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ARTICLE

Synthesis of Block or Graft Copolymers Containing Poly(*Styrene Derivatives*) Segments by Living Cationic Polymerization Using Acetal Moieties as Latent Initiating Sites

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Selective acetal-initiated living cationic polymerization was successfully employed for the precision synthesis of block and graft copolymers containing poly(*p*-methylstyrene) and poly(alkyl vinyl ether) segments. The synthesis involved the living cationic polymerization of *p*-methylstyrene from the acetal moieties at the chain ends or in the side chains of poly(alkyl vinyl ether). Quantitative initiation of the reaction from the acetal moieties and efficient propagation were achieved via the use of a combined initiating system, TiCl₄ and SnCl₄, in the presence of ethyl acetate as an added base and 2,6-di-*tert*-butylpyridine as a proton trap reagent in CH₂Cl₂ at 0 °C. Appropriate ratios of acetal units, TiCl₄, and SnCl₄ were indispensable for the quantitative reaction. Solubility and thermal analyses indicated that the properties of the block and graft copolymers were mainly governed by the poly(*p*-methylstyrene) segments. The synthesis of block and graft copolymers using a more reactive alkoxy styrene was also achieved via the initiation reaction from acetal moieties.

Introduction

Polymer synthesis using prepolymers containing initiating, terminating, and polymerizable units—i.e., macroinitiators, macroterminators, and macromonomers, respectively,—is a powerful tool for the production of copolymers with well-defined structures from different types of monomers. In peptide synthesis via fragment condensation, the use of prepolymers can be crucial to the synthesis of polymers with complicated structures. For a prepolymer in chain polymerization, a macroinitiator, a macroterminator, or a macromonomer is used: macroinitiator-initiated polymerization or the termination reaction of living polymerization by a macroterminator yields block or graft copolymers;^{1–3} the controlled polymerization of a macromonomer produces graft copolymers with branched chains having regular length.⁴

A distinct advantage of methods that use prepolymers over

one-pot sequential copolymerization is that each segment can be prepared under the best conditions for each monomer, enabling the synthesis of copolymers from monomers with completely different reactivities. In particular, an unusual combination of monomers that polymerize via different mechanisms, such as radically or cationically polymerizable monomers, can be employed for copolymer synthesis.^{5–7} The development of living polymerization has expanded the scope of macroinitiators, macroterminators, and macromonomers.

Our group recently achieved Lewis acid-selective activation of acetal functional groups for controlled cationic polymerization of vinyl ethers (VEs), leading to the facile synthesis of block or graft copolymers using only the cationic mechanism without post polymerization transformation of functional groups.⁸ Systematic investigation revealed that highly efficient acetal activation for the initiation of VE polymerization was achieved using an oxophilic metal chloride, such as TiCl₄ and ZrCl₄, whereas chlorophilic metal chlorides, such as ZnCl₂ and SnCl₄, were inert. Thus, an acetal-inert Lewis acid was used to prepare a macroinitiator with acetal moieties in the side chains via living cationic copolymerization of an acetal-containing VE monomer. The quantitative activation of the pendant acetals with a catalyst active in acetal-initiated living polymerization of another VE produced a graft

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copolymer. The macroinitiator method should be applicable to the synthesis of copolymers derived from comonomers that are cationically polymerizable but have very different reactivities. Although cationic polymerizations using acetals as a cationogen have been employed in several studies by other groups (e.g., aliphatic acetals treated with trimethylsilyl iodide^{9,10} or aromatic acetals coupled with AlCl_3 ¹¹), catalyst-selective synthesis has never been reported.

In this study, we examined the synthesis of block and graft copolymers containing poly(alkyl VE) and poly(styrene derivatives) segments via living cationic polymerization of styrene derivatives using acetal-containing macroinitiators. Prior to the macroinitiator synthesis, a low-molecular-weight acetal compound was first examined as a model cationogen for the polymerization of *p*-methylstyrene, a monomer that is much less reactive than alkyl VEs. The syntheses of block and graft copolymers containing poly(alkyl VE) and poly(pMeSt) segments were then examined using the initiating system designed based on the results of the model reaction. Block and graft copolymers containing poly(VE) and poly(alkoxystyrene) segments were synthesized in a similar manner.

Experimental section

Materials

Isobutyl VE (IBVE; TCI; >99%) and 1,1-dimethoxyethane (DME; TCI; >98.0%) were distilled twice over calcium hydride. *p*-Methylstyrene (pMeSt; TCI; >98%), *p*-*tert*-butoxystyrene (tBOS; Wako; >98%), *p*-methoxystyrene (pMOS; TCI; >95%), 1,1,2-trimethoxyethane (TME; TCI; >98.0%) and 2,6-di-*tert*-butylpyridine (DTBP; Aldrich; 97%) were distilled twice over calcium hydride under reduced pressure. Ethyl acetate (Wako; >99.5%) was dried overnight over molecular sieves 3A and 4A and distilled twice over calcium hydride. Toluene (Wako; >99.5%), dichloromethane (CH_2Cl_2 ; Wako; >99.0%), and hexane (Wako; 96.0%) were dried using solvent purification columns (Glass Counter; Solvent Dispensing System). The acetal-containing VE 2-(2,2-dimethoxy)ethoxyethyl VE (DMEVE) was prepared from addition reaction of 2-hydroxyethyl VE with bromoacetaldehyde dimethyl acetal according to a literature method⁸ and distilled three times over calcium hydride. The adducts of IBVE with HCl [IBVE-HCl; $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{Cl}$] or acetic acid [IBEA; $\text{CH}_3\text{CH}(\text{O}i\text{Bu})\text{OCOCH}_3$] were prepared from addition reaction of IBVE with HCl or acetic acid according to a literature method¹² respectively. LiBH_4 (Aldrich; 2.0 M solution in tetrahydrofuran) was used as received. TiCl_4 (Aldrich; 1.0 M solution in toluene), ZnCl_2 (Aldrich; 1.0 M solution in diethyl ether), SnCl_4 (Aldrich; 1.0 M solution in CH_2Cl_2), $\text{Et}_{1.5}\text{AlCl}_{1.5}$ (Nippon Aluminum Alkyls; 1.0 M solution in toluene), and EtAlCl_2 (Wako; 1.0 M solution in hexane) were used without further purification. All chemicals, except for toluene, dichloromethane, and hexane, were stored in brown ampules under dry nitrogen.

