathit{C}CH_3$), 42.6 ($ArCH_2$), 72.7 ($C\mathit{C}H_2O$), 108.6 ($CH_2\mathit{C}O$), 113.1 ($CH_2{=}$), 125.8 (Ar, C3), 130.7 (Ar, C2), 134.9 (Ar, C1), 135.9 ($-CH{=}$), 136.9 (Ar, C4); IR (KBr, $cm^{-1}$) 845, 899, 1007, 1044, 1050, 1397, 1628, 2878, 2925, 2958.

**4-(2-Chloroethyl)styrene** (bp 71−72 °C/2 mmHg) was prepared in 66% yield by the reaction of (2-hydroxyethyl)styrene and thionyl chloride in the presence of *N*,*N*-dimethylaniline in $CHCl_3$:[28] $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 3.04 (t, 2H, $J$ = 7 Hz, $ArCH_2$), 3.69 (t, 2H, $CH_2Cl$), 5.21 and 5.71 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.70 (dd 1H, $-CH{=}$), 7.0−7.5 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 38.8 ($ArCH_2$), 44.6 ($CH_2Cl$), 113.4 ($CH_2{=}$), 126.4 (Ar, C2), 128.8 (Ar, C3), 136.4 (Ar, C1), 136.5 ($-CH{=}$), 137.7 (Ar, C4).

**3-(4-Vinylphenyl)propionic acid** was synthesized as a white powder in 61% yield from the Grignard reagent of 4-(2-chloroethyl)styrene and carbon dioxide in THF: $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 2.6−2.8 (m, 2H, $C\mathit{H_2}COOH$), 2.8−3.1 (m, 2H, $ArCH_2$), 5.18 and 5.70 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.70 (dd, 1H, $-CH{=}$), 7.0−7.5 (m, 4H, aromatic), 10.3 (bs, 1H, COOH); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 30.5 ($\mathit{C}H_2COOH$), 35.5 ($ArCH_2$), 113.4 ($CH_2{=}$), 126.5 (Ar, C3), 128.8 (Ar, C2), 136.1 (Ar, C4), 136.7 ($-CH{=}$), 139.9 (Ar, C1), 178.6 (C=O).

**(3-Methyloxetan-3-yl)methyl 3-(4-Vinylphenyl)propionate** (bp 134−136 °C/mmHg) was prepared in 62% yield according to the above-described procedure using 3-(4-vinylphenyl)propionic acid (14.02 g, 19.7 mmol), 3-methyl-3-hydroxymethyloxetane (8.24 g, 80.8 mmol), DMAP (2.42 g, 19.8 mmol), and DCC (25.06 g, 122 mmol) in $CHCl_3$: $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 1.25 (s, 3H, $CH_3$), 2.5−2.8 (m, 2H, $CH_2COO$), 2.8−3.1 (m, 2H, $ArCH_2$), 4.13 (s, 2H, $COOCH_2$), 4.31 and 4.44 (2d, 4H, $J$ = 6 Hz, $CCH_2O$), 5.19 and 5.68 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.68 (dd, 1H, $-CH{=}$), 7.0−7.4 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 21.0 ($CH_3$), 30.6 ($\mathit{C}H_2COO$), 35.5 ($ArCH_2$), 39.0 ($CH_3\mathit{C}$), 68.6 ($C\mathit{C}H_2O$), 79.4 ($COO\mathit{C}H_2$), 113.2 ($CH_2{=}$), 126.2 (Ar, C3), 128.3 (Ar, C2), 135.7 (Ar, C4), 136.4 ($-CH{=}$), 139.9 (Ar, C1), 172.7 (C=O).

