Protection and Polymerization of Functional Monomers. 27. Synthesis of Well-Defined Poly(4-vinyl-α-methylcinnamic Acid) by Means of Anionic Living Polymerization of 2-[1-Methyl-2-(4-ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline

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Received March 25, 1998; Revised Manuscript Received June 11, 1998

ABSTRACT: Anionic polymerizations of 2-[2-(4-ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (**1**), 2-[2-(4-isopropenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (**2**), and 2-[1-methyl-2-(4-ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (**3**) were carried out in tetrahydrofuran at −78 °C with (1,1,4,4-tetraphenylbutanediyl)dipotassium. Poly(**1**) was quantitatively obtained after 24 h but the molecular weight distribution (MWD) of the polymer was relatively broad (M_w/M_n = 1.3−1.4). The ^{1}H NMR analysis of the polymer suggested that side reactions toward the conjugated C═C−oxazoline linkage occurred during the polymerization. No apparent polymerization of **2** was observed under similar condition. On the other hand, the polymerization of **3** proceeded rather rapidly within 1 h and quantitatively gave poly(**3**) having a narrow MWD (M_w/M_n < 1.1) and the predicted molecular weight based on the molar ratio of monomer to initiator. The living character of the propagating carbanion of poly(**3**) was confirmed by the quantitative initiation efficiency in the postpolymerization. Novel tailored block copolymers, poly(**3**-*b*-isoprene-*b*-**3**), poly(**3**-*b*-styrene-*b*-**3**), and poly(*tert*-butyl methacrylate-*b*-**3**-*b*-*tert*-butyl methacrylate), were synthesized by sequential block copolymerizations of **3** and corresponding comonomers. It was elucidated from the results of block copolymerization that anionic polymerizability of **3** was higher than that of styrene and could be estimated to be the same level of 2-vinylpyridine. The oxazoline protecting moiety of poly(**3**) was completely hydrolyzed by treating with 3 N HCl in THF and subsequently with 15% NaOH (aq) in MeOH to give a well-defined poly(4-vinyl-α-methylcinnamic acid). The resulting poly(4-vinyl-α-methylcinnamic acid) could be quantitatively converted into its methyl ester by the reaction with diazomethane. The UV irradiation of poly(**3**) and poly(methyl 4-vinyl-α-methylcinnamate) at room temperature gave insoluble materials in moderate yields, indicating the photo-cross-linkable potential of these polymers.

Introduction

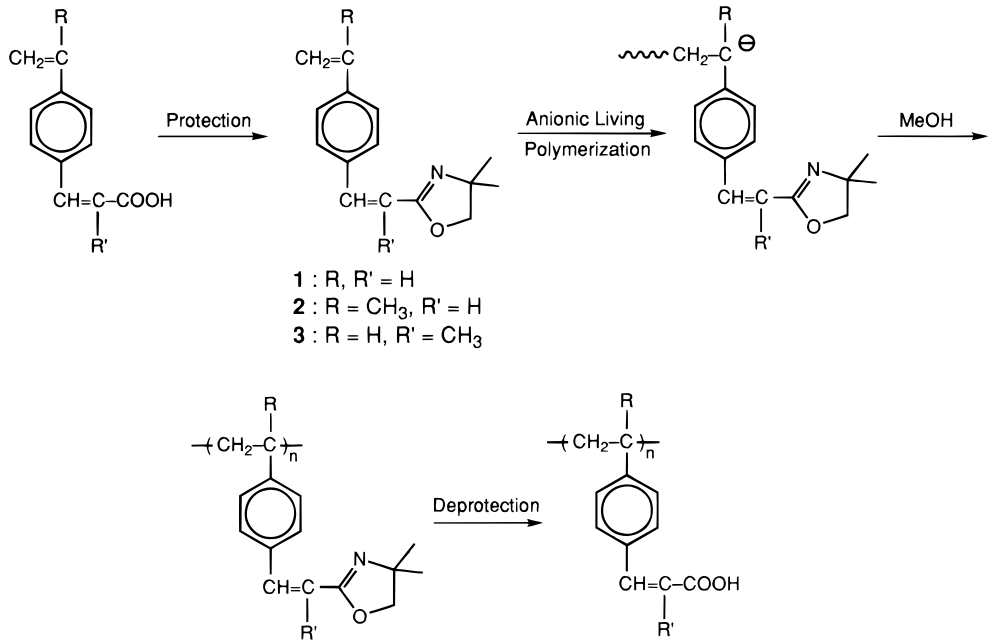
Photoreactive polymers have received great attention from the viewpoints of both academic interest and industrial application to be used as positive or negative photoresist.[1] The performance of these photoreactive polymers should strongly depend not only on inherent chemical structures and physical properties but also on primary structures of polymers such as molecular weight, molecular weight distribution (MWD), and tacticity. Photoreactive polymers are usually prepared by chemical modifications using commercially available and conventional polymers.[2−7] For instance, poly(vinyl cinnamate), a well-known negative acting photoresist, has been prepared by the polymer reaction of poly(vinyl alcohol) and cinnamoyl chloride.[2−6] Obviously, its primary structure was not regulated or well-controlled, although those features should be very important factors for the intermolecular photo-cross-linking. The controlled polymerization of monomers bearing a photosensitive moiety is a suitable route to obtain directly photoreactive polymers having well-defined architectures. However, the successful examples are extremely limited[8,9] because of the incompatibility of the photosensitive functional groups under polymerization conditions.

In the last 15 years, we developed a new strategy for the synthesis of a series of well-defined functional polymers via the anionic living polymerization of suitably protected functional monomers and the subsequent facile deprotection of the protecting groups from the resulting polymers.[10] The choice of protecting group is the most important key for the success of our methodology to synthesize the functional polymers. By using this methodology, polystyrenes containing OH,[11] NH_2,[12] SH,[13] CHO,[14] COOH,[15] $COCH_3$,[16] and C≡CH groups[17] and polymethacrylates bearing OH[18] and C≡CH functionalities[19] have been successfully synthesized. The resulting homopolymers and block copolymers possess the predicted molecular weights and the narrow MWDs in addition to the useful functional groups in each monomer unit.

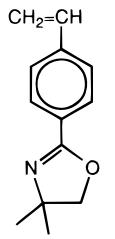
We herein focus on the anionic polymerization of monomers bearing photo-cross-linkable moieties as an extension of our continued effort. The controlled synthesis of poly(4-vinylcinnamic acid) derivatives by anionic living polymerization of protected monomers is our aim of this study. In the new protected monomers, **1**−**3**, the acid functions in the styrenes are purposefully masked with the oxazoline ring before their polymerizations as shown in Scheme 1. Meyers and co-workers demonstrated the utility of oxazoline moiety in organic synthesis as a versatile protecting group for various carboxylic acids and particularly its excellent stability under the basic conditions.[20] Furthermore, we have

S0024-9297(98)00478-1 CCC: $15.00
Published on Web 08/06/1998

Scheme 1



already succeeded in the anionic living polymerization of oxazoline-protected monomer, 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline, **4**, to give a polymer having a



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narrow MWD and a controlled M_n value.[15a,b] This substantiates that the coexistence of the polystyryl carbanion and the oxazoline moiety is possible under polymerization conditions.

In the anionic polymerizations of **1**−**3** used in this study, the inner C═C linkages conjugated with oxazoline ring are also seriously problematic in the presence of strong nucleophiles such as the anionic initiators and the propagating carbanions. In fact, nucleophilic conjugate additions[21] toward the activated C═C bonds are reported for the alkyl cinnamates and the related α,β-unsaturated enone compounds including oxazolines.[22] Thus, selective vinyl polymerization is much needed to afford linear polymers with precisely controlled chain structures, since **1**−**3** include another polymerizable function of the C═C linkage activated with the electron-withdrawing oxazoline moiety in the skeleton. After such selective polymerization and following deprotection, the cinnamoyl functions in the resulting polymers are expected to present the photosensitive features of the exposure to UV light irradiation.[7]

In this study, we report the results of anionic homopolymerization and sequential block copolymerization of **1**−**3** to elucidate the polymerization behavior and polymerizability of dual functional styrenes containing C═C-oxazoline moieties. The investigation of UV photosensitivity of the resulting polymers in their photochemical reactions is also discussed.