Polymerization procedure

Synthesis of the linear macroinitiator containing acetal groups in the side chains

The polymerization was performed under a dry nitrogen atmosphere in a glass tube with a three-way stopcock baked using a heat gun (Ishizaki; PJ-206A; blow temperature ~450 °C) under dry nitrogen for 10 min before use. The random copolymerization of DMEVE and IBVE in toluene at 0 °C is described as a representative example. The reaction was initiated by the addition of a prechilled $\text{Et}_{1.5}\text{AlCl}_{1.5}$ solution in toluene (0.20 mL; 200 mM) to a mixture of DMEVE, IBVE, ethyl acetate, and the cationogen (IBVE-HCl) (3.80 mL) at 0 °C using a dry syringe. After a certain period, the polymerization was terminated using a solution of LiBH_4 in tetrahydrofuran¹³ (0.20 mL; 2.0 M). The quenched reaction mixture was diluted with CH_2Cl_2 and washed with water to remove the initiator residues. The volatile materials were then removed under reduced pressure.

Synthesis of the block copolymer by sequential copolymerization

The first-stage polymerization of IBVE was started through the addition of an SnCl_4 solution (0.30 mL in toluene; 100 mM) to a solution (2.40 mL) containing toluene, IBVE, ethyl acetate, the cationogen (IBEA), and $\text{Et}_{1.5}\text{AlCl}_{1.5}$ using dry syringes. To this solution, pMeSt (0.30 mL) was added to start the second-stage polymerization. After a certain period, the polymerization was terminated using chilled methanol containing a small amount (0.1%) of an aqueous ammonia solution (3.0 mL). The quenched reaction mixture was diluted with CH_2Cl_2 and then washed with water to remove the initiator residues. The volatiles were then removed under reduced pressure at 50 °C, and the residue was vacuum-dried for more than 3 h at 60 °C.

Synthesis of the graft copolymer

For the graft copolymerization of pMeSt, a solution (2.10 mL) of predried poly(IBVE-*co*-DMEVE), ethyl acetate, DTBP solution in CH_2Cl_2 , and a solution of TiCl_4 in CH_2Cl_2 (0.30 mL; 50 mM) were successively added to the tube using dry syringes. To this solution, pMeSt (0.30 mL) and SnCl_4 in CH_2Cl_2 (0.30 mL; 200 mM) were successively added to start the pMeSt polymerization. After a certain period, the polymerization was terminated using chilled methanol containing a small amount (0.1%) of an aqueous ammonia solution (3.0 mL).

Characterization

The molecular weight distribution (MWD) of the polymers was measured by gel permeation chromatography (GPC) in chloroform at 40 °C with polystyrene gel columns [Tosoh; TSK gel G-4000H_{XL}, G-3000H_{XL}, and G-2000H_{XL} (exclusion limit molecular weight = 4×10^5 , 6×10^4 , and 1×10^4 , respectively; bead size = 5 μm; column size = 7.8 mm i.d. = 300 mm), TSKgel MultiporeH_{XL}-M × 3 (exclusion limit molecular weight

Table 1. Cationic Polymerization of pMeSt by TME/Lewis Acid Initiating Systems^a

entry	solvent	Lewis acid	additive	time	conv. (%)	$M_n \times 10^{-4}$ (GPC) ^b	$M_n \times 10^{-4}$ (calcd)	M_w/M_n (GPC) ^b
1	CH ₂ Cl ₂	ZnCl ₂	ethyl acetate, DTBP	24 h	0	–	–	–
2		SnCl ₄			2	0.42	0.04	2.02
3		Et _{1.5} AlCl _{1.5}			1	0.73	0.02	2.40
4		TiCl ₄			1	0.06	0.02	1.41
5		TiCl ₄ /SnCl ₄			98	2.00	2.20	1.15
6			none	8 h	97	0.91	2.19	2.05
7			ethyl acetate		99	0.66	2.22	1.24
8	toluene	TiCl ₄ /SnCl ₄	ethyl acetate, DTBP	72 h	4	0.11	0.09	1.22

^a [pMeSt]₀ = 0.76 M, [TME]₀ = 4.0 mM, [Lewis acid]₀ = 20 mM (entries 1, 3 and 4) or 10 mM (entry 2) or 5.0/10 mM (entries 5–8), [DTBP] = 10 mM (except for entries 6 and 7), [ethyl acetate] = 50 mM (except for entry 6), at 0 °C. ^b Determined by GPC with polystyrene calibration.

= 2×10^6 ; bead size = 5 μm; column size = 7.8 mm i.d. × 300 mm), or TSKgel GMH_{HR}-M × 3 or 2 (exclusion limit molecular weight = 4×10^5 ; bead size = 5 μm; column size = 7.8 mm i.d. × 300 mm) flow rate = 1.0 mL/min] connected to a Tosoh DP-8020 pump, a CO-8020 column oven, a UV-8020 ultraviolet detector, and an RI-8020 refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from the chromatographs with respect to 16 polystyrene standards (Tosoh; $M_n = 577\text{--}1.09 \times 10^6$, $M_w/M_n \leq 1.1$). The absolute weight-average molecular weight and the exponent a of the Mark–Houwink–Sakurada equation were determined using the GPC system comprised of a pump (Viscotek VE 1122), two polystyrene gel columns [TSKgel GMH_{HR}-M × 2 (exclusion limit molecular weight = 4×10^5 ; bead size = 5 μm; column size = 7.8 mm i.d. × 300 mm) flow rate = 0.7 mL/min], and a Viscotek TDA 305 triple detector [refractive index, laser light scattering ($\lambda = 670$ nm, 90° and 7°; RALS and LALS), and differential pressure viscometer]. NMR spectra were recorded using a JEOL JNM-ECA 500 spectrometer (500.16 MHz for ¹H). Differential scanning calorimetry (DSC; DSC-6220, Hitachi High-Tech Science) was used to determine the glass transition temperature (T_g) of product copolymers. The heating and cooling rates were 10 °C/min. The T_g of the copolymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan.

