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Anionic Polymerization of Monomers Containing Functional Groups. 8. Anionic Living Polymerization of 4-Cyano-α-methylstyrene

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ABSTRACT: The anionic polymerization of 4-cyano-α-methylstyrene (**1**) was carried out in THF at −78 °C with (1,1,4,4-tetraphenylbutanediyl)dipotassium and -dilithium, (diphenylmethyl)potassium, and (triphenylmethyl)potassium and -cesium. All the polymerizations of **1** quantitatively proceeded with each initiator, although the rates of polymerization were quite slow, especially in the case of organolithium initiator. The resulting poly(**1**)s always possessed narrow molecular weight distributions ($M_w/M_n < 1.13$) and predicted molecular weights based on the molar ratios of monomer to initiators. The living nature of the propagating carbanion derived from **1** was demonstrated by the postpolymerization. Novel well-defined block copolymers poly(**1**-*b*-styrene-*b*-**1**) and poly(**1**-*b*-*tert*-butyl methacrylate-*b*-**1**) were successfully synthesized by the sequential addition of **1** and styrene or *tert*-butyl methacrylate.

Introduction

Having realized the potential of the living polymerization systems as very useful methodology to synthesize tailor-made (co)polymers,[1] a number of studies have been so far dedicated to develop new living polymerization systems of various monomers[2] as well as the investigations concerning the kinetic and mechanistic features of the polymerization systems. Among these living polymerization systems, the anionic polymerization is still undoubtedly the best established method,[3] since it permits the precise control of the molecular structures of the resulting polymers, such as a wide range of controllable molecular weight, the narrowest molecular weight distribution, quantitative terminal functionality, and occasionally even high stereoregularity of the repeating unit[4] in addition to the synthesis of well-defined block copolymers. The stable but highly reactive propagating carbanion always plays a very important role in the anionic living polymerization to control such molecular structures of the polymers. However, these highly reactive carbanionic species of the resulting living polymers have simultaneously limited the range of the employable monomers to only conjugated hydrocarbons such as styrene, 1,3-butadiene, and isoprene and a few other monomers due to their incompatibility with functional groups.

We have successfully resolved this long-standing problem by introducing a series of electron-withdrawing groups into the framework of styrene monomer in order to change the reactivities of monomer and the resulting living polymer.[5] The electron-withdrawing groups introduced are *N,N*-dialkylamide,[6] *N*-alkylimino,[7] (trimethylsilyl)ethynyl,[8] oxazolinyl,[9] *tert*-butyl ester,[10] *N,N*-dialkylsulfonamide,[11] and cyano[12] groups, all of which are susceptible to react with strong nucleophiles such as butyllithiums and anionic living polystyrene. All the polymerizations of the styrenes *para*-substituted with these reactive functional groups afford the stable anionic living polymers having strictly controlled molecular structures without serious side reactions. In these systems, we have found two new findings with respect to the reactivities of the monomers and the carbanions produced. Primarily, the reactivities of the propagating carbanions of the living polymers are dramatically reduced by the electron-withdrawing effects of the substituents introduced purposefully to prevent serious side reactions of the carbanions toward the functional groups. The resonance stabilization of the terminal benzylic carbanion[13] through an extended π-conjugated system involving the multiple bond of $C{=}O$, $C{=}N$, $C{\equiv}C$, $S{=}O$, and $C{\equiv}N$ and the phenylene ring are also attained to suppress the undesirable side reactions. The reduced nucleophilicities of the living polymers are actually demonstrated by the crossover reactions with comonomers such as styrene and isoprene.[14] Secondarily, the anionic polymerizabilities (electrophilicities) of the *para*-substituted monomers are significantly enhanced by the similar electron-withdrawing effects of the substituents as expected. This is also evident from the fact that even low nucleophilic initiators that are ineffective in bringing about styrene polymerization can initiate the polymerizations of those monomers efficiently.[14] Thus, we have succeeded in a fine control of chain structures of the resulting polymers and changed both reactivities of the carbanions produced and the styrene monomers themselves by introducing the electron-withdrawing groups.

In this report, we extend this strategy to the framework of α-methylstyrene, which is less electrophilic than styrene under anionic conditions. The reactivity of α-methylstyrene should be also remarkably stimulated by the introduction of the electron-withdrawing group similar to the cases of styrene derivatives. In addition to this, the resulting substituted poly(α-methylstyrene)s are recognized as attractive materials because of their physical properties such as high T_gs[15,16] and degradable character to regenerate monomers quantitatively. Also of interest, the anionic polymerization systems of α-methylstyrenes often show fascinating equilibrium behaviors known as the typical example of the thermodynamically reversible polymerization due to the steric strain caused by α-methyl group.[16−21]

We hence introduce cyano group as a representative electron-withdrawing group to modify the reactivity of α-methylstyrene and report the synthesis of a novel