Results and Discussion

Anionic Polymerization of 1 and 2. Anionic polymerization of **1** was first carried out at −78 °C in THF with 1,1-diphenylethylene-capped carbanions associated with lithium or potassium countercations. The polymerization was terminated with methanol and the polymer was obtained by the precipitation on pouring the reaction mixture into a large excess of hexane. The polymerization results of **1** are shown in Table 1.

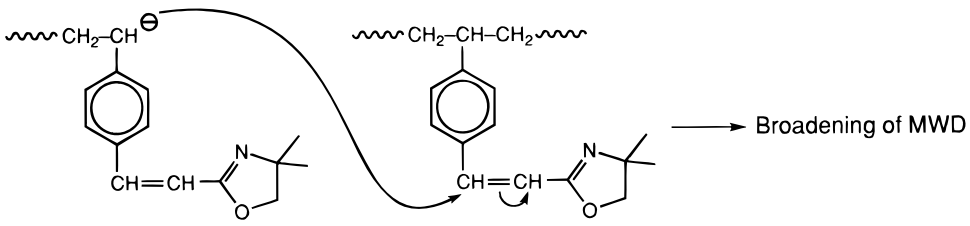
In the case of the organolithium initiator, no polymeric product was virtually obtained from the reaction mixture at −78 °C even after 24 h, although the polymerization system exhibited an intense reddish-violet color during the reaction. On the other hand, the corresponding organopotassium initiator unequivocally gave poly(**1**) under similar conditions. The yield of polymer was only 16% at −78 °C after 0.5 h, while the polymerization was certainly completed after 24 h, indicating that the rate of polymerization of **1** was very slow. Size exclusion chromatography (SEC) analysis of the polymer revealed that the MWD was initially unimodal and narrow but became broader with the polymerization time. The polydispersity index (M_w/M_n) was 1.10 after 0.5 h and around 1.4 after 24 h polymerization. Both the lowering of the polymerization temperature to −90 °C and the addition of potassium *tert*-butoxide to the system showed no effect on the MWDs of the resulting polymers. It was revealed from the ^{1}H NMR analysis of poly(**1**) that the vinyl polymerization on the styrene framework of **1** predominantly proceeded. However, small signal of unreacted vinyl group derived from **1** was still observed at 5.0−6.0 ppm in the spectrum. This suggests that the anionic polymerization of **1** involves two polymerization modes, which are the expected vinyl polymerization and the nucleophilic attack toward inner CH═CH bond activated with the electron-withdrawing C═N moiety on the oxazoline ring (Scheme 2),[22] although the latter mode is a very minor one. The intermolecular side reaction including nucleophilic addition might result in the broadening the MWDs of the polymers, particularly at the final stage of the polymerization as suggested above. Hence, the

Table 1. Anionic Polymerization of 1−3 at −78 °C in THF

run	monomer; amt, mmol	initiator; amt, mmol	amt of DPE,[a] mmol	time, h	yield, %	$10^{-3}M_n$ calcd[b]	$10^{-3}M_n$ obsd[c]	$10^{-3}M_w$ (LS)[d]	M_w/M_n[c]
1	**1**; 2.22	*n*-BuLi; 0.0985	0.131	24	0				
2	**1**; 3.05	cumyl−K;[e] 0.146	0.190	0.5	16	5.0	2.7		1.10
3	**1**; 2.12	cumyl−K; 0.0855	0.111	5	74	5.9	5.5		1.16
4	**1**; 2.71	cumyl−K; 0.0855	0.111	12	95	7.5	7.2		1.25
5	**1**; 2.48	cumyl−K; 0.0314	0.0471	12	84	18	14		1.30
6	**1**; 2.63	cumyl−K; 0.137	0.178	24	100	4.7	5.0		1.38
7	**1**; 1.67	K−naph;[f] 0.147	0.189	24	100	5.5	5.0		1.38
8	**1**; 4.03	Bz−K;[g] 0.0581	0.0755	24	100	16	10		1.32
9	**2**; 2.23	*n*-BuLi; 0.0849	0.142	24	0				
10	**2**; 2.19	cumyl−K; 0.147	0.191	24	0				
11	**2**; 2.33	K−naph; 0.113	0.253[h]	24	0				
12	**3**; 1.90	Li−naph;[i] 0.118	0.203	1	8.6	1.0	6.1		1.09
13	**3**; 3.38	*n*-BuLi; 0.0870	0.170	24	62	9.7	13[j]		1.55
14	**3**; 2.40	*n*-BuLi; 0.0468	0.114	72	86	11	13[j]		1.86
15[k]	**3**; 1.92	*sec*-BuLi; 0.0493	0.147	24	85	9.7	12[j]		1.24
16[k]	**3**; 2.37	*sec*-BuLi; 0.0550	0.147	72	100	11	15[j]		1.27
17	**3**; 2.19	Na−naph;[l] 0.107	0.164	1	100	10	9.4[j]		1.06
18	**3**; 2.35	K−naph; 0.0843		1	100	13	13[j]		1.05
19	**3**; 2.23	K−naph; 0.108	0.313[h]	1	100	11	12[j]		1.03
20	**3**; 2.11	K−naph; 0.0787	0.129	1	100	13	12[j]		1.04
21	**3**; 3.23	K−naph; 0.0831	0.137	1	100	19	18[j]		1.04
22	**3**; 3.58	K−naph; 0.0537	0.140	2	100	33	35[j]	39	1.05
23	**3**; 4.04	cumyl−K; 0.0276	0.105	21	100	36	64[j]	69	1.03
24	**3**; 2.92	cumyl−K; 0.0724	0.144	24	100	10	10[j]		1.05
25[m]	**3**; 2.34	K−naph; 0.0923	0.148	1	100	13	14[j]		1.08
26[n]	**3**; 1.78	K−naph; 0.0757	0.187	1	100	12	11[j]		1.16

[a] 1,1-Diphenylethylene. [b] M_n(calcd) = [monomer] × (MW of monomer) × conversion × *f*/[initiator] + MW of initiator; *f* = 1 or 2, corresponding to the functionality of the initiators. [c] M_n(obsd) and M_w/M_n were obtained by SEC calibration using standard polystyrenes in THF solution. [d] These weight-average molecular weights (M_w(LS)) were obtained by light scattering in benzene at 25 °C. [e] Cumylpotassium. [f] Potassium naphthalenide. [g] Benzylpotassium. [h] α-Methylstyrene was used as a capping reagent instead of DPE. [i] Lithium naphthalenide. [j] M_n(obsd) was obtained by VPO in benezene. [k] 3−5-fold-molar excess of LiCl was added to the reaction system. [l] Sodium naphthalenide. [m] At 0 °C. [n] At 26 °C.

Scheme 2



molecular structure of **1** seems to be unsuitable to produce a polymer having a uniform repeating unit under the anionic mechanism.

To prevent an undesirable nucleophilic attack toward the CH═CH−oxazoline moiety of **1**, we modified the molecular structure of **1** by introducing a methyl group on the α-carbon of the vinyl group. Namely, the α-methylstyrene derivative **2** is synthesized and polymerized. The expectation was that the steric hindrance of methyl group helps to prevent the propagating carbanion of poly(**2**) from the side reaction with the inner CH═CH bond. However, the starting monomer **2** was nearly quantitatively recovered from the reaction mixture at −78 °C even after a 24 h reaction regardless of the countercation of the anionic initiator. No apparent polymerization of **2**, the α-methylstyrene counterpart of **1**, took place as shown in Table 1. Although the reason is not clear yet, we consider that the above-mentioned side reaction toward CH═CH−oxazoline moiety also occurs at the initial stage of polymerization of **2**. Probably, the electron-donating character of the methyl group enhances the electron density of the terminal carbanion and results in serious side reactions.