**1-(2-(4-Vinylphenyl)ethyl)-4-methyl-2,6,7-trioxabicyclo[2.2.2]octane (2).** The same procedure was followed as described above for **1** using (3-methyloxetan-3-yl)methyl 3-(4-vinylphenyl)propionate (11.90 g, 45.8 mmol) and $BF_3$ etherate (3.0 mL, 23.9 mmol) in $CH_2Cl_2$ (50 mL) at −20 °C for 18 h. Column chromatography ($SiO_2$; hexane/ethyl acetate = 9/1) and recrystallizations from a mixed solvent of hexane and benzene gave as a colorless solid **2** (4.13 g, 15.9 mmol, 35%, mp 114−115 °C): $^1H$ NMR ($CDCl_3$, 90 MHz) $\delta$ 0.80 (s, 3H, $CH_3$), 1.8−2.1 (m, 2H, $CH_2CO$), 2.6−2.9 (m, 2H, $ArCH_2$), 3.92 (s, 6H, $CH_2O$), 5.17 and 5.67 (2d, 2H, $J$ = 11 and 18 Hz, $CH_2{=}$), 6.68 (dd, 1H, $-CH{=}$), 7.0−7.4 (m, 4H, aromatic); $^{13}C$ NMR ($CDCl_3$, 23 MHz) $\delta$ 14.6 ($CH_3$), 29.4 ($\mathit{C}H_2CO$), 30.3 ($CH_2\mathit{C}CH_3$), 38.4 ($ArCH_2$), 72.7 ($CH_2O$), 108.8 ($CH_2\mathit{C}O$), 112.9 ($CH_2{=}$), 126.2 (Ar, C3), 128.6 (Ar, C2), 136.7 (Ar, C4), 136.8 ($-CH{=}$), 146.7 (Ar, C1); IR (KBr, $cm^{-1}$) 854, 893, 991, 1029, 1048, 1397, 1629 (C=C), 2873, 2884, 2955.

**Purification.** After recrystallizations, the solid monomers, **1**−**4**, were dried over $P_2O_5$ in vacuo for 48 h at room temperature and sealed off in an apparatus equipped with breakseals under high-vacuum conditions ($10^{-6}$ mmHg). More effective purifications for **1** and **4** were achieved by vacuum distillations on a vacuum line after drying over $CaH_2$ at room temperature for 24 h in dry THF. *tert*-Butyl (4-vinylphenyl)acetic acid was distilled from phenylmagnesium chloride (3 mol %, THF solution) on a vacuum line. The monomers thus purified were diluted with dry THF in a glass ampule equipped with a breakseal, and the resulting monomer solutions were stored at −30 °C until needed for the polymerization.

**Anionic Polymerization.** All polymerizations were carried out at −78 °C in an all-glass apparatus equipped with breakseals under high-vacuum conditions ($10^{-6}$ mmHg).[26] Polymerizations were terminated with degassed MeOH. The reaction mixture was poured into a large excess of MeOH to precipitate a polymer. The polymers were further purified by reprecipitations in THF/hexane and by freeze-drying from their benzene solutions. The polymer was then characterized by $^1$H and $^{13}$C NMR and IR spectroscopies. The following is the complete list.

**Poly(1)**: $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 0.75 (3H, $CH_3$), 1.0−2.1 (2H, $CH_2CH$), 2.7 (2H, $ArCH_2$), 3.9 (6H, $CH_2O$), 6.2−7.1 (4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 15 ($CH_3$), 31 ($\mathit{C}CH_3$), 39−43 ($CH_2CH$), 43 ($ArCH_2$), 73 ($C\mathit{C}H_2O$), 109 ($CH_2\mathit{C}O$), 126−132 (Ar, C3, C2, C1), 144 (Ar, C4); IR (KBr, cm$^{-1}$) 990, 1011, 1056, 1273, 1346, 1368, 1397, 1471, 2930, 2958.

**Poly(2)**: $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 0.70 (3H, $CH_3$), 1.0−2.2 (5H, $CH_2CO$ and $CH_2CH$), 2.9 (2H, $ArCH_2$), 3.8 (6H, $CH_2O$), 6.3−7.2 (4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 15 ($CH_3$), 29 ($\mathit{C}H_2CO$), 30 ($CH_2\mathit{C}CH_3$), 38 ($ArCH_2$), 39−44 ($CH_2CH$), 73 ($CH_2O$), 109 ($CH_2\mathit{C}O$), 127−129 (Ar, C3, C2), 139 (Ar, C1), 143 (Ar, C4); IR (KBr, cm$^{-1}$) 896, 935, 995, 1059, 1192, 1255, 1304, 1353, 1378, 1397, 1458, 1511, 2875, 2929.