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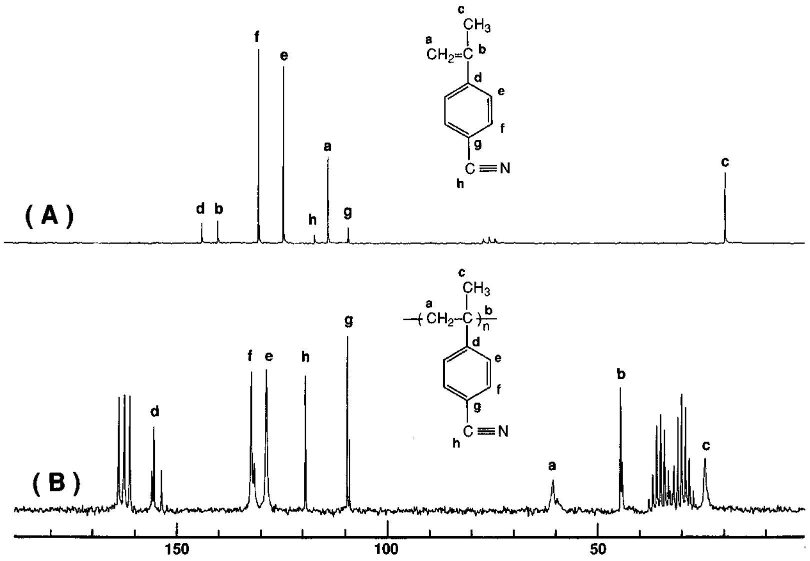
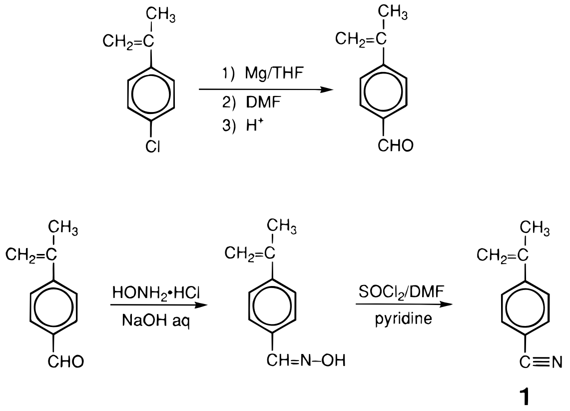


Figure 1. ^{13}C NMR spectra of **1** in $CDCl_3$ (A) and of poly(**1**) in DMF-d_7 (B).

Scheme 1



anionic living polymer derived from 4-cyano-α-methylstyrene (**1**). The substitution of electron-withdrawing cyano and α-methyl groups should considerably affect the polymerization behavior and the reactivity of **1** compared with those of α-methylstyrene and 4-cyanostyrene[12] analogues, respectively. In the forthcoming paper, we will discuss the behavior of anionic equilibrium polymerization of **1** characteristic to α-methylstyrene derivatives under the various thermodynamic conditions.

Results and Discussion

Synthesis of 1. The monomer **1** was synthesized by a two-step reaction from 4-chloro-α-methylstyrene as shown in Scheme 1. We have attempted two synthetic routes in the second-stage reaction from 4-formyl-α-methylstyrene to **1**. One is a one-pot reaction employed previously in the synthesis of 4-cyanostyrene,[12,22] which involves the formation of an oxime in situ and the subsequent dehydration of the resulting oxime. The other is a modified procedure reported by Arrieta *et al.* with a mixture of DMF and thionyl chloride as a dehydrating reagent of the isolated oxime.[23] In the former reaction, the dehydration of the oxime proceeded very slowly and the yield of **1** was moderate (49%), while the latter attained a 61% production of **1** within 1 h without difficulty. The ease of the purification for these α-methylstyrene derivatives is also noteworthy because of their low tendency toward thermal polymerization during the fractional distillation.

Anionic Polymerization of 1. Anionic polymerization of **1** was carried out in THF at −78 °C with various initiators. Since side reactions were previously suggested to occur to some extent at the initiation step of anionic polymerization of 4-cyanostyrene with *n*-butyllithium as an initiator,[12b] we employed here bulky and less nucleophilic initiators. They were (1,1,4,4-tetraphenylbutanediyl)dilithium[24] and dipotassium, and [1,1,4,4-tetrakis[4′-(trimethylsilyl)phenyl]butanediyl]-dipotassium,[25] all of which were found to be effective for the anionic living polymerization of 4-cyanostyrene.[12] Bulkier but less reactive (triphenylmethyl)potassium (Ph_3CK), and -cesium (Ph_3CCs) were also used to examine the anionic polymerizability of **1**.

