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R–Cl/$SnCl_4$/*n*-Bu_4NCl-induced direct living cationic polymerization of naturally-derived unprotected 4-vinylphenol, 4-vinylguaiacol, and 4-vinylcatechol in CH_3CN

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A combination of an alkyl chloride (R–Cl) as an initiator and $MtCl_n$ as an activator, which is a common initiating system for living cationic polymerizations, was used for the direct cationic polymerization of unprotected 4-vinylphenol or *p*-hydroxystyrene (pHOS), which were derived from naturally-occurring *p*-coumaric acid via decarboxylation, in the absence and presence of additives such as *n*-Bu_4NCl. The initiating system consisting of an HCl-adduct of *p*-methoxystyrene (pMOS–HCl), $SnCl_4$, and *n*-Bu_4NCl induced the direct living cationic polymerization of pHOS in CH_3CN at –40 °C without using any protective groups on the phenolic groups and resulted in well-defined poly(pHOS) with controlled molecular weights and narrow molecular weight distributions (MWDs) (M_w/M_n = 1.1–1.2). The pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl initiating system was also effective for living cationic polymerization of pMOS in CH_3CN even in the presence of phenol, where side reactions such as proton initiation and chain-transfer reactions caused by phenol were almost completely suppressed. ^1H and ^{119}Sn NMR analyses of the mixtures revealed that CH_3CN strongly interacted with both the phenol and $SnCl_4$ and thereby prevented the direct interaction between the phenol and $SnCl_4$, suppressing these side reactions. Similar direct living cationic polymerizations of 4-vinylguaiacol and 4-vinylcatechol, which were obtained via decarboxylation of naturally-occurring ferulic and caffeic acids, respectively, resulted in well-defined polymers (M_w/M_n = 1.1–1.2) in CH_3CN without protecting the phenol and catechol groups.

Introduction

Cationic polymerizations are generally conducted in the absence of polar functional groups such as hydroxyl moieties because these groups tend to react with the growing carbocations and metal halides as Lewis acid catalysts to terminate the propagation and/or to deactivate the catalysts.[1–3] Therefore, protic solvents are rarely used for cationic polymerizations, and polar functional groups in monomers are usually protected during these reactions.

Since the 1980s, living cationic polymerizations of various vinyl monomers, including vinyl ethers, isobutylene, and styrenes, have been developed using the reversible equilibrium between the growing cationic species and the dormant covalent bond species.[4–7] The living cationic polymerization can be achieved by an appropriate combination of an initiator, which is a protonic acid with a nucleophilic anion or its adduct with the monomer (R–X), and a Lewis acid catalyst (MtX_n), which can reversibly activate the dormant species to generate a small amount of the carbocation in an equilibrium. In addition to these two components, additives such as weak Lewis bases and salts with nucleophilic anions may be used to stabilize the growing carbocation and/or tune the Lewis acidity of the catalyst. Among the various initiating systems for living cationic polymerizations, a combination of alkyl chloride (R–Cl), $SnCl_4$, and *n*-Bu_4NCl is one of the most versatile systems for various cationically polymerizable monomers, such as styrenes and vinyl ethers.[8–19] However, polar hydroxy functional groups must be protected during living cationic polymerizations because they generally induce side reactions that deteriorate the livingness of the polymerization. In addition, most metal halide catalysts easily react with hydroxyl groups and lose their activity via the formation of a less Lewis acidic metal alkoxide or phenoxide.

4-Vinylphenol or *p*-hydroxystyrene (pHOS) is a representative functionalized styrene monomer, and the corresponding polymer is used for photoresists, epoxy-curing agents, adhesives, etc.[20–25] The phenol group in pHOS is usually protected by *tert*-butyl, *tert*-butoxycarbonyl, acetyl, benzoyl, benzyl, or trialkylsilyl groups[26–34] because it generally induces undesired side reactions such as protic initiation, chain transfer, and termination reactions during the cationic polymerization. However, once it is protected, some of the protected styrene monomers show high cationic polymerizability due to the electron-donating substituent and can be polymerized in a living fashion with an appropriate initiating system such as HI/ZnI_2, R–I/ZnI_2, R–Cl/$ZnCl_2$, R–Cl/$SnBr_4$, R–Cl/$TiCl_4$/Ti(O*i*-Pr)$_4$, R–Cl/$SnCl_4$/*n*-Bu_4NCl, and R–Cl/$SnCl_4$/EtOAc,[19,35–40] most of which are also effective for the living cationic polymerization of *p*-

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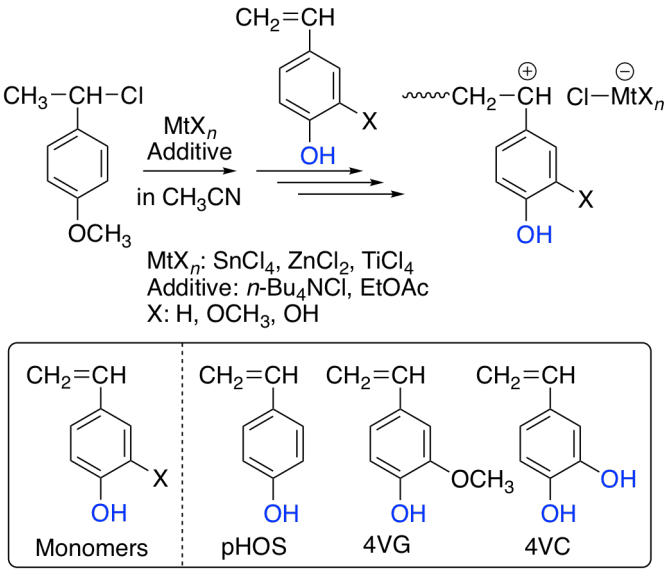
methoxystyrene (pMOS) with a similar electron-donating alkoxy substituent. Furthermore, not only in anionic but also in radical polymerizations, the phenolic groups must be protected because phenol moieties can serve as both a terminator of the growing carbanion and an inhibitor of the carbon radical species.[33,34,41–51] Therefore, protection of the phenol group in pHOS is required to prepare well-defined poly(pHOS) as well as the corresponding block copolymers by any living cationic, anionic, and radical polymerizations.