Anionic Polymerization of 3. Therefore, we newly designed another protected monomer, a 4-vinyl-α-methylcinnamic acid derivative, **3**, by introducing a methyl group on the α-carbon of the CH═CH−oxazoline moiety of **1**. In the case of **3**, the bulky and electron-donating methyl group is expected to suppress the nucleophilic addition to the vinylene linkage because of the steric hindrance and the enriched electron density of the C═C-oxazoline moiety. We then attempted to polymerize the alternative monomer **3** under similar conditions to **1** with various initiators including (1,1,4,4-tetraphenylbutanediyl)dilithium, -disodium, and -dipotassium, (1,1-diphenylhexyl)lithium, *n*-butyllithium, and potassium naphthalenide. All the reaction mixtures turned to reddish violet during the addition of THF solution of **3** to the initiators. No change of color was observed even after 72 h at −78 °C, but the violet color instantaneously disappeared when a few drops of methanol were added to quench the polymerization. This indicates the existence of the propagating carbanion during the polymerization. The polymers, which were white powders, were isolated by pouring the polymerization mixture into a large excess of hexane. The resulting polymer was purified by reprecipitations and finally freeze-dried from the benzene solution. In the ^{1}H NMR spectrum of the polymer, the signals of monomer vinyl group at 5.21−5.87 ppm completely disappeared. The signal intensity

was in accordance with the expected integral ratio of poly(**3**) obtained via exclusive vinyl polymerization. No residual vinyl group of the styrene framework was observed in poly(**3**) in contrast to the result for poly(**1**). This was also supported by the ^{13}C NMR spectrum of the polymer.[23]

The polymerization results of **3** are shown in Table 1. With organopotassium initiators, the polymerizations of **3** proceeded rapidly at −78 °C within 1 h always to quantitative yields. The SEC curves of the resulting polymers exhibited unimodal and sharp peaks, indicating the narrow distributions of the molecular weights. The M_w/M_n values were always around 1.1. Even when the reaction system was allowed to stand for 24 h at −78 °C, the polymer maintained its unimodal and narrow MWD after the completion of the polymerization. Moreover, the number-average molecular weights measured by vapor pressure osmometry (VPO) fairly agreed with the calculated values based on the molar ratios of monomer to initiators. The M_n values were well regulated in the range of 10 000 and 33 000. The M_w values of poly(**3**) samples obtained by the light scattering (LS) measurement also supported the fine molecular weight control.[24] The controlled polymerization of **3** can be achieved by the initiators varying from radical anion (run 18) to carbanion capped with α-methylstyrene or 1,1-diphenylethylene, including monofunctional and difunctional initiators. The high anionic polymerizability of **3** is suggested from the results of homopolymerization, where quantitative and rapid initiation of **3** occurred with low nucleophilic diphenylethylene-capped carbanions to produce the well-defined polymers. Even at 0 °C, a poly(**3**) having narrow MWD and predicted M_n value was still obtained with (1,1,4,4-tetraphenylbutanediyl)dipotassium. However, a broadening of the SEC curve took place when the polymerization of **3** was performed at 26 °C.

The organosodium initiator also gives satisfactory polymerization results in terms of molecular weight control (run 17). On the other hand, the rate of polymerization was considerably slow in the cases of lithium initiators. MWDs of the resulting polymers became broader with polymerization time. The SEC chromatogram was initially unimodal and narrow, but it became multimodal and showed an apparent high molecular shoulder after a longer reaction. When the polymerization was performed with organolithium initiators, the intermolecular side reactions between the resulting polymers derived from **3** were significant particularly at the late stage of the polymerization, as was observed in the polymerization of **1**. When lithium chloride was added to the reaction system as an additive,[25] the polymerization proceeded rather rapidly (run 15) up to quantitative conversion (run 16). Furthermore, the SEC curve of the resulting polymer was always unimodal and relatively narrow even after 72 h (M_w/M_n = 1.27). Thus, the added lithium chloride avoids the side reaction to a certain extent.

The postpolymerization was attempted in order to prove the living nature of the propagating carbanion derived from **3** at −78 °C in THF. By initiation with (1,1,4,4-tetraphenylbutanediyl)potassium, **3** underwent the first-stage polymerization quantitatively within 1 h. The second feed of **3** was added to the polymerization system and allowed to polymerize for a further 1 h to complete the second-stage polymerization. Quantitative yields of the polymers were obtained in both stages of

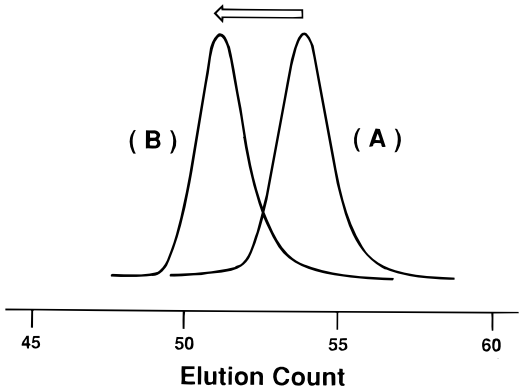


Figure 1. SEC curves of prepoly(**3**) (peak A, M_w/M_n = 1.04) and postpoly(**3**) (peak B, M_w/M_n = 1.04) produced at −78 °C in THF (second feed of monomer was added 1 h after the first-stage polymerization).

polymerization. The M_n values of the pre- and postpolymers, 9300 and 16 000, were in good accordance with the predicted ones from the molar ratio of **3** and initiator, 8500 and 18 000, respectively. Furthermore, the SEC trace of the postpolymer (M_w/M_n = 1.04) shifted completely toward the higher molecular weight side from that of the prepolymer (M_w/M_n = 1.04), keeping the narrow MWD (Figure 1). These results clearly demonstrate that the terminal carbanion of poly(**3**) is satisfactorily stable at −78 °C for 1 h to propagate in the second-stage polymerization with a quantitative initiation efficiency. It is substantiated that the introduction of the methyl group on the α-carbon of CH═CH−oxazoline moiety in **1** dramatically changes the polymerization behavior and successfully induces the anionic living polymerization of novel styrene monomer **3**.

Block Copolymerization of 3 with Isoprene (Isp), Styrene (St), 2-Vinylpyridine (2VP), and *tert*-Butyl Methacrylate (tBMA). The above success of the anionic living polymerization of novel monomer **3** prompts us to synthesize block copolymers containing functional poly(**3**) segments by sequential addition of monomers. We hence carried out the sequential copolymerization of **3** by using Isp, St, 2VP, and tBMA as comonomers to prepare new block copolymers. In addition to the synthetic viewpoint, the results obtained here will also demonstrate the relative reactivities of the new monomer **3** and the active chain end of the living polymer as we have previously reported.[26]

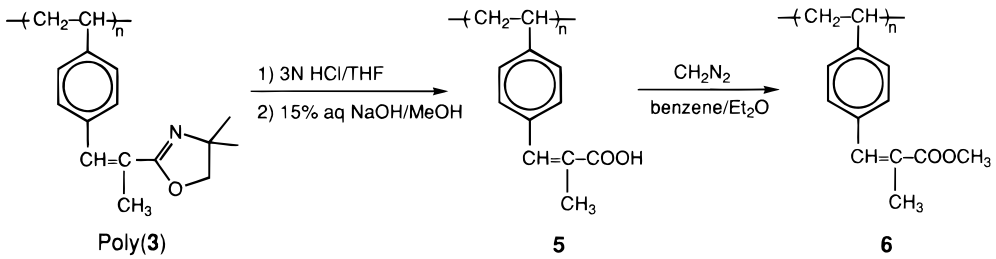
At first, the sequential polymerizations of **3** were carried out with the difunctional anionic living polymers of Isp, St, and 2VP. The polymerizations of Isp, St, and 2VP were initiated with potassium naphthalenide in THF at −78 °C to form their difunctional living polymers and then **3** was added sequentially to the reaction mixture. The color of the reaction mixture immediately changed to characteristic violet, and the copolymers were obtained quantitatively. The SEC curves of the resulting copolymers were relatively narrow (M_w/M_n < 1.2) and shifted from elution volumes of the homopolymers of Isp, St, and 2VP to higher molecular weight regions (Table 2). In each polymer, the composition of both polymer segments agreed well with the feed ratio of the comonomers. The molecular weights estimated from the ^1H NMR spectra agreed well with the predicted values as expected. Thus, well-defined triblock copolymers, poly(**3**-*b*-Isp-*b*-**3**), poly(**3**-*b*-St-*b*-**3**), and poly(**3**-*b*-2VP-*b*-**3**), were successfully synthesized.