Results and discussion

Catalyst survey for acetal-initiated living cationic polymerization of *p*-methylstyrene

To identify a suitable catalyst for the acetal-initiated living cationic polymerization of *p*-methylstyrene (pMeSt), various metal chlorides were examined for the polymerization of pMeSt using 1,1,2-trimethoxyethane (TME) as the cationogen. The reactions were conducted in CH₂Cl₂ at 0 °C in the presence of ethyl acetate as an added base and 2,6-di-*tert*-butylpyridine (DTBP) as a proton trap reagent (Table 1). The catalyst concentration was similar to that used for the living polymeriza-

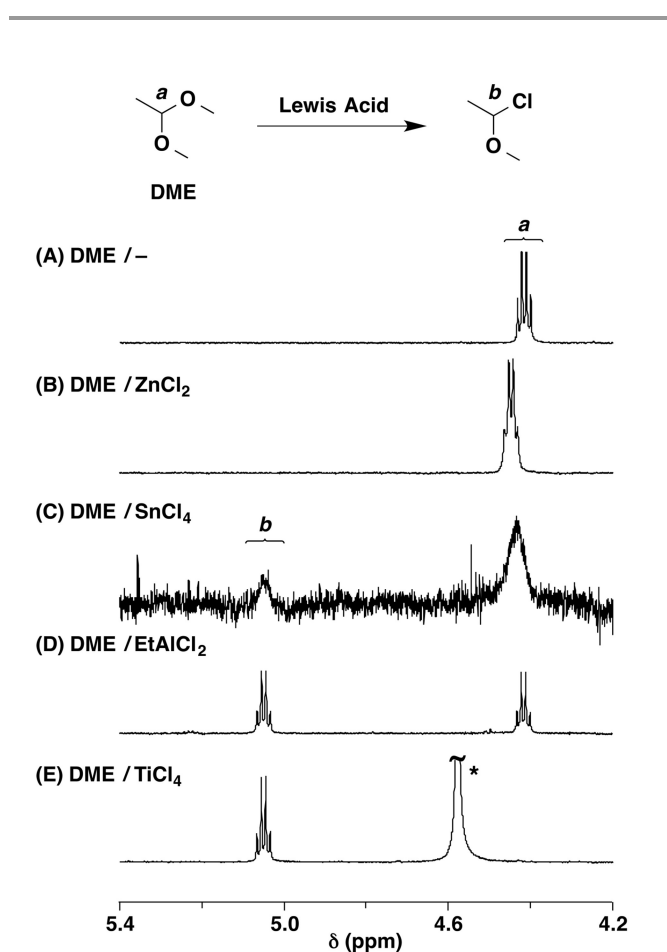
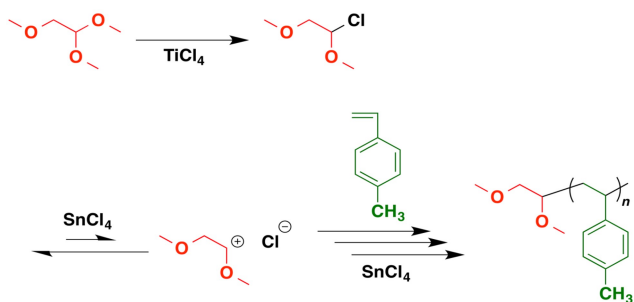


Figure 1. ¹H NMR spectra of (A) DME in toluene-*d*₈ and the mixtures of DME, ethyl acetate, and (B) ZnCl₂, (C) SnCl₄, (D) EtAlCl₂, and (E) TiCl₄ in toluene-*d*₈ at 0 °C: [DME]₀ = 10 mM, [ethyl acetate] = 100 mM, [Lewis acid]₀ = 10 mM. *The methoxy group that coordinated with Ti.

tion of pMeSt with a hydrogen chloride adduct of a styrene derivative or a VE as the cationogen.^{14,15} However, the Lewis acid catalysts used (ZnCl₂, SnCl₄, Et_{1.5}AlCl_{1.5}, and TiCl₄) induced almost no polymerization (entries 1–4 in Table 1). The most unexpected outcome was the lack of polymerization in the presence TiCl₄, which induces the living polymerization of IBVE using TME.⁸ One of the main roles of TiCl₄ is the generation of the real initiating species, i.e., a β -methoxy

methyl VE–hydrogen chloride adduct, via the exchange reaction between the methoxy group of TME and the chloride anion of TiCl_4 . This type of exchange reaction was confirmed by ^1H NMR analysis of the reactions of DME and TiCl_4 in the presence of ethyl acetate [Figure 1 (E)]. Thus, the inability of TiCl_4 in the presence of ethyl acetate to polymerize pMeSt may reflect insufficient Lewis acidity for the propagation of the polymerization of the much less reactive pMeSt. SnCl_4 , a stronger Lewis acid that enables living cationic polymerization of pMeSt with a different cationogen,^{14,15} did not induce polymerization due to the limited exchange reaction between the methoxy group of TME and the chloride anion of SnCl_4 [Figure 1 (C)].