However, despite such a pessimistic view of the direct living polymerization of pHOS without any protecting groups except via direct uncontrolled cationic and radical polymerizations,[52–54] we previously reported that a unique initiating system consisting of an appropriate alcohol (R–OH) as an initiator and $BF_3{\cdot}OEt_2$ as a Lewis acid catalyst induced the direct cationic polymerization of unprotected pHOS in acetonitrile (CH_3CN), which is a good solvent for both pHOS and the resulting poly(pHOS).[55,56] Furthermore, the addition of water gradually narrowed the molecular weight distribution (MWD) of the resulting polymer and finally resulted in poly(pHOS) with controlled molecular weights and relatively narrow MWDs (M_w/M_n ~ 1.3). The unique feature of the specific and controlled/living cationic polymerization is that $BF_3{\cdot}OEt_2$ is relatively stable even in the presence of hydroxyl groups and selectively activates the dormant C–OH terminal, which originates from the initiator as well as the added water because of its high oxophilicity. While this R–OH/$BF_3{\cdot}OEt_2$-based initiating system is applicable to various styrene derivatives, the controllability is moderate in terms of MWDs (M_w/M_n ~ 1.3 for pHOS and pMOS, M_w/M_n ~ 1.6 for *p*-methylstyrene and *p*-chlorostyrene, and M_w/M_n ~ 1.8 for styrene and *p*-chloromethylstyrene).[57–59] Other R–OH/boron-based Lewis acid systems have also been reported for pMOS in aqueous media.[60,61]



Scheme 1 Direct cationic polymerization of unprotected *p*-hydroxystyrene (pHOS), 4-vinylguaiacol, 4-vinylcatechol with pMOS–HCl/MtX_n/Additive in CH_3CN

In this study, we employed a more common living cationic polymerization system based on R–Cl/$MtCl_n$ to achieve the direct living cationic polymerization of unprotected pHOS in CH_3CN in the absence or presence of *n*-Bu_4NCl (Scheme 1). In particular, the effects of CH_3CN and *n*Bu_4NCl on the polymerization were investigated. Furthermore, the controlled/living cationic polymerization of pMOS with R–Cl/$SnCl_4$/*n*-Bu_4NCl in the presence of phenol was examined. The effects of CH_3CN on the polymerization of pMOS and the model reaction were studied. Finally, other biobased styrene monomers with hydroxyl groups on the aromatic ring, such as 4-vinyguaiacol (4VG) and 4-vinylcatechol (4VC), which can be easily prepared by decarboxylation of naturally occurring ferulic and caffeic acid, respectively,[62–64] were directly polymerized with R–Cl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN. This common initiating system for living cationic polymerization, R–Cl/$SnCl_4$/*n*-Bu_4NCl, enabled the direct controlled/living cationic polymerization of all the phenolic monomers without protecting groups in CH_3CN and provided well-controlled polymers with narrow MWDs (M_w/M_n = 1.1–1.2).

Results and discussion

Direct cationic polymerization of *p*-hydroxystyrene with R–Cl/$MtCl_n$ in CH_3CN

The direct cationic polymerization of unprotected pHOS was investigated using common living cationic polymerization systems, i.e., R–Cl/$MtCl_n$, where the adduct of HCl and *p*-methoxystyrene (pMOS–HCl) were used as the R–Cl initiator and various Lewis acids such as $SnCl_4$, $ZnCl_2$, and $TiCl_4$ were used as the activator in CH_3CN in the absence and presence of *n*-Bu_4NCl as an additive at –40 °C. Table 1 and Fig. S1 show the results of the direct polymerization of pHOS under various conditions. Here, pHOS, which was used in all experiments, was obtained via the simple decarboxylation of naturally-occurring *p*-coumaric acid in the presence of an amine at high temperature.

The pMOS–HCl/$SnCl_4$ initiating system induced rapid polymerization of pHOS (>99% conversion in 10 s) even without protection of the phenolic groups, resulting in polymers with high molecular weights and broad MWDs (entry 1 in Table 1 and Fig. S1A). This result indicates that $SnCl_4$ does not lose its activity in the presence of phenolic groups but does generate polymers with uncontrolled molecular weights. However, in the presence of *n*-Bu_4NCl, especially when used in slightly excess relative to $SnCl_4$ ($[n\text{-}Bu_4NCl]_0/[SnCl_4]_0$ = 30/20 mM), the obtained polymers showed very narrow MWDs (M_w/M_n = 1.15) (entry 3 and Fig. S1C). However, the number-average molecular weights (M_n(SEC) values) of the poly(pHOS), which were calibrated against polystyrene standards by size-exclusion chromatography (SEC) in DMF, were higher than the calculated values (M_n(calcd)), assuming that one molecule of pMOS–HCl generates one living polymer chain, due to their different hydrodynamic volumes. The M_n(SEC) values were then multiplied by a calibration factor (f = 0.396), which was obtained from the ratio of M_n measured by multiangle laser light scattering (M_n(MALLS)) and the M_n(SEC) of poly(pHOS), to give the corrected values (M_n(coor.)), which were close to M_n(calcd). These results suggest that pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl indeed