Table 2. Block Copolymerization of 3 with Isoprene, Styrene, 2-Vinylpyridine, and *tert*-Butyl Methacrylate at −78 °C in THF[a]

				block copolymer (homopolymer[b])		
				$10^{-3}M_n$		
run	block sequence	A monomer	B monomer	calcd[c]	obsd[d]	M_w/M_n[e]
27	A−B−A	**3**	Isp	27 (13)	27 (13)	1.06 (1.10)
28	A−B−A	**3**	St	23 (11)	21 (9.9)	1.05 (1.12)
29	A−B−A	**3**	2VP	42 (27)	39 (27)	1.20 (1.22)
30	A−B−A	**3**	tBMA	30 (19)	23[f] (15)	1.20[f] (1.07)
31	B−A−B	**3**	Isp	34 (13)	12[g] (12)	1.07[g] (1.05)
32	B−A−B	**3**	St	28 (12)	28[h] (12)	2.17[h] (1.03)
33	B−A−B	**3**	2VP	40 (15)	41[f] (13)	1.43[f] (1.05)
34	B−A−B	**3**	tBMA	28 (11)	25 (10)	1.06 (1.04)

[a] Difunctional initiators were used in all sequential block copolymerizations. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer) × 2/[initiator] + MW of initiator. [d] The M_ns of the block copolymers were determined by using the molecular weights of the homopolymers and the molar ratios of monomer units in the block copolymer analyzed by ^{1}H NMR. [e] M_w/M_n was obtained by SEC calibration using standard polystyrenes in THF solution. [f] Bimodal MWDs. [g] No second-stage polymerization proceeded. Homopoly(**3**) was quantitatively recovered. [h] Only partial initiation at the second-stage polymerization occurred. A mixture of homopoly(**3**) and block copolymer with extremely high M_n value was obtained.

Scheme 3



The polymerization of **3** could be also initiated with the living poly(tBMA) prepared with oligo(α-methylstyryl)dipotassium in THF at −78 °C. Quantitative conversion of **3** was achieved within 1 h at −78 °C. However, the SEC curve of the polymeric product presented a bimodal peak consisted of the homopolymer of tBMA and the block copolymers having a M_n value higher than the calculated one. This is probably due to the partial initiation and the subsequent rapid consumption of **3**. The initiator efficiency was estimated to be 30% from the SEC analyses of the product. Higher anionic polymerizability (electrophilicity) of **3** than that for St is demonstrated from this fact since no initiation of St occurs with the living poly(tBMA).[26]

Next, the living poly(**3**) was employed as macroinitiator for the sequential copolymerization of Isp, St, 2VP, and tBMA. In this reversed sequence, only tBMA accepted a quantitative initiation with difunctional living poly(**3**) to afford a tailored block copolymer having a narrow MWD and a predicted M_n value as shown in Table 2. Although 2VP was nearly quantitatively initiated with living polymer of **3**, the MWD of the resulting block copolymer was bimodal. This observation suggests the partial intermolecular side reaction of the propagating carbanion of newly formed poly(2VP) and the C═C-oxazoline pendant group of the poly(**3**) segment. This is somewhat curious because it is known that the living poly(2VP) anion is not very nucleophilic. St also could be initiated with living poly(**3**), but the SEC curve of the polymeric product involved a large content of homopoly(**3**) and the block copolymer had a larger M_n value than the predicted one. The initiation efficiency of St with living poly(**3**) was far from quantitative (∼3%) and only 21% of St was consumed at −78 °C for 1 h. As expected, no polymerization of Isp proceeded by the reaction with living poly(**3**), and the homopolymer of **3** was virtually recovered from the reaction mixture. Thus, Isp, St, and 2VP are not suitable second monomers for the sequential block copolymerization using living poly(**3**) as a macroinitiator. Lower nucleophilicity of the propagating carbanion of poly(**3**) compared with that of St is apparent from the results of the crossover initiations, considering the fact that the anionic living polystyrene induces the quantitative initiation of polymerizations of Isp and 2VP.[26]

Thus, a series of well-defined triblock copolymers including poly(**3**) segments can be synthesized by the sequential block copolymerization of **3** and comonomers, although this method involves a strict limit concerning the additional order of the comonomers as shown above. It is also confirmed from the results of block copolymerization that the anionic polymerizability of **3** is apparently higher than that of St and nearly comparable to that of 2VP. The polymerizability of **3** is estimated to have the same level as **4** as shown in the previous reports.[15b,26] On the other hand, the nucleophilicity of the propagating carbanion derived from **3** is remarkably reduced and comparable to those of living polymers of 2VP and **4**.

We previously found a good correlation between the anionic polymerizability of 4-substituted styrenes and their ^{13}C NMR chemical shifts of vinyl β-carbons.[26,27] Reflecting the difference in the electron density of the vinyl group, the monomers presenting the downfield chemical shifts show higher anionic polymerizability than the monomers of upfield shifts and vice versa. The observed anionic polymerizability of **3** is indeed grouped into the same level of **4**, and this is also predicted from the β-carbon chemical shifts of **3** (114.3 ppm) and **4** (115.3 ppm) which were observed considerably downfield compared with St (113.8 ppm). This can be reasonably explained by both electronic and resonance effects of **3** as follows. The electron-withdrawing oxazoline moiety[28] of **3** reduces the electron density of the

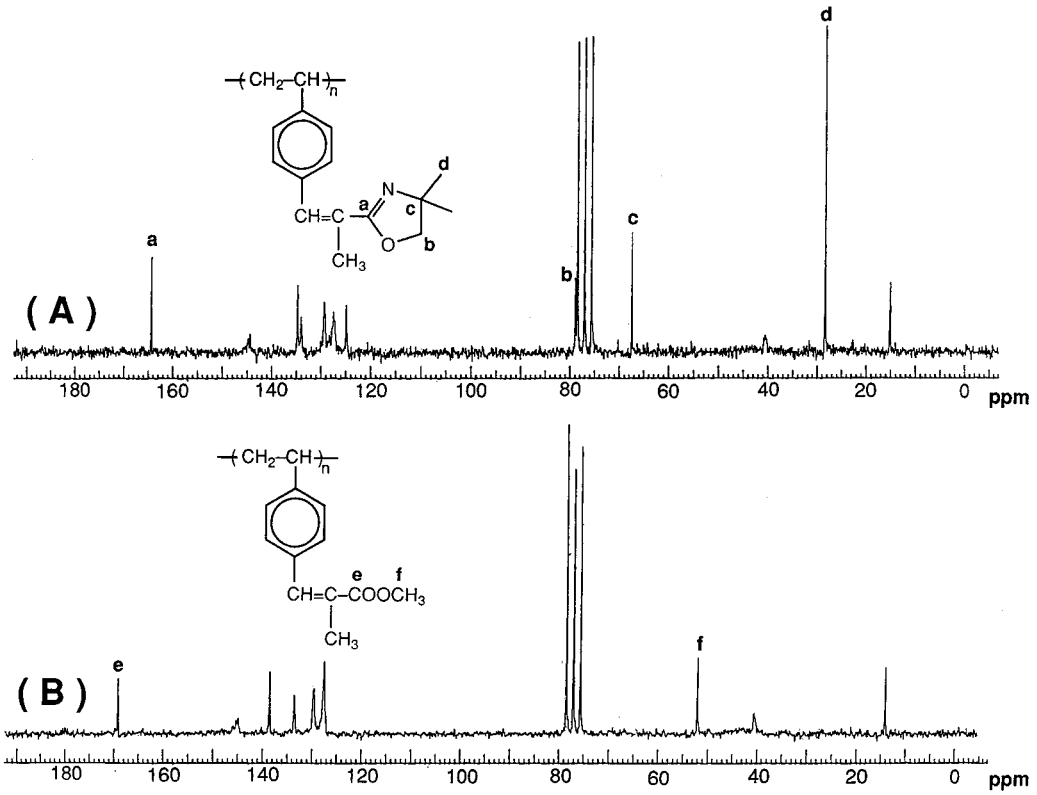


Figure 2. ^{13}C NMR spectra of poly(**3**) (A) and poly(methyl 4-vinyl-α-methylcinnamate) after deprotection and methylation (B) in $CDCl_3$.

vinyl group in the styrene skeleton through the π-electron conjugation system and enhances the anionic polymerizability as well as the case of **4**. Furthermore, the extended π-conjugation system including the *para*-substituted C═C−C═N linkage,[29] which is apparently longer than that of St, also induces the high polymerizability of **3** in addition to the electron-withdrawing nature of the substituent.