**Poly(3)**: $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 0.8 (3H, $CH_3$), 0.5−2.4 (3H, $CH_2CH$), 4.0 (6H, $CH_2O$), 6.2−8.0 (4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 14 ($CH_3$), 31 ($\mathit{C}CH_3$), 39−44 ($CH_2CH$), 73 ($CH_2O$), 108 (ArCO), 123−131 (Ar, C2, C6, C5, C4), 138 (Ar, C1), 146 (Ar, C3); IR (KBr, cm$^{-1}$) 979, 1005, 1097, 1189, 1338, 1394, 2876, 2928, 2956.

**Deprotection of Polymers.** A mixture of poly(**1**) (0.60 g, 2.4 mmol, based on monomer unit), THF (6 mL), MeOH (2 mL), and 6 N HCl (0.2 mL) was stirred at room temperature for 1 h. Then, 10% NaOH aqueous solution (2 mL) and THF (2 mL) were added to the mixture and stirred overnight at room temperature. The reaction mixture was poured into 60 mL of water containing 1 mL of 6 N HCl to precipitate a polymer. The resulting polymer (0.38 g, 95%) was purified by reprecipitations into MeOH/water and by freeze-drying from a mixed solvent of 1,4-dioxane and MeOH. The deprotections of poly(**2**) and -(**3**) were similarly carried out to afford the corresponding carboxylic acid polymers quantitatively, whereas a mixed solvent of DMF and THF was used for the hydrolysis of poly(**3**).[24] The polymers thus obtained were characterized by $^1$H and $^{13}$C NMR spectroscopies.

**Poly[(4-vinylphenyl)acetic acid]** from poly(**1**): $^1$H NMR ($CD_3OD$, 90 MHz) $\delta$ 1.1−2.4 (3H, $CH_2CH$), 3.6 (2H, $ArCH_2$), 6.3−7.3 (4H, aromatic); $^{13}$C NMR ($CD_3OD$, 23 MHz) $\delta$ 42 ($ArCH_2$), 40−46 ($CH_2CH$), 128−131 (Ar, C3, C2), 134 (Ar, C1), 146 (Ar, C4), 176 (C═O); IR (KBr, cm$^{-1}$) 1152, 1255, 1426, 1513, 1711 (C═O), 2500−3700 (OH).

**Poly[3-(4-vinylphenyl)propionic acid]** from poly(**2**): $^1$H NMR ($CD_3OD$, 90 MHz) $\delta$ 1.0−2.2 (3H, $CH_2CH$), 2.4−3.1 (4H, $ArC\mathit{H}_2C\mathit{H}_2$), 6.2−7.1 (4H, aromatic); $^{13}$C NMR ($CD_3OD$, 23 MHz) $\delta$ 31 ($\mathit{C}H_2COOH$), 37 ($ArCH_2$), 41−47 ($CH_2CH$), 129 (Ar, C3, C2), 139 (Ar, C1), 146 (Ar, C4), 177 (C═O); IR (KBr, cm$^{-1}$) 1157, 1214, 1248, 1295, 1421, 1512, 1709 (C═O), 2500−3700 (OH).

**Poly(3-vinylbenzoic acid)** from Poly(**3**): $^1$H NMR ($CD_3OD$, 90 MHz) $\delta$ 0.8−2.2 (3H, $CH_2CH$), 6.4−7.9 (4H, aromatic); $^{13}$C NMR ($CD_3OD$, 23 MHz) $\delta$ 44−50 ($CH_2CH$), 133−139 (Ar, C2, C5, C4, C1, C6), 152 (Ar, C3), 175 (C═O); IR (KBr, cm$^{-1}$) 1197, 1268, 1410, 1453, 1696 (C═O), 2500−3600 (OH).