Table 1 Direct cationic polymerization of unprotected pHOS in CH_3CN using various Lewis acids and additives[a]

entry	Lewis acid	Additive	time	conv. (%)[b]	M_n(calcd)[c]	M_n(SEC)[d]	M_n(corr.)[e]	M_w/M_n[d]
1	$SnCl_4$	none	10 sec	>99	6200	41800	16500	8.87
2	$SnCl_4$	nBu$_4$NCl (16 mM)	10 sec	>99	6200	45300	17900	6.35
3	$SnCl_4$	nBu$_4$NCl (30 mM)	6 h	96	5900	15800	6300	1.15
4	$SnCl_4$	EtOAc (1.0 M)	1 min	>99	6200	72600	28700	3.93
5[f]	$ZnCl_2$	none	20 min	>99	6200	19600	7800	1.58
6[f]	$ZnCl_2$	nBu$_4$NCl (16 mM)	8 h	90	5600	17800	7000	1.33
7[f]	$ZnCl_2$	nBu$_4$NCl (30 mM)	30 h	0	–	–	–	–
8	$TiCl_4$	none	12 h	>99	6200	6000	2400	3.47
9	$TiCl_4$	nBu$_4$NCl (16 mM)	12 h	30	2000	1500	600	1.45
10	$TiCl_4$	nBu$_4$NCl (30 mM)	12 h	23	–	–	–	–

[a] Polymerization condition: $[pHOS]_0$ = 500 mM, $[pMOS\text{-}HCl]_0$ = 10 mM, $[Lewis\ Acid]_0$ = 20 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40°C. [b] Determined by ^{1}H NMR. [c] M_n(calcd) = MW(pHOS) × ($[HOS]_0/[pMOS–HCl]_0$) × conv + MW(pMOS–HCl). [d] Determined by SEC using polystyrene standards. [e] Determined by SEC using polystyrene standards and the calibration factor (f = 0.396) which was obtained from the ratio between M_n (MALLS) and M_n (SEC) of poly(pHOS). [f] Containing 2 vol% of Et_2O.

enables the direct controlled/living cationic polymerization of pHOS in CH_3CN to give well-defined poly(pHOS) with controlled molecular weights and narrow MWDs. In contrast, polymerization with pMOS–HCl/$SnCl_4$ in the presence of ethyl acetate resulted in uncontrolled M_n values and broad MWDs (entry 4 and Fig. S1D) even though ethyl acetate is an effective additive for controlling the cationic polymerization of pMOS with R–Cl/$SnCl_4$ in toluene.[65]

A weaker Lewis acid, $ZnCl_2$, also induced the direct cationic polymerization of pHOS in conjunction with pMOS–HCl in CH_3CN (entry 5). The obtained polymer had a narrower MWD (M_w/M_n = 1.58) and an M_n(corr.) closer to M_n(calcd) than those obtained with R–Cl/$SnCl_4$ under the same conditions (entry 5). The addition of n-Bu$_4$NCl, which was used as a lower loading than $ZnCl_2$ ($[n\text{-}Bu_4NCl]_0/[ZnCl_2]_0$ = 16/20 mM), retarded the polymerization and narrowed the MWD (entry 6). The addition of excess nBu$_4$NCl relative to $ZnCl_2$ ($[n\text{-}Bu_4NCl]_0/[ZnCl_2]_0$ = 30/20 mM) stopped the polymerization (entry 7) due to loss of the activity. These results indicate that the direct controlled cationic polymerization of pHOS can also be achieved even with $ZnCl_2$ in CH_3CN.

As another $MtCl_n$, $TiCl_4$, which is a stronger Lewis acid than $SnCl_4$, also induced the direct polymerization but resulted in uncontrolled polymers with broad MWDs and low molecular weights (entry 8). Even in the presence of a small amount of n-Bu$_4$NCl ($[n\text{-}Bu_4NCl]_0/[TiCl_4]_0$ = 16/20 mM), the polymerization stopped at a low conversion and resulted in only low-molecular-weight oligomers (entry 9). Further addition of n-Bu$_4$NCl ($[n\text{-}Bu_4NCl]_0/[TiCl_4]_0$ = 30/20 mM) completely stopped the polymerization (entry 10). Unlike the previous two Lewis acids ($SnCl_4$ and $ZnCl_2$), in the case of $TiCl_4$, the reaction mixture immediately turned red upon addition of $TiCl_4$ to the monomer solution (Fig. S2). The color change showed that $TiCl_4$ was decomposed via a ligand-exchange reaction between Cl and phenoxide anions, which generated inactive phenoxy titanium compounds. Thus, $TiCl_4$ was not effective for the direct cationic polymerization of pHOS.

These results indicate that even common living cationic polymerization systems, such as R–Cl/$SnCl_4$/n-Bu$_4$NCl, are also effective for inducing and controlling the direct polymerization of pHOS without protecting the phenolic groups under appropriate conditions in CH_3CN.