Deprotection of Poly(3). We have already succeeded in the complete removal of oxazoline protecting group from poly(**4**),[15a,b] although it required a relatively severe condition compared to the deprotection procedure reported for low molecular weight compounds.[20] Similar to the case of the deprotection of poly(**4**),[15a,b] the oxazoline moiety of poly(**3**) was deprotected by treating poly(**3**) with 3N HCl-aqueous THF at reflux for 10 h and subsequently with 15% NaOH in H_2O/MeOH at reflux for 18 h (Scheme 3). Both reactions proceeded homogeneously. In the ^1H NMR spectrum of the resulting polymer, the signals of CH_2 and CH_3 protons on the oxazoline ring at 4.0 and 1.3 ppm completely disappeared. The IR absorptions due to the C═N linkage on the oxazoline ring at 1607 cm^{-1} disappeared and new absorptions corresponding to the C═O and OH groups of carboxylic acid at 1685 and 2500−3500 cm^{-1} strongly appeared. These gave a clear evidence that the quantitative removal of oxazoline moiety is attained to give a poly(4-vinyl-α-methylcinnamic acid), **5**, by the two-step deprotection reaction. Unfortunately, no SEC chromatogram of the deprotected polymer was obtained in THF solution, possibly due to the adsorption of the COOH group of **5** on the polystyrene gel columns.

Then, the polar acid function of the deprotected **5** was converted into its methyl ester, poly(methyl 4-vinyl-α-methylcinnamate), **6**, by treating with diazomethane in benzene/diethyl ether as shown in Scheme 3. The

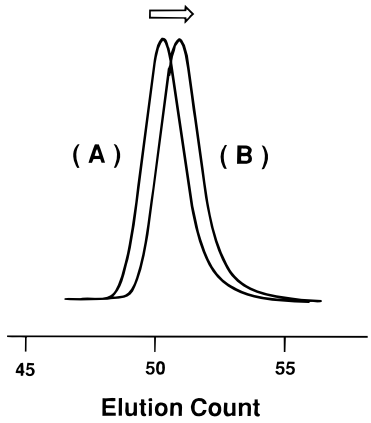


Figure 3. SEC curves of poly(**3**) (peak A, $M_w/M_n = 1.04$) and poly(methyl 4-vinyl-α-methylcinnamate) after deprotection and methylation (peak B, $M_w/M_n = 1.04$).

quantitative methylation was also confirmed by ^1H and ^{13}C NMR and IR spectroscopies. The typical ^{13}C NMR spectrum of **6** is shown in Figure 2. The SEC curve of the esterified polymer **6** maintains a unimodal and very narrow MWD ($M_w/M_n = 1.04$) as can be seen in Figure 3. It reasonably shifts from that of poly(**3**) ($M_w/M_n = 1.04$, $M_n = 15\,000$) toward the lower molecular weight region ($M_n = 13\,000$) due to the structural change of the repeating units. This strongly indicates the absence of cross-linking and degradation of polymer main chains during the three-step polymer reactions including acid hydrolysis, saponification, and methylation. Thus, we successfully opened a new synthetic path to the well-defined poly(4-vinyl-α-methylcinnamic acid) having narrow MWD and well-controlled M_n by means of anionic living polymerization of **3** and complete removal of the oxazoline protecting group.

Table 3. Weight Fraction of Insoluble Part of the UV-Irradiated Polymers

polymer	irradiation time, min	weight fraction,[a] %
poly(**3**)	0	0
poly(**3**)	5	2.9
poly(**3**)	90	20
6	0	0
6	5	9.3
6	90	61

[a] Insoluble part in THF.

Photoreaction of the Polymers. The [2 + 2] photocycloaddition is a powerful carbon−carbon bond forming reaction in organic chemistry and has attracted remarkable attention from both a synthetic viewpoint and its mechanism.[30] Poly(vinyl cinnamate) readily underwent this photocyclization to form a four-membered ring to be used as a well-known negative-type photoresist.[1−6] Since **6** and poly(**3**) included either the cinnamate moiety or conjugated carbon−carbon double bonds activated by the electron-withdrawing C═N group, they are also expected to act as photo-cross-linkable polymers.

To check the photoreactivity of **6** and poly(**3**), the UV irradiation was carried out onto their polymer films at room temperature under air. On exposure to UV light, the transparent polymer films slowly turned pale yellow. The irradiated polymer film was immersed in THF and washed out to examine how much of the content of insolubilized materials formed by cross-linking was caused by the [2 + 2] cyclization. Table 3 shows the weight fraction of insoluble polymeric material after the irradiation. Obviously, the weight fraction of the insoluble part increased with the irradiation time in both polymers. It was found that **6** underwent photo-cross-linking much faster than poly(**3**). After a 90 min dose, 61% of **6** became insoluble, while the insoluble fraction of poly(**3**) was around 20%. No apparent insolubilization of polystyrene occurred under the same irradiation conditions.

The THF soluble parts of both polymers were characterized by SEC, ^{1}H NMR, and IR spectroscopy. The poly(**3**) and **6** possess unimodal and very narrow MWDs and are suitable candidates to check the MWD change during the UV irradiation. The SEC curves of the irradiated polymers present multimodal broad MWDs and have high molecular side peaks along with the main sharp chromatograms, as can be seen in Figure 4. These SEC changes clearly proved the presence of intermolecular photo-cross-linking of the polymers along with the intramolecular reactions. In the ^{1}H NMR spectra of soluble parts of irradiated poly(**3**) and **6**, the new signals were observed at 3.4 and 4.7 ppm along with the previous signals, which can be assigned to methine protons on a cyclobutane ring formed by the [2 + 2] photocyclization. Similar spectroscopic information was obtained by the IR spectra of the irradiated polymer films. In the case of **6**, the absorption of C═C bond at 1630 cm^{-1} decreased with the irradiation time and almost diminished after 90 min. On the other hand, the C═O absorption at 1710 cm^{-1} became broad and shifted toward 1730 cm^{-1}, indicating the disappearance of the conjugation system of C═C−C═O. Thus, these spectroscopic changes of the irradiated polymer samples further support the point that the expected [2 + 2] photocyclizations proceeded intermolecularly to give insoluble polymeric materials (Scheme 4), suggesting their potentials for the negative photoresists. Furthermore, the novel block copolymers containing photo-cross-linkable poly(**3**) and **6** segments newly synthesized here are also of great interest. They are the new heterophasic materials which will form the selectively cross-linked polymer micelles in solution or polymer films in bulk, where the micelles[31] or the microphase separated structure[32] are effectively fixed as recently demonstrated by Liu and co-workers.

Solubility and Glass Transition Temperatures of the Polymers. Polymers obtained in this study were white powders and could be cast into colorless films from their solutions. Table 4 summarizes the solubility of polymers obtained in this study. Poly(**1**) and poly(**3**) were soluble in a wide range of organic solvents including nonpolar and polar ones. In particular, their good solubility in methanol and ethanol indicated the high polarity of the introduced oxazoline moiety as observed in the case of poly(**4**).[15a] Small differences in solubility of poly(**1**) and poly(**3**) suggested the effect of the introduced α-methyl substituent on the side chain. After hydrolysis of the oxazoline protecting group, the solubility of the polymer dramatically changed. The resultant **5** was readily soluble in 1,4-dioxane, THF, DMF, DMSO, ethanol, and methanol but was insoluble in nonpolar solvent, indicating its high polarity. With the exception of DMSO, the methyl ester **6** showed a solubility similar to that of polystyrene.