On mixing each of these initiators with **1**, the reaction mixture always showed a deep red color which resembled that of living anionic poly(α-methylstyrene) during the course of the polymerization. The intense red color remained at −78 °C even after 264 h but immediately disappeared upon the addition of a small amount of methanol to quench the polymerization at −78 °C , indicating the existence of the propagating species. After termination, the conversion of **1** was analyzed by GC and the reaction mixture was poured into a large excess of methanol to precipitate the polymer. After reprecipitation from DMF/methanol, the resulting polymer was characterized by ^{1}H, and ^{13}C NMR and IR spectroscopy. In ^{1}H NMR, the signals of the $CH_2{=}$ moiety of **1** at 5.25 and 5.47 ppm disappeared completely and a broad signal corresponding to the methylene group of the polymer main chain appeared at 1.8 ppm after the polymerization. Figure 1 shows the ^{13}C NMR spectra of **1** and poly(**1**) obtained with Ph_3CCs. The two signals corresponding to the carbon−carbon double bond (115.6 and 141.8 ppm) are no longer present in the resulting polymer, and alternatively, the signals of the polymer backbone appeared at 44.6 (quaternary) and 60.6 ppm (methylene). Some carbon signals of the poly(**1**) are observed to be split into doublets or triplets possibly due to the tacticity of the resulting polymer. In the IR spectrum of poly(**1**), a strong and characteristic $C{\equiv}N$ stretching absorption at 2227 cm^{-1} was observed, and as expected, the absorption at 904 cm^{-1} for $C{=}C$ bond of **1** disappeared. It is thus evident from these spectroscopic observations that the vinyl polymerization of **1** proceeded.

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

					$10^{-3}M_n$			
run	**1**, mmol	initiator, mmol	time, h	yield, %	calcd[a]	obsd[b]	$10^{-3}M_w$(LS)[c]	M_w/M_n[b]
1	4.67	Li-Naph,[d] 0.156/DPE,[e] 0.160	2	12	1.0	1.2		1.06
2	6.86	Li-Naph, 0.164/DPE, 0.261	48	61	8.2	7.3		1.11
3	6.70	Li-Naph, 0.0984/DPE, 0.110	168	100	18	11		1.10
4	5.18	K-Naph,[f] 0.116/TMS_2DPE,[g] 0.128	8	58	7.5	5.8		1.06
5	3.73	K-Naph, 0.0964/TMS_2DPE, 0.105	24	82	9.8	6.8		1.06
6	10.6	Ph_2CHK,[h] 0.156	100	100	9.9	6.9		1.06
7	3.95	K-Naph, 0.0709/DPE, 0.128	48	100	16	13		1.06
8	7.63	K-Naph, 0.157/DPE, 0.169	96	100	14	12	13	1.07
9	3.14	K-Naph, 0.0557/TMS_2DPE, 0.0755	96	100	17	12		1.06
10	5.58	Ph_3CK,[i] 0.106	40	100	7.6	5.4		1.04
11	4.18	Ph_3CK, 0.0519	48	100	12	11		1.06
12	4.45	Ph_3CK, 0.0188	168	100	34	34	41	1.10
13	3.97	Ph_3CCs,[j] 0.0280	48	88	18	15		1.05
14	11.2	Ph_3CCs, 0.0263	264	100	61	50	71	1.13

[a] M_n (calcd) = [monomer] × (MW of monomer) × f/[initiator] + MW of intiator residue; f = 1 or 2, corresponding to the functionality of the initiators. [b] M_n (obsd) and M_w/M_n were obtained by SEC calibration using standard poly(4-cyanostyrene)s in DMF. [c] M_w(LS) was obtained by light scattering in acetone at 25 °C. [d] Lithium naphthalenide. [e] 1,1-Diphenylethylene. [f] Potassium naphthalenide. [g] 1,1-Bis[4′-(trimethylsilyl)phenyl]ethylene. [h] (Diphenylmethyl)potassium. [i] (Triphenylmethyl)potassium. [j] (Triphenylmethyl)cesium.

Table 1 summarizes the results of polymerization of **1** in THF at −78 °C . The molecular weight and molecular weight distribution were measured by size exclusion chromatography (SEC) using DMF containing 0.01 M LiBr as an eluent and estimated from the calibration of several poly(4-cyanostyrene)s having known M_ns and narrow molecular weight distributions ($M_w/M_n < 1.1$) as previously synthesized in our laboratory.[12]

The rate of polymerization for **1** seemed significantly slower than that of α-methylstyrene by using the anionic initiators associated with lithium countercation (runs 1−3). The yield of poly(**1**) was only 12% at −78 °C for 2 h, while the polymerization of α-methylstyrene was completed under identical conditions. Even after 48 h polymerization, the conversion was still 61%, but the polymerization was finally completed after 168 h to give poly(**1**) quantitatively. In contrast to the organolithium initiators, the polymerization using organopotassium and -cesium initiators proceeded rather rapidly at −78 °C and was completed within 48 h at similar monomer concentrations. This dependence on countercation is in sharp contrast to the case of α-methylstyrene. In the case of α-methylstyrene, it was observed that the polymerization rate with organopotassium initiators was much slower than that of organolithiums under the identical conditions.