Direct living cationic polymerization of *p*-hydroxystyrene with

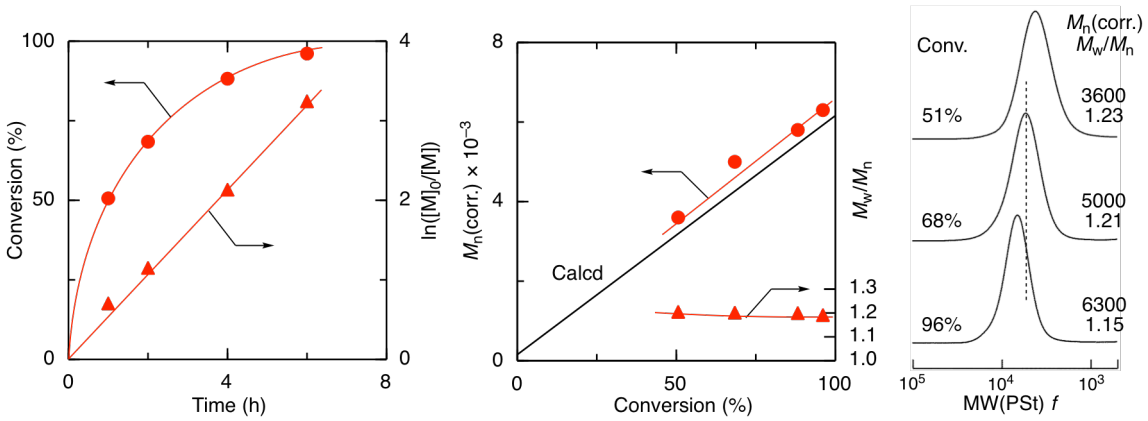


Fig. 1 Time-conversion and SEC curves for direct cationic polymerization of unprotected pHOS with pMOS–HCl/$SnCl_4$/n-Bu$_4$NCl in CH_3CN: $[pHOS]_0/[pMOS\text{–}HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 500/10/20/30 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C. M_n(corr.) was determined by SEC using polystyrene standard and the calibration factor (f = 0.396).

R–Cl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN

To further evaluate the living cationic polymerization of pHOS with R–Cl/$SnCl_4$/*n*-Bu_4NCl, the kinetics of the polymerization were studied in CH_3CN at –40 °C. As shown in Fig. 1, the first-order plots of $(\ln[M]_0/\ln[M])$ versus time were linear, indicating that the concentration of growing carbocations was constant during the polymerization. As the polymerization proceeded, size-exclusion chromatography (SEC) curves of the obtained polymers shifted to a higher molecular weight region and retained the narrow MWD (M_w/M_n = 1.1–1.2). In addition, the M_n(corr.) values increased in direct proportion to the monomer conversion and agreed well with the calculated value assuming that one pMOS–HCl initiator generates one polymer chain. These results indicate that the direct living cationic polymerization of unprotected pHOS proceeded despite the presence of unprotected phenolic hydroxyl groups in the monomer.

Furthermore, monomer addition experiments were carried out; a new batch of monomer was added when the first batch of monomer was almost fully consumed (conversion = 93%). Even after the monomer addition, the M_n(corr.) further increased linearly and agreed with the calculated values (Fig. 2). Furthermore, no tailing was observed in the SEC curves. These results again indicate that almost no side reactions occurred during the direct cationic polymerization of pHOS with R–Cl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN at –40 °C.

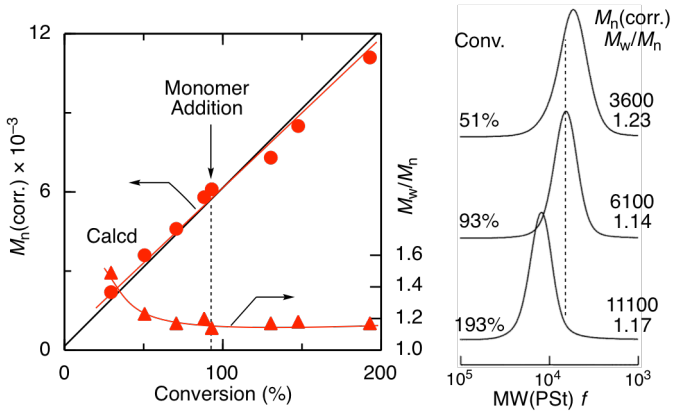


Fig. 2 M_n, M_w/M_n, and SEC curves for monomer-addition experiment in direct cationic polymerization of unprotected pHOS with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN: $[pHOS]_0/[HOS]_{add}/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 500/500/10/20/30 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C. M_n(corr.) was determined by SEC using polystyrene standard and the calibration factor (f = 0.396).

The polymer obtained with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN was analyzed by ^{1}H NMR spectroscopy and MALDI-TOF-MS (Fig. 3). The ^{1}H NMR spectrum showed signals for the repeating pHOS unit, including the main-chain methylene and methine (*a*, *b*), the aromatic (*c*), and the phenolic hydroxyl (*d*) protons (Fig. 3A). In addition to these signals, signals characteristic of the end groups were also observed. They are the methyl (α) and methoxy (β) groups derived from the initiator (pMOS–HCl) and a methoxy group (ω) from quenching the polymerization with methanol. The M_n value (M_n(NMR)) was determined from the peak intensity ratio of the aromatic ring (*c*) of the pHOS units to the initiating terminal methyl groups (α) because the methoxy proton (β) was slightly overlapped with the ω-terminal methine proton. The value was 3500 and was close to the theoretical value (M_n(calcd) = 3200) as well as that measured by MALLS (M_n(MALLS) = 3600). These results indicate that one initiator generated one polymer chain without any side reactions, such as the undesired protic initiation or chain transfer reaction by the phenolic hydroxyl groups.

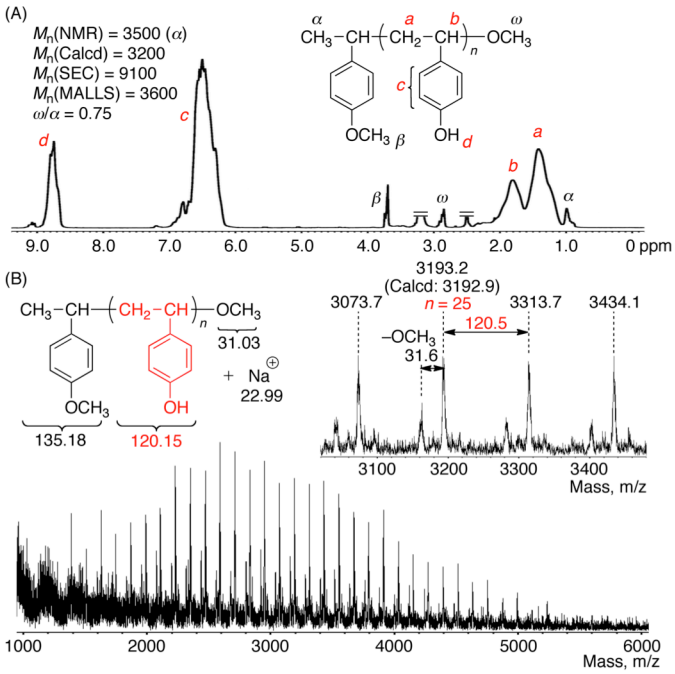


Fig. 3 ^{1}H NMR (DMSO-d_6, 70 °C) (A) and MALDI-TOF-MS (B) spectra of poly(pHOS) obtained with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C.