The glass transition temperatures (T_gs) of the polymers are shown in Table 5. The poly(**3**) samples are suitable to discuss M_n effects on the T_g values, since they have very narrow MWDs and well-defined chain structures. Poly(**1**) and poly(**3**) presented higher T_g values at 165 and 157 °C, respectively, compared with that of polystyrene (T_g = 100 °C). The T_g values of poly(**3**) actually increased with M_ns as expected. The free-radically prepared poly(**3**) having broad MWD showed a T_g at 154 °C, which was close to that of anionically obtained poly(**3**) (T_g = 157 °C) having a comparable molecular weight. Poly(methyl 4-vinyl-α-methylcinnamic acid) bearing a CH═C(CH$_3$)COOCH$_3$ moiety had a T_g at 104 °C, which is comparable with that of polystyrene. Two T_g values at 18 and 95 °C were observed for the triblock block copolymer, poly(**3**-*b*-Isp-*b*-**3**), indicating the microphase separation of this block copolymer in bulk.

In conclusion, we have successfully demonstrated the anionic living polymerization of **3**, where the COOH functionality of 4-vinyl-α-methylcinnamic acid is masked with a oxazoline protecting group. Precise controls of molecular weight and its distribution are indeed attained. The living nature of the polymerization enables us to perform the tailored syntheses of novel block copolymers containing poly(**3**) segments by sequential copolymerization of **3** and other comonomers. Quantitative acid hydrolysis and the following saponification of poly(**3**) afford a poly(4-vinyl-α-methylcinnamic acid) having well-defined chain structures. UV irradiation on poly(**3**) and poly(methyl 4-vinyl-α-methylcinnamate) effectively induces their cross-linking to afford the insoluble materials.

Experimental Section

Materials. 4-Chlorostyrene, 4-chloro-α-methylstyrene, and 1,1-diphenylethylene (DPE) were kindly supplied by Hokko Chemical Industry Co., Ltd. DMF was dried and distilled over CaH_2 in vacuo. Commercially available magnesium, acetic

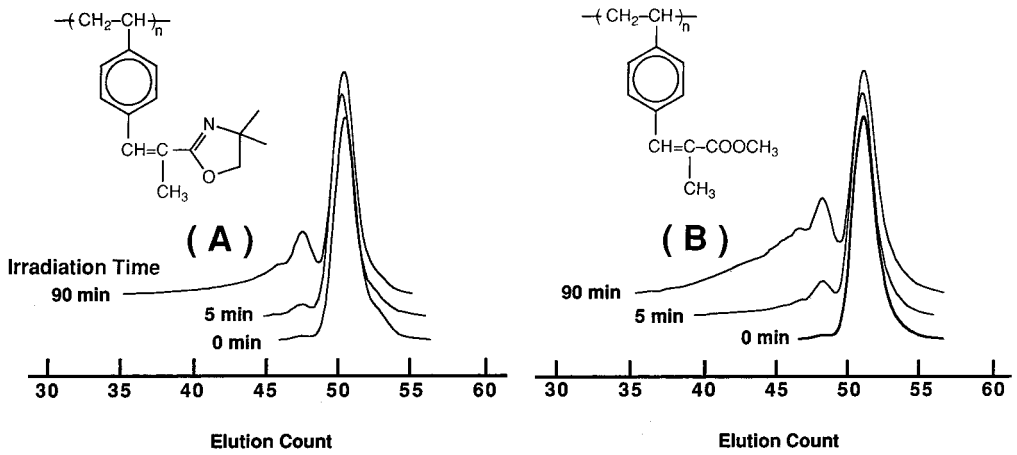


Figure 4. SEC curves of soluble portions of the irradiated poly(**3**)s (series A) and the irradiated poly(methyl 4-vinyl-α-methylcinnamate)s (series B).

Scheme 4

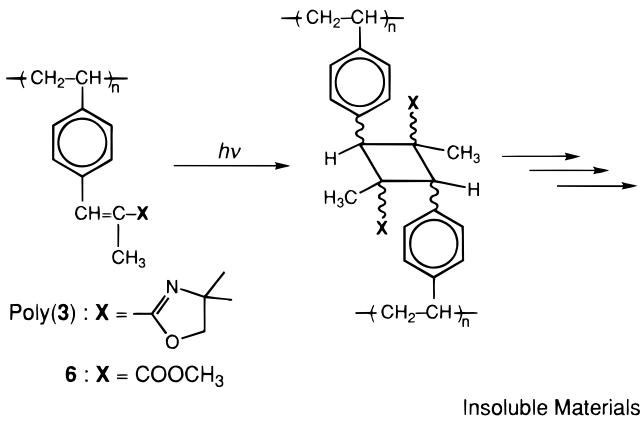


Table 4. Solubilities of the Resulting Polymers[a]

	polymer					
solvent	poly(**1**)	poly(**3**)	**5**	**6**	poly(**4**)[b]	polystyrene
hexane	I	I	I	I	I	I
benzene	S	S	I	S	S	S
carbon tetrachloride	S	S	I	S	S	S
diethyl ether	I	S	I	S	S	S
ethyl acetate	S	S	I	S	S	S
chloroform	S	S	I	S	S	S
acetone	S	S	I	S	S	S
methyl ethyl ketone	S	S	I	S	S	S
1,4-dioxane	S	S	S	S	S	S
THF	S	S	S	S	S	S
N,*N*-dimethylformamide	S	S	S	S	S	S
dimethyl sulfoxide	Sw	S	S	S	Sw	I
ethanol	S	S	S	I	S	I
methanol	S	S	S	I	S	I
water	I	I	I	I	I	I

[a] Key: I, insoluble; S, soluble; Sw, swelling. [b] Poly[2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline].

acid, propionic acid, and 2-amino-2-methylpropanol were used without purification. 4-Formylstyrene was synthesized by the Grignard reaction of 4-chlorostyrene and DMF according to our previous report.[14c] α-Methylstyrene and styrene were washed with 5% NaOH solution and with water and then dried over anhydrous $MgSO_4$. The styrenes and DPE were distilled over CaH_2 under vacuum. *tert*-Butyl methacrylate and isoprene were dried over CaH_2 and distilled on the vacuum line. 2-Vinylpyridine was first dried with potassium hydroxide and then distilled over CaH_2 under vacuum. THF was refluxed over sodium wire for 5 h and distilled from $LiAlH_4$ and finally under vacuum from sodium naphthalenide solution.

Table 5. Glass Transition Temperatures (T_g) of Polymers[a]

polymer	$10^{-3}M_n$(obsd)	M_w/M_n	T_g, °C
poly(**1**)	14	1.30	165
poly(**3**)	10	1.05	143
poly(**3**)	18	1.04	149
poly(**3**)	35	1.05	147
poly(**3**)	64	1.03	157
poly(**3**)[b]	62	1.88	154
6[c]	14	1.05	104

[a] T_g was measured in the second heating scan at a rate of 20 °C/min. [b] Obtained by the free-radical polymerization. [c] Obtained by the hydrolysis and the following methylation of poly(**3**).

Initiators. *sec*-BuLi as a 1.05 M solution in cyclohexane (Kanto Chemical Co., Ltd.) was diluted with heptane and used as an initiator. Metal naphthalenides were prepared by the reactions of a small excess of naphthalene with the corresponding alkali metal in THF. Oligo(α-methylstyryl)dilithium, -disodium, and -dipotassium were freshly prepared prior to polymerizations 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. (1,1,4,4-Tetraphenylbutanediyl)dilithium, -disodium, and -dipotassium were prepared from the corresponding metal naphthalenides and a 1.5−2 M quantity of DPE at −78 °C for 10 min. Similarly, DPE was reacted in THF at −78 °C with *n*-BuLi, *sec*-BuLi, cumylpotassium, and benzylpotassium to produce the monoadducts having lowered nucleophilicities. These initiators were stored in ampules equipped with breakseals. The concentration of initiator was determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum as previously reported.[33] α,α′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol.