It should be emphasized that all the SEC curves of poly(**1**) produced at −78 °C possessed unimodal and sharp peaks without any shoulders. The sharp and narrow molecular weight distributions of the resulting poly(**1**)s ($M_w/M_n < 1.13$) clearly reflected the absence of chain termination reactions as well as the rapid initiation and the slow propagation in the polymerization systems employed. Their M_n values determined by using the SEC calibration of poly(4-cyanostyrene)s linearly increased with the molar ratios of monomer to initiator. The values were close to but in most cases slightly lower than those calculated on the basis of the molar ratios. To determine absolute values of molecular weights, the molecular weights (M_w value in this case) of some polymers were measured by a light scattering method. As you can see, the M_w values of three polymer samples are found to agree reasonably well with the molecular weights calculated (see runs 8, 12, and 14). These results clearly indicate that real values of M_n are estimated to be very close to those calculated values and the M_n values determined by the calibration of poly(4-cyanostyrene)s may possibly be slightly underestimated.

In order to prove the living character of the propagating carbanion derived from **1** more clearly, a postpolymerization was carried out with Ph_3CK as an initiator at −78 °C. After the completion of the first-stage polymerization for 48 h, a second feed of **1** was added to the polymerization system. It was allowed to react at −78 °C for a further 48 h to complete the second-stage polymerization. The yields of both pre- and postpolymers were quantitative. They possessed the molecular weights of 5900 and 12 000, close to the theoretical values of 6900 and 14 000, respectively. Figure 2 shows that the SEC curve of the postpoly(**1**) obtained by the second-stage polymerization clearly shifts from that of prepolymer toward the higher molecular weight side, keeping the narrow molecular weight distribution (M_w/M_n = 1.07). This provides direct evidence for the living character of the polymerization of **1** under the conditions employed here.

Interestingly, the less nucleophilic Ph_3CK and Ph_3CCs initiators are also effective for the polymerization, giving the poly(**1**)s with predicted molecular weights and narrow molecular weight distributions. This indicates a high anionic polymerizability of **1**, since both Ph_3CK and Ph_3CCs are not able to initiate the polymerization of styrene and α-methylstyrene at all.

In conclusion, the result of the postpolymerization and those listed in Table 1 clearly demonstrate the anionic living polymerization of **1**, an α-methylstyrene derivative, *para*-substituted with reactive cyano group. The resulting poly(**1**)s possess predicted M_ns and very narrow molecular weight distributions as well as the polystyrene counterpart, poly(4-cyanostyrene).[12]

Block Copolymerization of 1 with Styrene and *tert*-Butyl Methacrylate. In recent years, block copolymers attracted great interest due to their unique character shown in the solutions and in the solid state.[26] The attainment of the living polymerization of **1** allows the controlled synthesis of block copolymers containing polar and reactive poly(**1**) segments by the sequential addition of **1** and comonomers. In addition to the synthetic viewpoint, the results of block copolymerization provide important information on the relative reactivities of **1** itself and the terminal carbanion of living polymer derived from **1**. For these purposes, we have employed two representative comonomers for **1**, styrene and *tert*-butyl methacrylate (tBMA), and their anionic living polymers. As is well-known, tBMA is more reactive than styrene under the conditions of

Table 2. Block Copolymerization of 1 with Styrene and *tert*-Butyl Methacrylate in THF at −78 °C[a]

run	first monomer	second monomer	block copolymer (homopolymer[b]) $10^{-3}M_n$ calcd[c]	obsd[d]	M_w/M_n[e]
15	styrene	**1**	16 (8.3)	17 (9.4)	1.05 (1.06)
16	tBMA	**1**	23 (13)	19 (11)	1.07 (1.07)
17[f]	**1**	styrene	25 (9.3)	7.3[f] (7.3)	1.05[f] (1.05)
15	**1**	tBMA	18 (7.6)	22[e] (5.4)	1.28[g] (1.03)
19	**1**	tBMA	20 (7.5)	27[e] (6.3)	1.18[g] (1.04)

[a] Yields of polymers were always quantitative except for run 17. [b] Homopolymers were obtained at the first-stage polymerization. [c] M_n(calcd) = [monomer] × (MW of monomer)/[initiator] + MW of initiator. [d] The molecular wights 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 and M_n were obtained by SEC calibration using standard poly(4-cyanostyrene)s in DMF solution. [f] No second-stage polymerization proceeded. The homopoly(**1**) was recovered quantitatively. [g] Bimodal MWDs.

anionic polymerization, while the living polymer of styrene has higher reactivity than that of tBMA, which is not able to initiate the anionic polymerization of styrene. All the sequential copolymerizations were carried out at −78 °C by using the anionic initiators associated with a potassium countercation to examine the polymerizability under similar conditions.