Based on the results above, the polymerization of pMeSt was conducted with an initiating system comprising both TiCl_4 and SnCl_4 , which respectively induces the quantitative generation of the real initiating species through the exchange reaction between the methoxy group and the chloride anion [Figure 1 (E)], and catalyzes the efficient propagation reaction as a real activator (Scheme 1). Polymerization using the $\text{TiCl}_4/\text{SnCl}_4$ dual catalysts in conjunction with TME proceeded smoothly, with near quantitative conversion in 24 h. Furthermore, the product polymer had a narrow MWD ($M_w/M_n = 1.15$) and an M_n value consistent with that calculated from the



Scheme 1. Living cationic polymerization of pMeSt using TME- $\text{TiCl}_4/\text{SnCl}_4$ system.

monomer-to-initiator ratio (entry 5 in Table 1; Figure 2). The linear increase in the M_n values is consistent with the theoretical value and indicates that the living polymerization proceeded under these conditions (the acetal-initiated cationic polymerization of styrene was also examined¹⁶).

The use of appropriate additives was very important for the living polymerization of pMeSt using TME as a cationogen. When the polymerization using the $\text{TiCl}_4/\text{SnCl}_4$ initiating system was performed in the absence of additives, the reaction was uncontrolled and yielded poly(pMeSt) with a broad MWD ($M_w/M_n = 2.05$), most likely because the Lewis acidity of the catalysts was not moderated and/or the propagating carbocation was not stabilized in the absence of a weak Lewis base (entry 6 in Table 1). The polymerization using ethyl acetate alone as an additive was controlled, but the molecular weight of the resulting polymer was lower than the calculated value, likely due to the occurrence of initiation reactions from protic impurities other than TME, such as adventitious water (entry 7 in Table 1). A proton trap reagent, DTBP, was essential for the suppression of such undesired initiation reactions. In addition, a lower polarity solvent was not suitable for the polymerization. Almost no polymerization of pMeSt occurred when toluene was used as the polymerization medium instead of CH_2Cl_2 (entry 8 in Table 1). Thus, the use of the $\text{TiCl}_4/\text{SnCl}_4$ initiating system in CH_2Cl_2 with an added base and a proton trap reagent was indispensable for the living cationic polymerization of pMeSt using acetal as a cationogen.

Macroinitiator-initiated block copolymerization of pMeSt

The synthesis of a block copolymer composed of poly(IBVE) and poly(pMeSt) segments using a poly(IBVE) macroinitiator with an acetal moiety at the chain end was examined (Scheme 2). The macroinitiator with the methoxy- and isobutoxy-containing acetal group was prepared simply by quenching the living cationic polymerization of IBVE with methanol.¹⁷ This macroinitiator quantitatively initiated the polymerization of pMeSt using the $\text{TiCl}_4/\text{SnCl}_4$ initiating system in a manner sim-

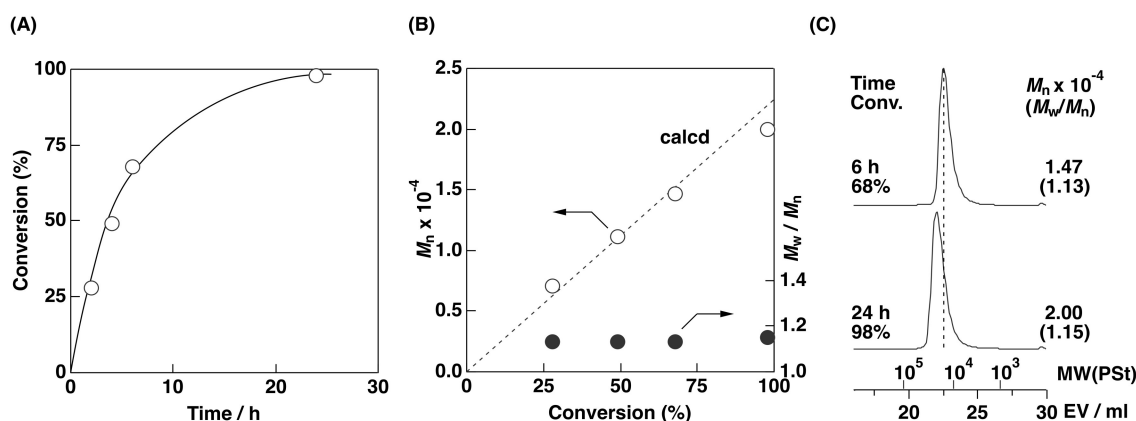
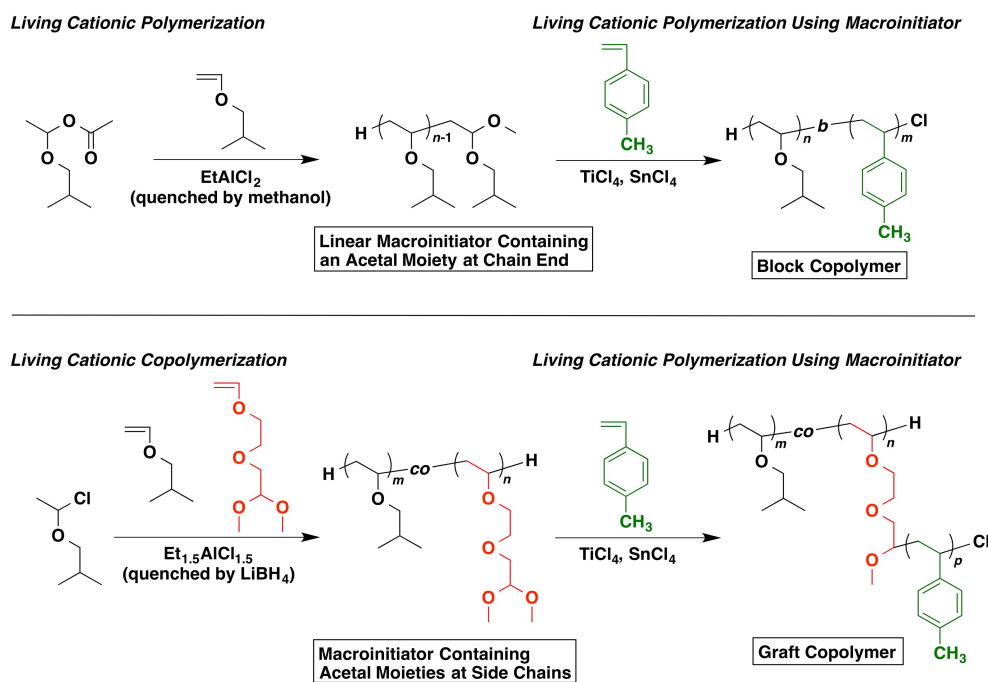