2,4,4-Trimethyl-2-oxazoline.[20] A mixture of glacial acetic acid (30.43 g, 508 mmol) and 2-amino-2-methylpropanol (44.50 g, 500 mmol) was heated under stirring at 180 °C for 17 h. The yielded oxazoline and water were azeotropically distilled at 97−105 °C, and hexane (100 mL) was added to the distillate. The organic layer was separated, and the water phase was further extracted with hexane (50 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ for 2 h, and concentration gave a colorless liquid of 2,4,4-trimethyl-2-oxazoline (45.0 g, 398 mmol, 80%). The resulting compound was directly used for the following reaction without further purification: ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.19 (s, 6H, $(CH_3)_2C-N$), 1.88 (s, 3H, CH_3CO), 3.84 (s, 2H, CH_2).

2-[2-(4-Ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (1) was prepared according to the procedure reported by Wehrmeister et al.[34] A mixture of 4-formylstyrene (15.13 g, 115 mmol), 2,4,4-trimethyl-2-oxazoline (24.93 g, 221 mmol), 4-toluenesulfonic acid (1.06 g, 5.58 mmol), *p*-*tert*-butylpyrocatechol (10 mg), and toluene (70 mL) was refluxed under

stirring for 35 h. The yielded water was removed from the reaction mixture by azeotropic distillation using a Dean−Stark head. After cooling, the mixture was diluted with ether (100 mL). The organic layer was washed with $NaHSO_3$ solution (50 mL × 2), a 5% NaOH solution (50 mL × 2), and water (50 mL × 2) and finally dried over anhydrous $MgSO_4$. After concentration, the viscous residue was purified by flash column chromatography (silica gel) using a mixed solvent (hexane: ethyl acetate = 3:1) to give yellowish crystals of **1** (13.33 g, 60.3 mmol, 52%). Five recrystallizations from hexane gave a white crystal of **1** (6.02 g, 26.5 mmol, 23%, mp 35.0−36.0 °C). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.34 (s, 6H, CH_3), 4.03 (s, 2H, CH_2), 5.28 and 5.78 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.58 (d, 1H, J = 16 Hz, =CH−oxazoline), 6.71(dd, 1H, vinyl, −CH=), 7.41 (s, 4H, aromatic). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 28.2 (CH_3), 67.2 (CCH_3), 78.7 (CH_2), 114.6 (vinyl, CH_2=), 115.3 (=CH−oxazoline), 126.5 (Ar, C2), 127.5 (Ar, C3), 134.7 (Ar, C4), 136.1 (vinyl, −CH=), 138.6 (Ar, C1), 139.0 (vinylene, Ar−CH=) 161.9 (C=N). IR (KBr, cm^{-1}): 3000−2900, 1657 (C=C), 1604 (C=N), 1355, 1308, 1202 (C−O), 1008, 977, 899, 826. Anal. Calcd for $C_{15}H_{17}NO$: C, 79.29; H, 7.54; N, 6.16. Found: C, 78.64; H, 7.63; N, 6.01.

4-Formyl-α-methylstyrene.[35] To a suspension of magnesium turnings (2.89 g, 119 mmol) in dry THF (10 mL), was added 4-chloro-α-methylstyrene (10.30 g, 67.5 mmol) in dry THF (50 mL) dropwise over 1 h at reflux temperature under nitrogen. After further refluxing for 1 h, the reaction mixture was cooled to 0 °C. Freshly distilled DMF (31.40 g, 430 mmol) was added dropwise at 0 °C for 0.5 h. After being stirred for 1 h at room temperature, the reaction mixture was poured into 2 N HCl (200 mL) and the layers were separated. The aqueous layer was extracted three times with diethyl ether. The organic phase was combined and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, vacuum distillation gave a colorless liquid of 4-formyl-α-methylstyrene (6.07 g, 41.6 mmol, 62%, bp 47−51 °C/0.5 mmHg). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 2.18 (s, 3H, CH_3), 5.24 and 5.52 (2s, 2H, CH_2=), 7.55−7.89 (m, 4H, aromatic), 9.99 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 21.6 (CH_3), 115.4 (CH_2=), 126.1 (Ar, C2), 139.8 (Ar, C3), 135.5 (Ar, C4), 142.4 (Ar, C1), 147.3 (CH_2=*C*), 191.7 (CHO).

2-[2-(4-Isopropenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (2) was prepared according to the similar procedure for **1** by using 4-formyl-α-methylstyrene (5.75 g, 39.4 mmol) and 2,4,4-trimethyl-2-oxazoline (9.28 g, 82.1 mmol). The resulting yellow crystals of **2** (13.33 g, 60.3 mmol, 52%) were purified by flash column chromatography (silica gel, hexane: ethyl acetate = 3:1). Five recrystallizations from hexane gave white crystals of **2** (1.05 g, 4.36 mmol, 11%, mp 51.5−53.0 °C). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.34 (s, 6H, CH_3), 2.15 (s, 3H, =CCH_3), 4.03 (s, 2H, CH_2), 5.11 and 5.42 (2s, 2H, CH_2=), 6.59 (d, 1H, J = 16 Hz, =CH−oxazoline), 7.34 (d, 1H), 7.45 (s, 4H, aromatic). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 21.6 (=C*C*H_3), 28.4 (CH_3), 67.3 (CCH_3), 78.9 (CH_2), 113.2 (CH_2=), 115.5 (=CH−oxazoline), 125.9 (Ar, C2), 127.3 (Ar, C3), 134.4 (Ar, C4), 139.2 (=CH−Ar), 142.2 (=*C*CH_3), 142.5 (Ar, C1), 161.8 (C=N). IR (KBr, cm^{-1}): 3000−2900, 1656 (C=C), 1624, 1606 (C=N), 1355, 1312, 1202 (C−O), 1007, 982, 896, 831. Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63, H, 7.94, N, 5.80. Found: C, 79.28, H, 8.33, N, 5.70.

2-Ethyl-4,4-dimethyl-2-oxazoline.[36] A mixture of propionic acid (37.7 g, 509 mmol) and 2-amino-2-methylpropanol (44.7 g, 502 mmol) was heated under stirring at 180 °C for 9 h. The yielded oxazoline and water were azeotropically distilled at 95−105 °C, and hexane (100 mL) was added to the distillate. The organic layer was separated, and the water phase was extracted with hexane (50 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ for 2 h. Concentration gave a colorless liquid of 2-ethyl-4,4-dimethyl-2-oxazoline (44.7 g, 352 mmol, 70%). The resulting compound was directly used for the following reaction without further purification. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.09 (t, 3H, CH_2CH_3), 1.27 (s, 6H, $(CH_3)_2$C−N), 2.26 (q, 2H, CH_2CH_3), 3.90 (s, 2H, CH_2).

2-[1-Methyl-2-(4-ethenylphenyl)ethenyl]-4,4-dimethyl-2-oxazoline (3) was prepared according to the similar procedure for **1** by using 4-formylstyrene (10.35 g, 78.4 mmol) and 2-ethyl-4,4-dimethyl-2-oxazoline (19.57 g, 154 mmol). The resulting yellow crystals of **3** (10.14 g, 42.1 mmol, 54%) were purified by flash column chromatography (silica gel, hexane: ethyl acetate = 3:1). After five recrystallizations from hexane, white crystals of **3** (5.49 g, 22.8 mmol, 29%, mp 48.7−49.4 °C) were obtained: ^{1}H NMR ($CDCl_3$, 90 MHz): δ 1.35 (s, 6H, =N−CCH_3), 2.21 (s, 3H, =C−CH_3), 4.03 (s, 2H, CH_2), 5.27 and 5.77 (2d, 2H, J = 11 and 18 Hz, CH_2=), 6.73(dd, 1H, −CH=, vinyl), 7.38−7.49 (m, 5H, overlapping, aromatic and Ar−CH=). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 15.2 (=CH*C*H_3), 28.3 (=N−C−*C*H_3), 67.4 (=N−*C*−CH_3), 78.9 (CH_2), 114.3 (vinyl, CH_2=), 125.6 (=*C*CH_3), 126.1 (Ar, C2), 129.7 (Ar, C3), 134.4 (Ar−CH=), 135.9 (Ar, C4), 136.3 (vinyl, −CH=), 136.9 (Ar, C1), 164.1 (C=N). IR (KBr, cm^{-1}): 3000−2900, 1629, (C=C), 1608 (C=N), 1463, 1386, 1207 (C−O), 1087, 1006, 962, 906. Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63, H, 7.94, N, 5.80. Found: C, 79.49, H, 7.82, N, 5.72.