The MALDI-TOF-MS spectrum showed a series of peaks each separated by 120-Da intervals, which corresponds to the molecular weight of pHOS (Fig. 3B). The molar mass of each individual peak was close to the calculated value for the expected polymer structure $[CH_3–CH(Ph–OCH_3)–(CH_2–CH(Ph–OH))_n–OCH_3 + Na^+]$, i.e., poly(pHOS) with a pMOS unit at the α-end and a methoxy group at the ω-end along with a sodium ion originating from the ionization agent (CF_3CO_2Na). A minor series of peaks, with masses indicating the loss of 32 Da, can be attributed to loss of the terminal methoxy group during laser-induced ionization. These results also support that pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl induces the direct living cationic polymerization of unprotected pHOS without any significant side reactions in CH_3CN under appropriate conditions and results in the well-defined poly(pHOS).

Polymerization of *p*-methoxystyrene in the presence of phenol: effect of CH_3CN

The direct living cationic polymerization of pHOS without protecting the phenolic groups was thus accomplished using pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN. Although phenolic hydroxyl groups generally interact with $SnCl_4$ and may cause undesired

protonic initiation, such side reactions were hardly observed during this polymerization. We speculated that CH_3CN as the solvent was key to suppressing such side reactions because the nitrile groups can interact with phenol and $SnCl_4$ as a Lewis base. To confirm the effect of CH_3CN, the cationic polymerization of pMOS was investigated in the presence of phenol in CH_2Cl_2 using the same pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl initiating system (Fig. 4 and S3).

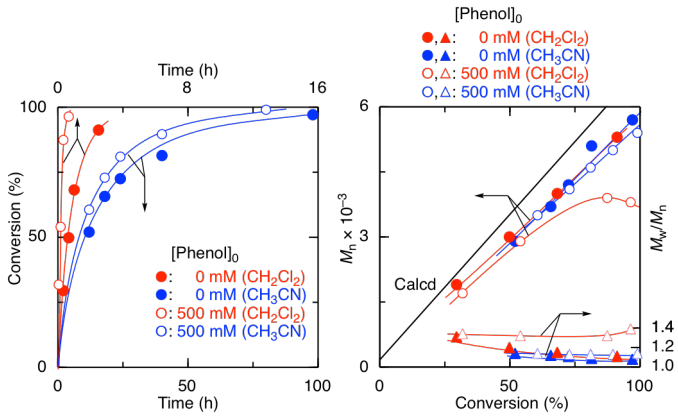


Fig. 4 Time-conversion, M_n, and M_w/M_n curves for cationic polymerization of pMOS with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in the presence or absence of phenol: $[pMOS]_0/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0/[Phenol]_0$ = 500/10/10/15/0 or 500 mM in CH_2Cl_2 at –40 °C, or $[pMOS]_0/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0/[Phenol]_0$ = 500/10/20/30/0 or 500 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C.

The pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl initiating system induced relatively fast polymerization (91% conversion in 150 min) in CH_2Cl_2 at –40 °C and afforded in polymers with controlled molecular weights and narrow MWDs (M_w/M_n ~ 1.1). Whereas the polymerization in CH_3CN/CH_2Cl_2 (9/1) under similar conditions was much slower (97% conversion in 98 h), and the similar living polymerization proceeded to give well-controlled polymers (M_w/M_n ~ 1.1). This indicates that CH_3CN interacts with $SnCl_4$ or the formed carbocation to retard the polymerization but does not have any adverse effects on the livingness of the polymerization.

Upon the addition of an equimolar amount of phenol to pMOS in CH_2Cl_2 at –40 °C, the polymerization became faster (96% conversion in 40 min). However, as the polymerization proceeded, the M_n values of the obtained polymers declined from the calculated values, and the MWDs became broader. These results suggest that protic initiation and/or chain transfer caused by the phenol moiety occurred during the polymerization. Even in CH_3CN/CH_2Cl_2 (9/1), upon addition of the same amount of phenol, a slight increase in the polymerization rate was observed (99% conversion in 80 h) in comparison to that in the absence of phenol. However, in contrast to the polymerization in CH_2Cl_2 without CH_3CN, the M_n values of the polymers obtained in CH_3CN/CH_2Cl_2 (9/1) with phenol increased in direct proportion to the monomer conversion up to high conversion (> 95%) while retaining the narrow MWDs (M_w/M_n ~ 1.1). These results demonstrate that CH_3CN inhibits protic initiation and chain transfer caused by phenol and is a key component for the living cationic polymerization of pMOS in the presence of phenol as well as pHOS without protecting the phenol groups.