Figure 2. (A) Time–conversion curve, (B) M_n – and M_w/M_n –conversion plots, and (C) MWD curves of the obtained poly(pMeSt)s using TME- $\text{TiCl}_4/\text{SnCl}_4$ system: $[\text{pMeSt}]_0 = 0.76$ M, $[\text{TME}]_0 = 4.0$ mM, $[\text{TiCl}_4]_0 = 5.0$ mM, $[\text{SnCl}_4]_0 = 10$ mM, $[\text{DTBP}] = 10$ mM, $[\text{ethyl acetate}] = 50$ mM, in CH_2Cl_2 at 0°C .



Scheme 2. Synthetic routes of the block and graft copolymers via living cationic polymerization using macroinitiator.

ilar to the reaction using TME as the cationogen. The reaction yielded a block copolymer with a very narrow MWD ($M_w/M_n = 1.08$) without unreacted macroinitiator, suggesting that the terminal acetal moiety was quantitatively activated to function as an initiating site for the polymerization (Figure 3).

A considerable benefit of polymerization using acetal-containing macroinitiators is that both segments can be prepared under completely different reaction conditions. Although a past report¹⁸ showed the successful sequential block copolymerization of methyl VE and styrene, i.e., monomers with a very large difference in reactivity, a drastic change of

reaction conditions (the addition of a catalyst and the rise of temperature) after the addition of styrene was needed for the efficient synthesis of block copolymers. To confirm the superiority of the current method, sequential block copolymerizations of IBVE and pMeSt were examined under conditions suitable for the living polymerization of either of the two monomers. When the sequential block copolymerization was performed under the conditions optimized for IBVE, the polymerization of IBVE proceeded in a living manner, but the subsequent reaction of pMeSt did not occur [Figure S4 (A)]. The use of an additional SnCl_4 catalyst for the second-stage pMeSt polymerization was also ineffective [Figure S4 (B)]. By contrast, the polymerization of IBVE was uncontrolled under the conditions suitable for the living cationic polymerization of pMeSt, yielding a polymer with a broad MWD [Figure S4 (C)]. These results demonstrate that poly(IBVE)-*block*-poly(pMeSt) is difficult to synthesize via sequential block copolymerization with the present system because of the significantly large differences in reactivity between IBVE and pMeSt.

Precision synthesis of graft copolymer via the polymerization of pMeSt using a macroinitiator containing acetal moieties in its side chains

The synthesis of graft copolymers was examined via the initiation of living cationic polymerization of pMeSt from the acetal groups in the side chains of a poly(VE). Poly(IBVE_{78-co}-DMEVE₄) (Scheme 2), a macroinitiator, was prepared via the living cationic copolymerization of IBVE with DMEVE, an acetal-containing monomer.⁸ The acetal moieties were intact during the copolymerization with $\text{Et}_{1.5}\text{AlCl}_{1.5}$ as a catalyst.

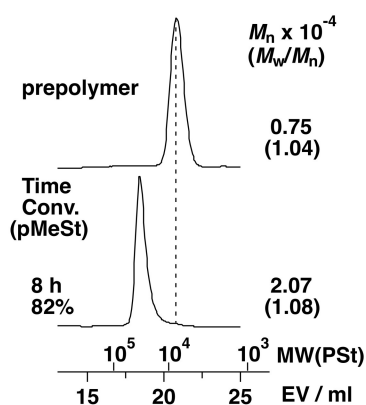


Figure 3. MWD curves for the synthesis of poly(IBVE)-*block*-poly(pMeSt) using poly(IBVE) as a macroinitiator: $[\text{pMeSt}]_0 = 0.76 \text{ M}$, $[\text{poly}(\text{IBVE})]_0 = 4.0 \text{ mM}$, $[\text{TiCl}_4]_0 = 5.0 \text{ mM}$, $[\text{SnCl}_4]_0 = 10 \text{ mM}$, $[\text{DTBP}] = 10 \text{ mM}$, $[\text{ethyl acetate}] = 50 \text{ mM}$, in CH_2Cl_2 at 0°C .

Table 2. Synthesis of Graft Copolymer Containing Poly(pMeSt) by Macroinitiator-TiCl₄/SnCl₄ Initiating Systems^a

entry	[TiCl ₄] ₀ (mM)	[SnCl ₄] ₀ (mM)	time	conv. (%)	$M_n \times 10^{-4}$ (GPC) ^b	M_w/M_n (GPC) ^b	NB ^c
1	5.0	10	20 h	40	2.85	1.20	4
2	10	10	24 h	100	2.44	2.10	–
3	5.0	20	2 h	94	5.69	1.22	4

^a [pMeSt]₀ = 0.76 M, [acetal units]₀ = 4.0 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C. ^b Determined by GPC with polystyrene calibration. ^c The number of branches: calculated from ¹H NMR integral ratios.