The first attempt was the synthesis of a block copolymer by the sequential addition of styrene and **1**. First-stage polymerization of styrene was initiated with potassium naphthalenide in THF at −78 °C for 10 min and then **1** was added to the reaction mixture. It was allowed to stand for 48 h to complete the polymerization of **1**. From the analysis of ^{1}H NMR data of the resulting polymer after addition of **1**, a good agreement was observed between the composition of each polymer segment and the feed composition of styrene and **1**. The SEC trace of the polymer clearly shifted toward the higher molecular weight region while the narrow distribution after addition of **1** was maintained. The molecular weights of the homopolystyrene and the resulting polymer were consistent with the calculated values (Table 2, run 15). These results demonstrate the successful formation of a tailored triblock copolymer, poly(**1**-*b*-styrene-*b*-**1**), as expected.

Similarly, another triblock copolymer with well-regulated chain structures could be synthesized by sequential addition of **1** to living poly(tBMA) (run 16). When **1** was added to the living poly(tBMA) at −78 °C, the color change of the reaction mixture was immediately observed from pale violet to intense red, which suggested the formation of the benzylic carbanion from **1**. The SEC curve of the resulting block copolymer shifts completely from the starting homopolymer of tBMA, as can be seen in Figure 3. This finding that living poly(tBMA) can initiate the polymerization of **1** is surprising, since the enolate anion of living poly(tBMA) is known not to initiate the polymerization of either styrene or α-methylstyrene. The result obtained in the block copolymerization indicates that the reactivity of **1** toward carbanions is undoubtedly higher than those of α-methylstyrene and styrene and it is comparable with that of tBMA. Thus, it is obvious that the electrophilicity of **1** was extremely enhanced by the presence of the C≡N group.

The syntheses of the block copolymer of **1** and the comonomers with the reversed sequence were next examined. Styrene was sequentially added to the living polymer of **1**, prepared with Ph_2CHK in THF at −78 °C for 48 h. No appreciable polymerization of styrene was observed and the homopoly(**1**) was recovered from the system after 2 h at −78 °C, showing that the propagating carbanion of poly(**1**) has no ability to initiate the polymerization of styrene under these conditions. This is similar to the fact that no initiation reaction takes place between the living poly(4-cyanostyrene) and styrene under similar conditions.[12] On the other hand, tBMA was found to undergo further polymerization by the living poly(**1**). A rapid increase of viscosity and the complete consumption of tBMA were observed in this case. Unexpectedly, the color of the polymerization system was unchanged. The SEC curve of the copolymerization product was bimodal and showed a considerable amount of the starting homopoly(**1**), indicating that partial initiation of tBMA by the poly(**1**) anion and rapid further polymerization occurred to yield a mixture of the homopolymer of **1** and the block copolymer with an unexpected chain structure. From the SEC peak areas, the initiation efficiency of the second-stage polymerization of tBMA was estimated to be nearly 50%. This is a sharp contrast to the previous result that the living polymer of 4-cyanostyrene can initiate the po-

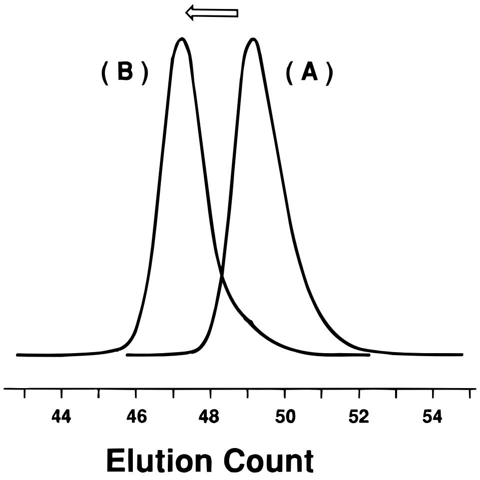


Figure 2. SEC curves of poly(**1**)s obtained at −78 °C: (A) the first-stage polymerization, M_n(obsd) = 5900, M_w/M_n = 1.04; (B) the second-stage polymerization, M_n(obsd) = 12 000, M_w/M_n = 1.07 (the second feed of monomer was added 48 h after the first-stage polymerization).

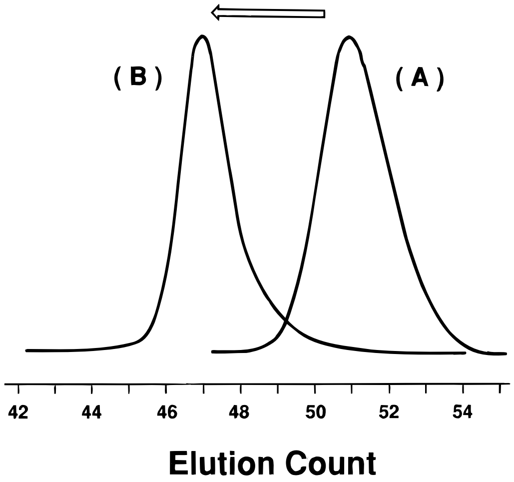


Figure 3. SEC curves of poly(tBMA) at the first-stage polymerization (A) and of poly(**1**-*b*-tBMA-*b*-**1**) obtained at −78 °C (B): peak A, M_n(obsd) = 11 000, M_w/M_n = 1.07; peak B, M_n(obsd) = 19 000, M_w/M_n = 1.07 (the second monomer was added 2 h after the first-stage polymerization).