^{1}H and ^{119}Sn NMR analysis: interaction of CH_3CN with phenol and $SnCl_4$

To clarify the role of CH_3CN in the polymerization, the interactions between CH_3CN, phenol, and $SnCl_4$ were analyzed by ^{1}H and ^{119}Sn NMR spectroscopy of those reaction mixtures. Fig. 5 shows a series of ^{1}H NMR spectra of phenol in the absence or presence of $SnCl_4$ in CH_2Cl_2 or CH_3CN at –40 °C using acetone-d_6 in an inner capillary tube for locking the deuterium signal. In CH_2Cl_2, the addition of $SnCl_4$ induced a downfield shift of both the aromatic (*a*–*c*) and phenolic protons (*d*) as well as broadening of the latter protons, indicating that $SnCl_4$ most likely coordinates to the phenolic oxygen and changes the acidity of the phenol (Fig. 5A and 5B). In contrast, in CH_3CN, the spectrum changed very little upon the addition of $SnCl_4$. In the ^{1}H NMR spectrum of phenol in CH_3CN, the aromatic signals (*a*–*c*) were shifted slightly upfield and the sharp phenolic proton (*d*) was shifted downfield compared with those in CH_2Cl_2 (Fig. 5C and 5A), which indicates an interaction between the phenolic proton and CH_3CN as a Lewis base. However, in CH_3CN, these signals shifted very little upon the addition of $SnCl_4$ (Fig. 5C and 5D). These results indicate that the phenolic hydroxyl groups interact more strongly with CH_3CN than with $SnCl_4$, most likely due to another strong interaction between $SnCl_4$ and CH_3CN, which will be clarified below.

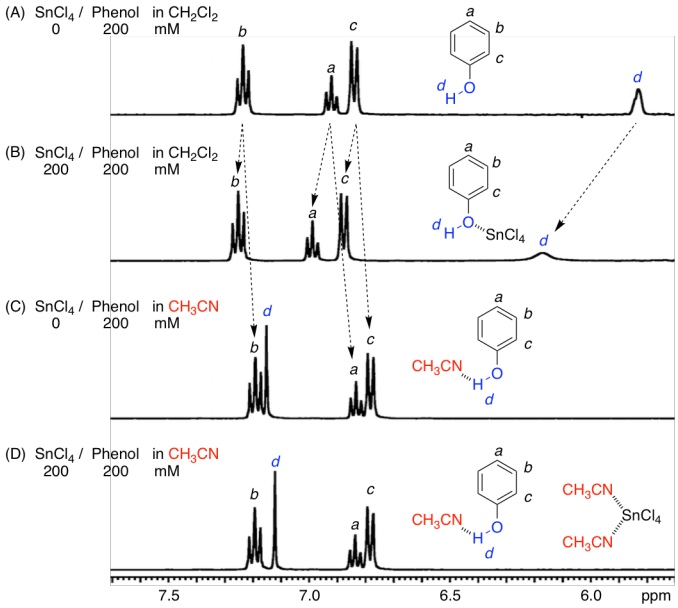


Fig. 5 ^{1}H NMR spectra of phenol in the presence or absence of $SnCl_4$ in CH_2Cl_2 (A, B) or CH_3CN/CH_2Cl_2 = 8/2 (C, D) at –40 °C.

Then, the interactions of $SnCl_4$ with phenol and CH_3CN were analyzed by ^{119}Sn NMR at –40 °C (Fig. 6). Upon the addition of an equimolar amount of phenol to $SnCl_4$ in CH_2Cl_2, the broad signal of $SnCl_4$ at –161 ppm[16] moved upfield to –189 ppm (Fig. 6A and 6B). This upfield shift also indicates an interaction between $SnCl_4$ and the phenolic group in CH_2Cl_2, which may induce protic initiation from

phenol in the cationic polymerization. In contrast, in CH_3CN, no changes in the spectrum were observed upon the addition of phenol. In CH_3CN, $SnCl_4$ showed a sharp signal at –690 ppm, which was upfield relative to that in CH_2Cl_2 (Fig. 6C and 6A) due to the coordination of CH_3CN to $SnCl_4$. However, upon the addition of an equimolar amount of phenol, no changes were observed (Fig. 6D). These results indicate that $SnCl_4$ strongly interacts with CH_3CN rather than with phenol.

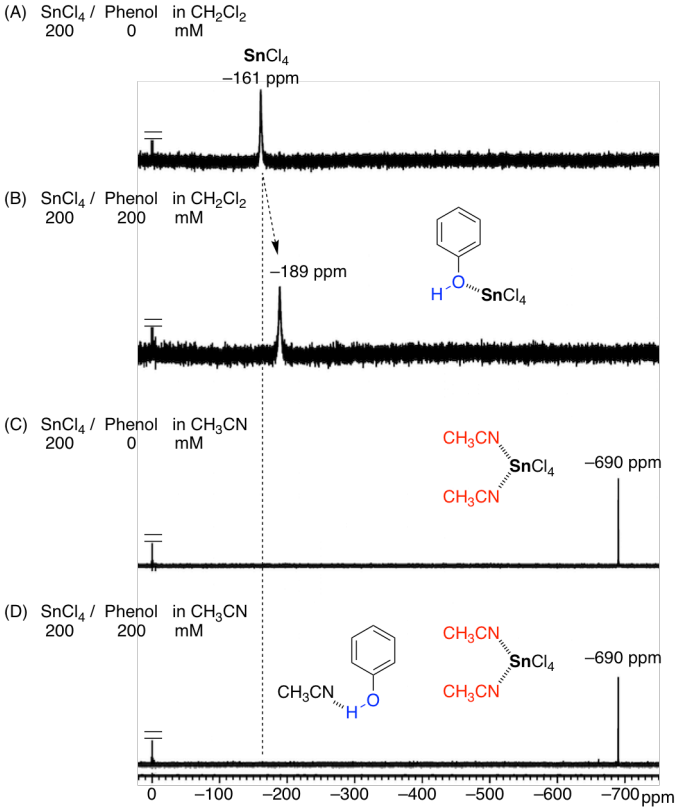


Fig. 6 ^{119}Sn NMR spectra of $SnCl_4$ in the presence or absence of phenol in CH_2Cl_2 (A, B) or CH_3CN/CH_2Cl_2 = 8/2 (C, D) at –40 °C.