Using this copolymer as a macroinitiator, the polymerization of pMeSt was conducted under similar conditions as those for the polymerization using TME as a cationogen and the synthesis of poly(IBVE)-*block*-poly(pMeSt). The polymerizations at the [acetal units]₀/[TiCl₄]₀/[SnCl₄]₀ ratio of 4.0 mM/5.0 mM/10 mM or 4.0 mM/10 mM/10 mM yielded the product with a narrow MWD, but the conversion of pMeSt plateaued (entry 1 in Table 2; circle symbols in Figure 4) or the product had a multimodal MWD (entry 2 in Table 2; square symbols in Figure 4; Figure S5), respectively. The lower reactivity of the acetal moieties on the side chain than that at the chain end may be due to the electron-withdrawing inductive effect of the oxygen atom adjacent to the β-carbon. Quantitative consumption of pMeSt was achieved when the amount of SnCl₄ was increased ([acetal units]₀/[TiCl₄]₀/[SnCl₄]₀ = 4.0 mM/5.0 mM/20 mM). The monomer conversion neared 100% within 2 h, and a product with a unimodal MWD was obtained without the generation of any byproducts (entry 3 in Table 2; triangle symbols in Figure 4; Figure 5). ¹H NMR analysis (Figure 6) revealed the disappearance of the acetal peak (peak *k*) and the appearance of the methine peak of the carbon–chlorine end at the poly(pMeSt) chain end (peak *q*) after the polymerization. Because these peaks had similar chemical shifts (4.2–4.3 ppm), acid hydrolysis of the product was conducted to estimate the

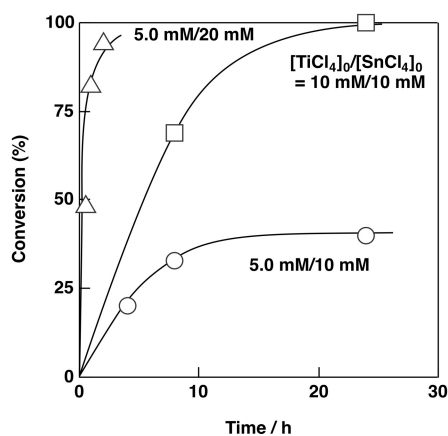


Figure 4. Time-conversion curves for the synthesis of poly(IBVE-co-DMEVE)-*graft*-poly(pMeSt) using poly(IBVE-co-DMEVE) as a macroinitiator: [pMeSt]₀ = 0.76 M, [acetal units]₀ = 4.0 mM, [TiCl₄]₀ = 5.0 or 10 mM, [SnCl₄]₀ = 10 or 20 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C; the data correspond to those listed in Table 2.

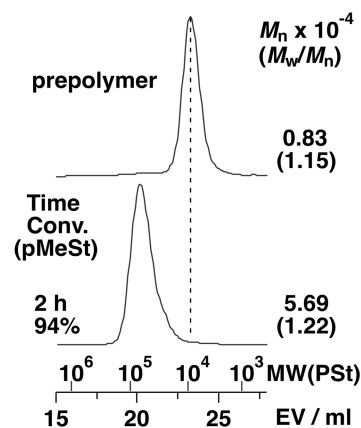


Figure 5. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-*graft*-poly(pMeSt) using poly(IBVE-co-DMEVE) as a macroinitiator: [pMeSt]₀ = 0.76 M, [acetal units]₀ = 4.0 mM, [TiCl₄]₀ = 5.0 mM, [SnCl₄]₀ = 20 mM, [DTBP] = 10 mM, [ethyl acetate] = 50 mM, in CH₂Cl₂ at 0 °C.

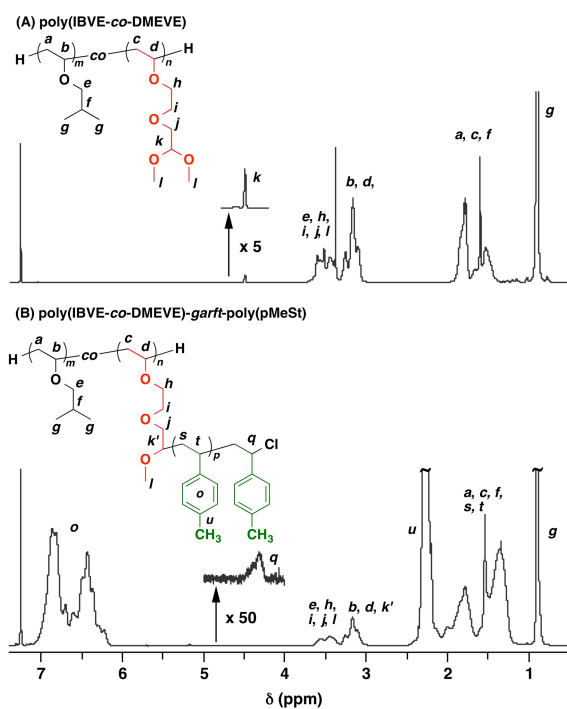


Figure 6. ¹H NMR spectra of poly(IBVE-co-DMEVE)-*graft*-poly(pMeSt) ($M_n = 5.02 \times 10^4$, $M_w/M_n = 1.24$) (B) and the linear macroinitiator ($M_n = 0.83 \times 10^4$, $M_w/M_n = 1.15$) (A) (500.16 MHz, CDCl₃, 30 °C).

amount of residual acetal moieties.¹⁹ No peak assignable to aldehyde protons, which would be generated by the hydrolysis of the acetal group, was observed (Figure S6). These results indicated that the pendant acetal groups of the macroinitiator were activated quantitatively for the initiation reactions, and a graft copolymer of poly(pMeSt) graft chains was successfully synthesized with the use of the initiating system composed of appropriate concentrations of TiCl₄ and SnCl₄. The number of branch chains was estimated to be approximately 4 by ¹H NMR, indicating quantitative initiation of the reaction by the copolymer macroinitiator.