**Methylation of Deprotected Polymers with Diazomethane.** Poly[(4-vinylphenyl)acetic acid] (0.18 g, 1.1 mmol based on monomer unit) was suspended in benzene (15 mL) and 1.6 M of diazomethane (20 mL, 32 mmol; Caution: Explosive!) solution in ether[29] was added at room temperature. The polymer was slowly dissolved into the solution during the reaction. The resulting yellow solution was allowed to stand at room temperature in a well-ventilated hood overnight. The reaction was quenched with acetic acid and poured into a large excess of hexane to precipitate poly[methyl (4-vinylphenyl)acetate] (0.16 g, 82%). The resulting polymer was purified by reprecipitations in THF/methanol and freeze-drying from the benzene solution. The methylations of poly(3-vinylbenzoic acid) and poly[3-(4-vinylphenyl)propionic acid] were similarly carried out to afford their methyl esters.

**Poly[methyl (4-vinylphenyl)acetate]:** $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 0.9−2.2 (3H, $CH_2CH$), 3.5 (2H, $ArCH_2$), 3.6 (3H, $CH_3O$), 6.2−7.2 (4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 41 ($ArCH_2$), 40−45 ($CH_2CH$), 52 ($CH_3O$), 127−129 (Ar, C3, C2), 131 (Ar, C1), 145 (Ar, C4), 172 (C═O); IR (KBr, cm$^{-1}$) 1014, 1157, 1258, 1338, 1436, 1511, 1735 (C═O), 2846, 2926, 2949, 3023.

**Poly[methyl 3-(4-vinylphenyl)propionate]:** $^1$H NMR ($CD_3OD$, 90 MHz) $\delta$ 1.0−2.2 (3H, $CH_2CH$), 2.4−3.0 (4H, $ArC\mathit{H}_2C\mathit{H}_2$), 3.65 (3H, $CH_3O$), 6.1−7.0 (4H, aromatic); $^{13}$C NMR ($CD_3OD$, 23 MHz) $\delta$ 31 ($\mathit{C}H_2COOR$), 36 ($ArCH_2$), 40−42 ($CH_2CH$), 52 ($CH_3O$), 128 (Ar, C3, C2), 138 (Ar, C1), 144 (Ar, C4), 173 (C═O); IR (KBr, cm$^{-1}$) 1021, 1111, 1168, 1197, 1250, 1293, 1363, 1436, 1513, 1738 (C═O), 2848, 2926, 3013.

**Poly(methyl 3-vinylbenzoate):** $^1$H NMR ($CDCl_3$, 90 MHz) $\delta$ 0.8−2.2 (3H, $CH_2CH$), 3.8 (3H, $CH_3O$), 6.4−7.8 (4H, aromatic); $^{13}$C NMR ($CDCl_3$, 23 MHz) $\delta$ 40−44 ($CH_2CH$), 52 ($CH_3O$), 127−133 (Ar, C2, C5, C4, C1, C6), 145 (Ar, C3), 167 (C═O); IR (KBr, cm$^{-1}$) 1108, 1199, 1286, 1431, 1447, 1722 (C═O), 2928, 2949.

**Measurements.** Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. $^1$H NMR and $^{13}$C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz for $^1$H and 22.53 MHz for $^{13}$C) in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane ($\delta$ 0) for $^1$H NMR and to $CDCl_3$ ($\delta$ 77.1) for $^{13}$C NMR as standard. SEC data for MWD determination were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with three polystyrene gel columns (TOSOH G5000H$_{XL}$, G4000H$_{XL}$, and G3000H$_{XL}$) with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent with a flow rate of 1.0 mL min$^{-1}$. VPO measurements for $M_n$ determination were made with a Corona 117 instrument in benzene solution. The glass-transition temperatures of the polymers were measured by DSC using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 200 °C, cooled rapidly to −20 °C, and then scanned again at a rate of 20 °C min$^{-1}$.

**Acknowledgment.** This study was partially supported by Grant-in Aid No. 05750781 from the Ministry of Education, Science, Sports, and Culture, Japan. T.I. thanks the Watanabe Memorial Fund for their financial support.

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MA981492R