Purification. After repeated recrystallizations, the purified monomers were dried over P_2O_5 for 48 h at ambient temperature and sealed off in an all-glass apparatus equipped with a breakseal under high vacuum conditions (10^{-6} mmHg). The monomers were then diluted with dry THF, and the resulting monomer solutions (0.3−0.5 M in THF) were stored at −30 °C.

Anionic Polymerization. All anionic polymerizations were carried out with vigorous shaking under high vacuum conditions in the all-glass apparatus equipped with breakseals as previously reported.[33] The polymerization reaction was terminated with degassed methanol. The reaction mixture was poured into hexane to precipitate the polymer. The polymers collected by filtration were further purified by reprecipitations from THF/water and THF/hexane systems and finally freeze-dried from the benzene solution. The resulting polymers were 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): δ 0.5−2.2 (m, 9H, CH_2-CH and CH_3), 4.0 (2H, CH_2), 5.0−7.5 (broad, aromatic and CH=CH). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 28.4 (CH_3), 38−43 (CH_2CH), 67.3 (CH_2), 114.7, 127, 133, 127, 140 (Ar and CH=CH including CH_2=CH), 162.0 (C=O). IR (KBr, cm^{-1}): 2970, 1659 (C=C), 1604 (C=N), 1363, 1289, 1202, 1004, 975.

Poly(3). ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.9−2.2 (m, 3H, CH_2-CH), 1.33 (s, 6H, N−C−CH_3), 2.1 (s, 3H, CH_3), 4.0 (s, 2H, CH_2), 6.2−7.4 (m, 5H, Ar−CH=). ^{13}C NMR ($CDCl_3$, 23 MHz): δ 15.3 (=C−*C*H_3), 28.5 (CH_3), 39−43 (CH_2CH), 67.5 (CH_2), 79.0 (*C*CH_3), 125.0 (=*C*CH_3), 127.6 (Ar, C2), 129.5 (Ar, C3), 134.1 (Ar, C1), 134.8 (Ar−CH=), 144.5 (Ar, C4), 164.4 (C=N). IR (KBr, cm^{-1}): 2966, 1641 (C=C), 1607 (C=N), 1363, 1192, 1089, 1008, 962.

Radical Polymerization. Radical polymerization of **3** was carried out in a sealed tube with AIBN as an initiator in benzene at 70 °C. After 6 h, the reaction mixture was poured into hexane to obtain the polymer (M_n = 62 000, M_w/M_n = 1.88) in 48% yield. All the polymeric products obtained from the radical process were soluble, similar to the cases of anionic polymerization.

Deprotection of Poly(3). A mixture of poly(**3**) (0.74 g, 3.1 mmol based on monomer unit), 3 N HCl (20 mL), and THF (6 mL) was heated at reflux temperature for 10 h. After evaporation of the solvent, the residue was neutralized with 15% sodium hydroxide solution (MeOH/water = 1/1). After a further 40 mL of 15% sodium hydroxide solution was added, the reaction system was heated at reflux temperature for 18 h. After concentration, the residue was poured into a large excess of 2 N HCl to precipitate a white powder of poly(4-vinyl-α-methylcinnamic acid) (0.58 g, 3.1 mmol based on monomer unit, 100%). The resulting polymer was converted into the corresponding methyl ester without further purification.

Poly(4-vinyl-α-methylcinnamic acid), 5. ^{1}H NMR ($CDCl_3$ and DMSO-d_6, 90 MHz): δ 0.8−2.0 (m, 3H, CH_2CH), 1.6 (s, 3H, CH_3), 6.1−7.3 (m, 5H, Ar−CH=). ^{13}C NMR ($CDCl_3$ and DMSO-d_6, 23 MHz): δ 13.2 (=C−*C*H_3), 38−45 (CH_2CH), 127

(Ar, C2), 127.2 (=*C*CH_3), 128.7 (Ar, C3), 132.8 (Ar, C1), 137.4 (Ar−CH=), 144.0 (Ar, C4), 169.4 (C=O). IR (KBr, cm^{-1}): 3500−2500 (OH), 1685 (C=O), 1629 (C=C), 1416, 1263, 1211, 1129.

Methylation of Poly(4-vinyl-α-methylcinnamic acid) with Diazomethane. To a suspension of poly(4-vinyl-α-methylcinnamic acid) (0.51 g, 2.7 mmol based on monomer unit) in benzene was added 1.6 M of diazomethane (90 mL, 14 mmol, *Caution*! *Explosive*!) solution in ether[37] at room temperature. During the reaction, the precipitated polymer dissolved slowly in the solution. The resulting yellow solution was allowed to stand at room temperature in a well-ventilated hood overnight. The reaction system was quenched with acetic acid and poured into a large excess of hexane to precipitate the poly(methyl 4-vinyl-α-methylcinnamate) (0.57 g). The isolated polymer was purified by reprecipitations in a THF/methanol system and freeze-dried from the benzene solution.

Poly(methyl 4-vinyl-α-methylcinnamate), 6. ^{1}H NMR ($CDCl_3$, 90 MHz): δ 0.9−2.2 (m, 3H, CH_2CH), 2.0 (s, 3H, CH_3), 3.8 (OCH_3), 6.2−7.3 (m, 4H, Ar), 7.5 (s, 1H, −CH=). ^{13}C NMR ($CDCl_3$ and DMSO-d_6, 23 MHz): δ 14 (=C*C*H_3), 38−43 (CH_2-CH), 52 (OCH_3), 127 (Ar, C2 and =*C*CH_3), 129 (Ar, C3), 133 (Ar, C1), 138 (Ar−CH=), 145 (Ar, C4), 169 (C=O). IR (KBr, cm^{-1}): 2926, 1712 (C=O), 1636 (C=C), 1436, 1261, 1208, 1121.

Photoreaction of the Polymers. The poly(**3**) and **5** (30 mg) were cast from their benzene solutions (1 mL) on a Teflon sheet. The solvent was slowly evaporated from the sheet to prepare a transparent film overnight. The photoreactions of the polymers were carried out with an Ushio super high-pressure mercury lamp, USH-500D (500 W). The irradiation of the polymer films was performed at room temperature for 5 or 90 min under air. After irradiation, the polymer films were immersed in 20 mL of dry THF for 1 h to wash out the soluble part. The insoluble part on the Teflon sheet was further washed with 5 mL of dry THF and dried in vacuo to obtain a constant weight. The THF soluble part was freeze-dried from the benzene solution and characterized by ^{1}H NMR and IR spectroscopies and SEC measurements.

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 (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) 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}) and with ultraviolet (254 nm) or refractive index detection. THF was a carrier solvent at a flow rate of 1.0 mL min^{-1}. Vapor pressure osmometry (VPO) measurements for M_n determination were made with a Corona 117 instrument in benzene. The glass transition temperatures of the polymers were measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The samples were first heated to 240 °C, cooled rapidly to −20 °C, and then scanned again at a rate of 20 °C min^{-1}.

Acknowledgment. This work was partially supported by a Grant-in Aid (No. 03855202 and 09750965) from the Ministry of Education, Science, and Culture, Japan. T.I. thanks the Kawakami Foundation and the Kurata Foundation for their financial supports. The authors thank Prof. Kazuhiko Saigo and Dr. Yutaka Adegawa at the University of Tokyo for their support in the experiment of UV irradiation.

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MA980478B