Table 3. Solubilities of Poly(1), Poly(4-cyanostyrene), Poly(α-methylstyrene), and Polystyrene[a]

solvent	polymer			
	poly(**1**)	poly(4-cyanostyrene)	poly(α-methylstyrene)	polystyrene
hexane	I	I	I	I
benzene	I	I	S	S
carbon tetrachloride	I	I	S	S
diethyl ether	I	I	Sw	S
ethyl acetate	I	I	Sw	S
chloroform	Sw	Sw	S	S
acetone	S	S	I	S
1,4-dioxane	I	I	S	S
tetrahydrofuran	Sw	Sw	S	S
N,*N*-dimethylformamide	S	S	S	S
dimethyl sulfoxide	S	S	I	I
nitromethane	S	S	I	I
acetonitrile	Sw	S	I	I
ethanol	I	I	I	I
methanol	I	I	I	I
water	I	I	I	I

[a] I, insoluble; S, soluble; Sw, swelling.

lymerization of tBMA in quantitative initiation efficiencies to produce well-defined block copolymers.[12b,14] We speculate that this difference in the reactivity between living poly(**1**) and living poly(4-cyanostyrene) may arise from the steric hindrance of the terminal carbanion. The steric effect of methyl group on the α-carbon and the electron-withdrawing effect of the cyano group remarkably decrease the nucleophilicity of the resulting tertiary carbanion derived from **1**.

In our previous paper, we successfully correlated the reactivities of the styrene monomers containing electron-withdrawing groups and their living polymers with the ^{13}C NMR chemical shifts of β-carbon of vinyl groups.[14] The introduction of the electron-withdrawing group at the *para*-position of styrene causes a downfield shift of the vinyl β-carbon and induces remarkably the high anionic polymerizability of the monomer and a low nucleophilicity of the resulting terminal carbanion. A similar relationship between the ^{13}C NMR chemical shift and the reactivity will be expected to hold for a series of *para*-substituted α-methylstyrenes. In fact, the chemical shift of the β-carbon of **1** is 115.6 ppm and it apparently shifts toward a lower field compared to that of α-methylstyrene itself (112.4 ppm). The high electrophilicity of **1** and the low nucleophilicity of the living polymer derived from **1** can be well-accounted for by this substituent effect of cyano group. A strong electron-withdrawing cyano group enhances the electrophilic nature of the carbon−carbon double bond of **1** and simultaneously stabilizes the propagating carbanion effectively to form a stable living polymer of **1**. The extension of π-conjugated system including the C≡N group[13] may also play an important role in stabilizing the benzylic carbanion yielded at termini of the living poly(**1**). This stabilized propagating carbanion permits 4-cyano-α-methylstyrene to produce a novel living polymer and to prevent side reactions toward the cyano group under the conditions employed here.

Solubilities of the Polymers. The poly(**1**) was a white powder and could be cast into transparent and brittle films from the solution. Table 3 summarizes the solubilities of poly(**1**) for various organic solvents. The solubilities of poly(4-cyanostyrene), poly(α-methylstyrene), and polystyrene are also listed as references. All these samples synthesized by anionic polymerizations possessed narrow molecular weight distributions with M_n values close to 20 000. Poly(**1**) is soluble in acetone, DMF, DMSO, and nitromethane and swells in chloroform, THF, and acetonitrile. It was insoluble in most of the nonpolar solvents employed here. The solubility of poly(**1**) resembles that of poly(4-cyanostyrene), as expected. As can be seen in Table 3, the solubility is greatly affected by introducing polar cyano group into poly(α-methylstyrene).

Table 4. Glass Transition Temperatures of Poly(1)s[a]

$10^{-3}M_n$	M_w/M_n	Tg, °C
5.4	1.04	214
6.9	1.06	232
8.6	1.06	241
11	1.06	249
34	1.10	249
50	1.13	260

[a] The glass transition temperature was measured in the second heating scan at a rate of 10 °C min^{-1}.

The glass transition temperatures (Tg) of the resulting poly(**1**)s having narrow molecular weight distributions were measured by differential scanning calorimetry (DSC) (Table 4). The Tg values apparently increased with the molecular weight of poly(**1**) and became constant at about 260 °C. This is significantly higher than the Tg values of poly(4-cyanostyrene), poly(α-methylstyrene), and polystyrene of comparable molecular weights, 180, 168, and 101 °C, respectively. The introduction of both the cyano group on the phenyl ring and the methyl group on the polystyrene backbone increases the Tg value of poly(**1**) more than that of polystyrene. This high Tg value of poly(**1**) may open a possible way to a new high performance material.