The absolute molecular weight of the resulting poly(IBVE-*co*-DMEVE)-*graft*-poly(pMeSt) was determined by GPC analysis using RALS and LALS detectors. The resulting value ($M_w = 11 \times 10^4$) was in good agreement with the calculated value ($M_w = 9.8 \times 10^4$) and was larger than the relative M_w value obtained from the GPC analysis with polystyrene standards ($M_w = 7.0 \times 10^4$), supporting the formation of a branched and compact structure. In addition, the exponent a of the Mark–Houwink–Sakurada equation was calculated to be 0.34 from the GPC data obtained with a viscosity detector. The a value of less than 0.5 also indicates the formation of a branched structure in the copolymer synthesized using the linear macroinitiator.

Solubility and thermal properties of the resulting copolymers

The solubilities of the resulting copolymers composed of poly(IBVE) and poly(pMeSt) segments were investigated. Although poly(IBVE) and poly(pMeSt) exhibit similar solubilities in various solvents, poly(IBVE) is soluble in acetone, whereas poly(pMeSt) exhibits upper critical solution temperature (UCST)-type phase separation. The resulting graft copolymer exhibited UCST-type phase separation in acetone, indicating that the solubilities of the resulting copolymers are likely governed largely by the poly(pMeSt) branches.

DSC analysis was also conducted to assess the thermal properties of the copolymers (Table 3; Figure S7). The resulting block copolymer had two glass transition temperatures (T_g s) of -19 °C and 110 °C. These values correspond to the T_g s of the poly(IBVE) and poly(pMeSt) segments, respectively. The T_g of the poly(pMeSt) segment was slightly higher than that of a pMeSt homopolymer because the former has a molecular weight larger than that of the analyzed homopolymer.²⁰ By con-

Table 3. T_g Values of Polymers

polymer	T_g (°C) ^a
poly(IBVE)	-19 ^b
poly(IBVE ₁₁₀ - <i>co</i> -DMEVE ₅) ^c	-27
poly(pMeSt ₈₈) ^d	100
poly(IBVE ₁₃₈)- <i>block</i> -poly(pMeSt ₁₄₄) ^e	-19, 110
poly(IBVE ₇₈ - <i>co</i> -DMEVE ₄)- <i>graft</i> -poly(pMeSt ₁₇₉) ^f	85

^a The heating and cooling rates were 10 °C/min. ^b Reference 22. ^c $M_n = 1.19 \times 10^4$, $M_w/M_n = 1.13$. ^d $M_n = 1.04 \times 10^4$, $M_w/M_n = 1.19$. ^e $M_n = 3.81 \times 10^4$, $M_w/M_n = 1.12$. ^f $M_n = 5.69 \times 10^4$, $M_w/M_n = 1.22$.

trast, the graft copolymer exhibited a single T_g of 85 °C, most likely because the thermal properties of the graft copolymer are governed mainly by the properties of the branch segments. The lower T_g of the graft copolymer is attributable to the larger amount of terminal end groups and larger free volume.²¹

Polymerizations of alkoxy styrenes using macroinitiators

Copolymer syntheses using acetal-containing macroinitiators were also examined for the polymerization of alkoxy styrenes, which are styrene derivatives that are more reactive than pMeSt²³ (past studies showed that the sequential block copolymerization of IBVE and alkoxy styrenes proceed²⁴). The cationic polymerizations of pMOS or tBOS were performed using an acetal end-containing poly(IBVE) as a macroinitiator under conditions similar to those for the polymerization of pMeSt, except that a larger amount of ethyl acetate was employed. The polymerizations proceeded smoothly, selectively producing block copolymers with narrow MWDs ($M_w/M_n < 1.1$) (Figure 7). These polymerizations were not accompanied by side reactions or unreacted macroinitiators.

For the syntheses of graft copolymers containing poly(alkoxy styrene) segments the cationic polymerization of pMOS using poly(IBVE-*co*-DMEVE) as a macroinitiator was performed under similar conditions as for the synthesis of poly(IBVE)-*block*-poly(pMOS). The initiation efficiency of the synthesis of graft copolymers using pMOS was low when equimolar amounts of TiCl₄ and acetal units were employed (entry 1 in Table 4). In turn, the reaction using a higher concentration of TiCl₄ proceeded without the occurrence of any side reactions unlike the case of tBOS (vide infra). Very high initiation efficiencies were accomplished with the use of a five-fold molar excess of TiCl₄ to acetal units. The polymerization was complete in 3 min, yielding a product with a relatively narrow MWD ($M_w/M_n = 1.30$) [entry 2 in Table 4; Figure 8 (A)]. Approximately 90% of the acetal units on the side chains of the macroinitiator were activated during the polymerization, as confirmed by ¹H NMR spectroscopy (Figure S8). The graft co-

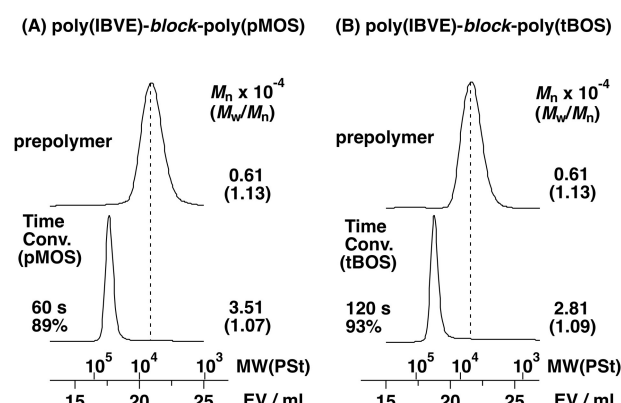


Figure 7. MWD curves for the synthesis of poly(IBVE)-*block*-poly(alkoxy styrene)s using poly(IBVE) as a macroinitiator: [monomer]₀ = 0.75 M (A) or 0.53 M (B), [poly(IBVE)]₀ = 4.0 mM, [TiCl₄]₀ = 5.0 mM, [SnCl₄]₀ = 10 mM, [DTBP] = 10 mM, [ethyl acetate] = 1.0 M (A) or 0.50 M (B), in CH₂Cl₂ at 0 °C.