As a summary of the ^{1}H and ^{119}Sn NMR analyses, CH_3CN strongly interacts with both $SnCl_4$ and phenol and prevents the direct interaction between $SnCl_4$ and phenol. Therefore, the use of CH_3CN is important for inducing the direct living cationic polymerization of pHOS without protecting the phenolic groups, as the protic initiation is suppressed by CH_3CN.

Direct living cationic polymerization of naturally-derived 4-vinylguaiacol and 4-vinylcatechol using R–Cl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN

In addition to *p*-coumaric acid, there are various naturally-occurring cinnamic acid derivatives with hydroxyl groups on the aromatic ring, such as ferulic and caffeic acids.[66] As in the case of *p*-coumaric acid, they are easily decarboxylated by heating in the presence of an amine and can be converted into styrene derivatives with phenolic protons, such as 4-vinylguaiacol (4VG) and 4-vinylcatechol (4VC).[52,63,67,68] We recently reported the synthesis and controlled radical polymerization of various protected 4VG and 4VC monomers; however, protection was required prior to the radical polymerization due to the inhibition of the radical reaction caused by the phenolic groups.[62,63] More recently, we reported that the R–OH/BF_3·OEt_2-based initiating system induces direct controlled cationic polymerization of 4VG;[64] however, no other systems have been used for the direct cationic polymerization of 4VG and 4VC.

Here, the direct living cationic polymerization of unprotected 4VG and 4VC was also investigated using pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl in CH_3CN at –40 °C to expand the versatility of this system. The common initiating system similarly induced the direct polymerization of 4VG and 4VC without protection of not only the substituted phenol but also catechol to result in quantitative consumption of the monomers in 2–4 h (Fig. 7). The rate of the polymerizations increased in the following order: pHOS < 4VC < 4VG. Although the reactivity order often correlates with the chemical shift of the vinyl β-carbon, which reflects the electron density on the vinyl group, in this case, the values were not correlated: 111.7 ppm (4VG) > 111.5 ppm (pHOS) > 111.2 ppm

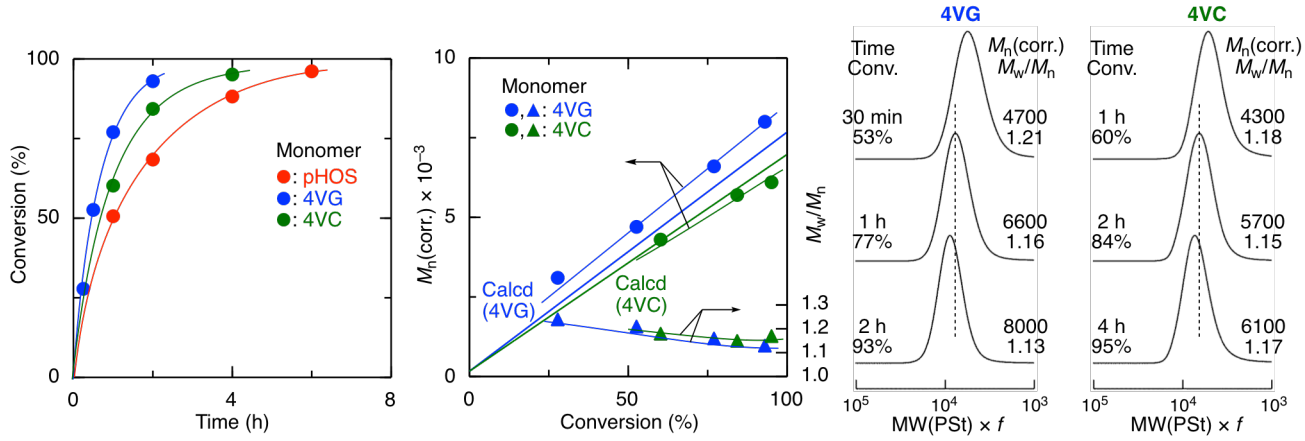


Fig. 7 Time-conversion, M_n, M_w/M_n, and SEC curves for direct cationic polymerization of unprotected pHOS, 4VG, and 4VC: $[Monomer]_0/[pMOS–HCl]_0/[SnCl_4]_0/[n\text{-}Bu_4NCl]_0$ = 500/10/20/30 mM in CH_3CN/CH_2Cl_2 = 9/1 at –40 °C. M_n(corr.) was determined by SEC using polystyrene standard and calibration factor (f = 0.653 (4VG), 0.410 (4VC)).

(4VC); they were all measured in CD_3CN.

The SEC curves of the obtained poly(4VG) and poly(4VC) shifted to a higher molecular weight region and retained the narrow MWDs (M_w/M_n = 1.1–1.2), as in the case of poly(pHOS). Additionally, the M_n(corr.) values of the obtained polymers increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of pMOS–HCl generates one polymer chain, where M_n(corr.) was obtained by using f = 0.653 for poly(4VG) and 0.410 for poly(4VC) based on the ratios of M_n(MALLS) and M_n(SEC). These results indicate that pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl is also effective for the direct cationic polymerization of 4VG and 4VC in CH_3CN without protection of the phenol and catechol substituents.

More interestingly, with the R–OH/BF_3·OEt_2 initiating system, which is effective for controlling the direct cationic polymerization of pHOS[55] and 4VG,[64] the direct polymerization of 4VC stopped around 60% and resulted in uncontrolled molecular weights (Fig. S4) most probably due to chelating of the catechol moiety to boron. These results indicate that the pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl is more tolerant to the phenol and catechol moieties.

The ^{1}H NMR spectra of the poly(4VG) and poly(4VC) obtained with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl showed signals corresponding to each repeating monomer unit and the initiator moiety of the pMOS unit (Fig. S5). The M_n(NMR) values, which were measured from the peak intensity ratio of the repeating units to the methyl proton of the α-end group, were close to the calculated values, indicating that one pMOS–HCl initiator generates one polymer chain without any considerable side reactions caused by phenol and catechol groups during the cationic polymerization. The terminal methoxy group generated by quenching with methanol was nearly quantitatively observed for poly(4VG) but could not be detected for poly(4VC).