In conclusion, we have shown that the anionic living polymerization of 4-cyano-α-methylstyrene (**1**) in THF at −78 °C gives polymers of predicted molecular weights and narrow molecular weight distributions in quantitative yields. From the results of block copolymerizations, the reactivity of **1** is found to be remarkably enhanced compared with that of α-methylstyrene by the electron-withdrawing effect of the cyano group. Surprisingly, the estimated anionic polymerizability of **1** is roughly comparable to that of tBMA. On the other hand, the carbanion derived from **1** has a lower reactivity than that from α-methylstyrene and is unable to initiate the polymerization of styrene.

Experimental Section

Materials. 4-Chloro-α-methylstyrene, kindly supplied by Hokko Chemical Industry Co., Ltd., was used for the monomer synthesis without further purification. *N*,*N*-Dimethylformamide (DMF) and diphenylmethane were dried and distilled from calcium hydride under vacuum. *tert*-Butyl methacrylate (tBMA) was distilled over calcium hydride and subsequently distilled from trioctylaluminum on a vacuum line.[27] 1,1-Diphenylethylene (DPE), supplied by Hokko Chemical Industry Co., Ltd., was purified by fractional distillation over calcium hydride and finally distilled from *n*-BuLi/heptane under vacuum. 1,1-Bis[4′-(trimethylsilyl)phenyl]ethylene (TMS$_2$-DPE) was synthesized by the reaction of Grignard reagent of 4-(trimethylsilyl)chlorobenzene with ethyl acetate and the subsequent dehydration of the resulting carbinol as previously reported.[11]

Initiators. Lithium naphthalenide, potassium naphthalenide, and cumylpotassium were prepared as previously reported.[12] (Diphenylmethyl)potassium was prepared by the reaction of potassium naphthalenide and 1.5 molar excess of diphenylmethane in dry THF at 25 °C for 72 h. (Triphenylmethyl)potassium and -cesium were synthesized from the corresponding alkali metals and 1.2 molar excess of triphenylmethane in dry THF at room temperature for 48 h. These initiators were sealed off under high vacuum conditions in ampules equipped with breakseals and stored at −30 °C. The concentrations of initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under high-vacuum conditions as previously reported.[28]

4-Formyl-α-methylstyrene. To a suspension of dry, clean magnesium turnings (5.84 g, 240 mmol) in dry THF (20 mL) under nitrogen was added 4-chloro-α-methylstyrene (21.41 g, 140 mmol) in dry THF (120 mL) dropwise at reflux temperature over 1 h. The heating was continued for a further 2 h to complete the reaction. In some cases, longer reaction time is required. To the reaction mixture, dry DMF (22.60 g, 309 mmol) was added dropwise with cooling in an ice bath, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with 2 N HCl, and the layers were separated. The aqueous layer was extracted three times with ether. The combined organic phase was washed with water and dried over anhydrous $MgSO_4$. After removal of the solvent under reduced pressure, the residue was distilled over calcium hydride under vacuum to give a colorless liquid of 4-formyl-α-methylstyrene (11.62 g, 79.6 mmol, 57%) at bp 58−62 °C/0.2 mmHg: ^{1}H NMR ($CDCl_3$) δ 2.18 (m, 3H, CH_3), 5.24 and 5.51 (2m, 2H, $CH_2{=}$), 7.55−7.89 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.6 (CH_3), 115.4 ($CH_2{=}$), 126.1 (Ar, C2), 129.8 (Ar, C3), 135.5 (Ar, C4), 142.4 (${=}C{-}CH_3$), 147.3 (Ar, C1), 191.7 (CHO); IR (KBr, cm^{-1}) 3100−2700, 1705 (C=O), 1604, 1558, 1386, 1308, 1215, 1174, 1113, 902, 838, 721.

4-Cyano-α-methylstyrene (1). Method A.[22] To a mixture of hydroxylamine hydrochloride (6.84 g, 98.4 mmol) and pyridine (20 mL) was added 4-formyl-α-methylstyrene (11.62 g, 79.4 mmol) in one portion at room temperature. After 5 min of stirring, 200 mL of toluene was added, and the mixture was heated for 25 h under reflux with azeotropic separation of water by means of a Dean−Stark water trap. The cooled solution was filtered from pyridinium chloride. The filtrate was washed twice with 1 N HCl, twice with saturated $NaHSO_3$ solution and once with H_2O and dried over anhydrous $MgSO_4$. After concentration in vacuo, distillation gave 5.58 g (39.9 mmol, 49%) of **1** as a colorless liquid at 56−59 °C/0.3 mmHg.

Method B.[23] To a stirred mixture of 4-formyl-α-methylstyrene (8.50 g, 55.1 mmol) and 40% solution of NaOH (10 mL) was added hydroxylamine hydrochloride (4.38 g, 63.0 mmol) in water (20 mL) dropwise with cooling in an ice bath. After stirring for 1 h at room temperature, 50 mL of water was added and the reaction mixture was neutralized with bubbling of CO_2 gas for 0.5 h. The white precipitate yielded was collected by suction filtration and then dried in vacuo. The resulting 4-isopropenylbenzaldoxime, a white powder (9.12 g), was used for the next reaction without further purification.