Table 4. Synthesis of Graft Copolymer Containing Poly(alkoxystyrene) by Macroinitiator-TiCl₄/SnCl₄ Initiating Systems^a

entry	monomer	[TiCl ₄] ₀ (mM)	time	conv. (%)	$M_n \times 10^{-4}$ (GPC) ^b	M_w/M_n (GPC) ^b	initiation efficiency (%) ^c	NB ^d
1	pMOS	10	3 min	59	2.86	1.34	~40	2
2		20	3 min	98	6.71	1.30	~90	4
3	tBOS	5.0	10 min	99	13.8	1.58	~50	4

^a [monomer]₀ = 0.75 M (entries 1 and 2) or 0.53 M (entry 3), [acetal units]₀ = 4.0 mM (entries 1 and 2) or 4.8 mM (entry 3), [SnCl₄]₀ = 10 mM, [DTBP] = 10 mM (entries 1 and 3) or 20 mM (entry 2), [ethyl acetate] = 1.0 M (entries 1 and 2) or 0.50 M (entry 3), in CH₂Cl₂ at 0 °C. ^b Determined by GPC with polystyrene calibration. ^c Determined by ¹H NMR analysis. ^d The number of branches: calculated from ¹H NMR integral ratios.

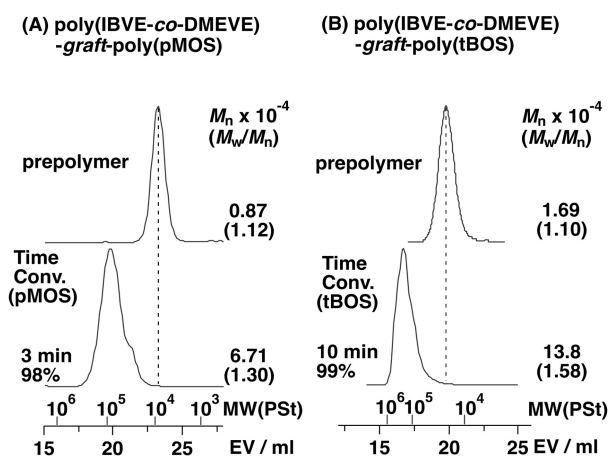


Figure 8. MWD curves for the synthesis of poly(IBVE-co-DMEVE)-graft-poly(alkoxystyrene)s using poly(IBVE-co-DMEVE) as a macroinitiator: [monomer]₀ = 0.75 M (A) or 0.53 M (B), [acetal units]₀ = 4.0 mM (A) or 4.8 mM (B), [TiCl₄]₀ = 20 mM (A) or 5.0 mM (B), [SnCl₄]₀ = 10 mM, [DTBP] = 20 mM (A) or 10 mM (B), [ethyl acetate] = 1.0 M (A) or 0.50 M (B), in CH₂Cl₂ at 0 °C.

polymerization using tBOS proceeded also smoothly, and a product with a unimodal MWD was obtained [entry 3 in Table 4; Figure 8 (B)]. However, detailed ¹H NMR analysis revealed that half of the acetal moieties on the macroinitiator remained unactivated (Figure S9). The polymerization was conducted with a larger concentration of TiCl₄ (10 mM) to improve the initiation efficiency. However, the polymerization was hampered by the side reaction between TiCl₄ and the *tert*-butoxy group²⁵ on tBOS (Figure S10).

The absolute molecular weight of the resulting poly(IBVE-co-DMEVE)-graft-poly(pMOS) (entry 2 in Table 4) was determined by GPC analysis using light scattering detectors. The resulting value ($M_w = 15 \times 10^4$) was close to the calculated value ($M_w = 11 \times 10^4$) and was larger than the relative M_w value obtained from the GPC analysis with polystyrene standards ($M_w = 8.7 \times 10^4$). The exponent a of the Mark–Houwink–Sakurada equation was calculated to be 0.31. These results indicate the obtained copolymer having branched structure.

Conclusions

The precise synthesis of block and graft copolymers containing poly(alkyl VE) and poly(styrene derivatives) segments was

successfully achieved using macroinitiators featuring acetal moieties at the chain ends or on the side chains. Living cationic polymerization of pMeSt, pMOS, or tBOS proceeded via initiation reactions from the acetal units with the use of the TiCl₄/SnCl₄ initiating system at appropriate concentration ratios. A notable benefit of the method used in this study is that each segment of the block or graft copolymers can be synthesized under completely different reaction conditions. In particular, a block copolymer was successfully obtained from IBVE and pMeSt, monomers that are incompatible under identical conditions and cannot be copolymerized via the sequential addition method. Thus, the synthetic method using macroinitiators with acetal units as latent initiating sites is expected to expand the strategies for the precise synthesis of copolymers with well-defined structures from monomers with very different reactivities.

Acknowledgments

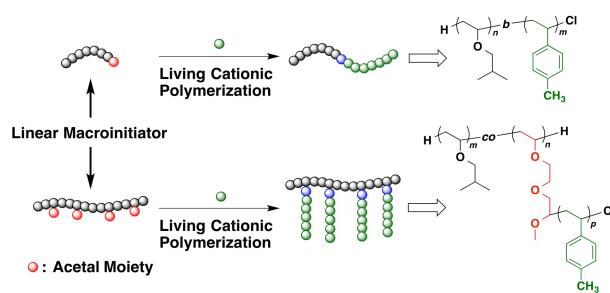
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Block and graft copolymers containing poly(*p*-methylstyrene) and poly(alkyl vinyl ether) segments were synthesized via selective acetal-initiated living cationic polymerizations of *p*-methylstyrene using poly(alkyl vinyl ether)s with acetal moieties as macroinitiators.