Dehydration of the aldoxime was carried out according to the reported procedure.[23] In a dropping funnel, to a mixture of benzene (100 mL) and DMF (17.80 g, 243 mmol), thionyl chloride (29.0 g, 243 mmol) was added at room temperature, and the layers were separated. The lower layer was added dropwise to a solution of 4-isopropenylbenzaldoxime (31.7 g, 197 mmol) in pyridine (40 mL) with cooling in an ice bath. After stirring for 1 h at ambient temperature, the reaction was quenched with water and then 2 N HCl (100 mL) was added. The reaction mixture was extracted with ether (150 mL × 3). The combined ether layer was washed twice with saturated $NaHSO_3$, twice with 5% NaOH, and twice with water and then dried over anhydrous $MgSO_4$. After concentration in vacuo, distillation gave 17.30 g (121 mmol, 61%) of **1** as a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 2.17 (m, 3H, CH_3), 5.25 and 5.47 (2m, 2H, $CH_2{=}$), 7.47−7.81 (m, 4H, aromatic); ^{13}C NMR ($CDCl_3$, Figure 1A) δ 21.3 (CH_3), 110.9 (Ar, C4), 115.6 ($CH_2{=}$), 118.8 (CN), 126.9 (Ar, C2), 132.0 (Ar, C3), 141.8 (${=}C{-}CH_3$), 145.6 (Ar, C1); IR (KBr, cm^{-1}) 3000−2900, 2228 (CN), 1629, 1606, 1506, 1440, 1408, 904, 845.

Purification. After careful fractional distillations over calcium hydride, the purified monomer was sealed off in an apparatus equipped with a breakseal under high-vacuum conditions (10^{-6} mmHg). To purify **1** more rigorously, phenylmagnesium chloride (4.0 mL, 0.20 M solution of THF) was added to the monomer (4.60 g, 32 mmol) at −78 °C, and the mixture was stirred for 0.5 h at ambient temperature. It was then distilled under vacuum into the apparatus equipped with breakseals and successively diluted with dry THF. The resulting monomer solution (0.3−0.5 M in THF) was stored at −30 °C until ready to use for the polymerization.

Polymerization Procedures. All polymerizations were carried out at −78 °C in an all-glass apparatus equipped with breakseals with vigorous shaking under high-vacuum conditions as previously reported.[28] In some cases, polymeric product, especially when M_n was higher than 20 000, precipitated in the reactor, as the polymerization proceeded. The polymerization was terminated with degassed methanol at −78 °C and DMF was added to dissolve the precipitated polymer again. The reaction mixture was poured into a large excess of methanol to precipitate a polymer. The resulting polymer was purified by reprecipitations in DMF/MeOH and dried under vacuum condition. The polymer was then characterized by ^{1}H and ^{13}C NMR and IR spectroscopies. **Poly(1):** ^{1}H NMR (DMF-d_7) δ −0.2−1.0 (m, 3H, CH_3), 1.5−2.3 (2H, CH_2), 6.8−7.9 (m, 4H, aromatic); ^{13}C NMR (DMF-d_7, Figure 1B) δ 24.5 (CH_3), 44.6 (quaternary C), 60.6 (CH_2), 109.6 (Ar, C4), 119.4 (CN), 128.7 (Ar, C2), 132.2 (Ar, C3), 155.4 (Ar, C4); IR (KBr, cm^{-1}) 3000−2900, 2227 (CN), 1671, 1604, 1505, 1453, 1408, 1016, 828.

Measurements. Infrared spectra (KBr disk) were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6 MHz for ^{1}H, 22.53 MHz for ^{13}C) in $CDCl_3$ or DMF-d_7. 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. Chemical shifts of poly(**1**) were reported in ppm downfield relative to DMF-d_7 (δ 8.05) for ^{1}H NMR and (δ 162.5) for ^{13}C NMR as standard. Size exclusion chromatograms (SEC) for determination of M_n and MWD were obtained at 40 °C with a TOSOH HLC-8020 instrument equipped with two polystyrene gel columns (TOSOH GMH$_{XL}$x2) with ultraviolet (270 nm) or refractive index detection. DMF containing 0.01 M LiBr was a carrier solvent at a flow rate of 0.8 mL min^{-1}. Laser light scattering (LS) measurements for weight-average molecular weight determination were performed with an Ootsuka Electronics DSL-600R instrument at 25 °C in acetone. The glass transition temperature of poly(**1**) was measured by differential scanning calorimetry using a Seiko Instrument DSC220 apparatus and analyzed by a SSC5200TA station. The sample was first heated to 280 °C, cooled rapidly to 20 °C, and then scanned again at a rate of 10 °C min^{-1}.

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