Conclusions

The pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl initiating system, which is common for living cationic polymerizations of various cationically polymerizable monomers, proved to be highly effective for the direct living cationic polymerization of *p*-hydroxystyrene without using any protecting groups in CH_3CN. In this direct polymerization, CH_3CN plays an important role: CH_3CN strongly interacts with both phenol and $SnCl_4$, prevents the direct interaction between phenol and $SnCl_4$, and then suppresses the possible proton initiation and chain-transfer reactions caused by phenol. Furthermore, the direct cationic polymerizations of other naturally-derived functional styrenes, such as 4-vinylguacol and 4-vinylcatechol with similar hydroxyl groups on the aromatic rings, were also accomplished in a living fashion by the same initiating system in CH_3CN. This study not only broadens the scope of living cationic polymerizations for unprotected monomers but also provides a more facile method for directly preparing well-defined functionalized polymers without tedious protection and deprotection procedures.

Experimental section

Materials

p-Coumaric acid (Tokyo Kasei, >98.0%), ferulic acid (Aldrich, >99%), caffeic acid (KANTO, >98.0%), triethylamine (Tokyo Kasei, >99.0%), *N*,*N*-dimethylformamide (DMF) (KANTO, >99.5%; H_2O <0.001%), $SnCl_4$ (Aldrich, 1.0 M solution in CH_2Cl_2), $ZnCl_2$ (Aldrich, 1.0 M solution in Et_2O), $TiCl_4$ (Aldrich, 1.0 M solution in CH_2Cl_2) and *n*-Bu_4NCl (Tokyo Kasei, >98.0%) were used as received. *p*-Methoxystyrene (pMOS) (Tokyo Kasei, >98.0%), acetonitrile (CH_3CN) (KANTO, >99.5%; H_2O <0.001%), ethyl acetate (KANTO, >99.5%; H_2O <0.001%), and *o*-dichlorobenzene (Tokyo Kasei, >99.0%) were distilled over calcium hydride under reduced pressure before use. CH_2Cl_2 (KANTO, >99.5%; H_2O <0.001%) was dried and deoxygenized by passage through columns of a Glass Contour Solvent System before use. The HCl adduct of pMOS (pMOS-HCl) was prepared from HCl and pMOS as previously reported.[69]

Synthesis of *p*-hydroxystyrene (pHOS)

p-Hydroxystyrene (pHOS) was synthesized from *p*-coumaric acid via decarboxylation as described below. *p*-Coumaric acid (40.5 g, 246.5 mmol) was dissolved in DMF (170 mL). Into this solution, triethylamine (34.0 mL, 243.9 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 10 h, the reaction mixture was cooled to room temperature, and the conversion of *p*-coumaric acid into pHOS as measured by ^{1}H NMR was quantitative (>99%). The reaction mixture was concentrated by rotary evaporation to remove the triethylamine. The residue was diluted with Et_2O and washed with water. The organic layer was dried with Na_2SO_4 and then concentrated by rotary evaporation. The yellowish crude product was purified by recrystallization from *n*-hexane to yield pHOS as a white solid (25.9 g, 88%). The obtained pHOS was stored as a methanol solution at –20 °C and was further purified by azeotropic drying with toluene just before use.

Synthesis of 4-vinylguaiacol (4VG)

4-Vinylguaiacol was synthesized from ferulic acid via decarboxylation as described below. Ferulic acid (20.1 g, 103.5 mmol) was dissolved in DMF (55 mL). Into this solution, triethylamine (29.0 mL, 208.1 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 2 h, the reaction mixture was cooled to room temperature, and the conversion of ferulic acid into 4VG as measured by ^{1}H NMR was quantitative (>99%). The reaction mixture was concentrated by rotary evaporation to remove the triethylamine. The residue was diluted with Et_2O and washed with water. The organic layer was dried with Na_2SO_4 and then concentrated by rotary evaporation. The yellowish crude product was purified by distillation under reduced pressure to yield 4VG as a colorless liquid (14.0 g, 90%).

Synthesis of 4-vinylcatechol (4VC)

4-Vinylcatechol (4VC) was synthesized from caffeic acid via decarboxylation as described below. Caffeic acid (10.8 g, 59.7 mmol) was dissolved in DMF (38 mL). Into this solution, triethylamine (7.7 mL, 55.2 mmol) was added, and then the mixture was heated to 100 °C under stirring. After 3 h, the reaction mixture was cooled to room temperature, and the conversion of caffeic acid

into 4VC as measured by ^{1}H NMR was quantitative (>99%). The reaction mixture was concentrated by rotary evaporation to remove the triethylamine. The residue was diluted with Et_2O and washed with water. The organic layer was dried with Na_2SO_4 and then concentrated by rotary evaporation. The yellowish crude product was passed through a silica gel column (silica gel 60 N, CH_2Cl_2/Et_2O = 9/1), and then 4VC was stored as a CH_3CN solution (2.13 M in CH_3CN) in sealed brown ampules at –20 °C.

Direct living cationic polymerization

The direct living cationic polymerizations were carried out by a syringe technique under dry nitrogen in sealed glassware equipped with a three-way stopcock. A typical example of the polymerization of pHOS with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl is given below. The reaction was initiated by the sequential addition of pMOS–HCl (100 mM in CH_2Cl_2; 0.30 mL) and a mixture of $SnCl_4$ and *n*-Bu_4NCl (200 mM of $SnCl_4$ and 300 mM of *n*-Bu_4NCl in CH_3CN and CH_2Cl_2 (1/1); 0.30 mL) via a dry syringe into the monomer solution (2.40 mL) containing pHOS (0.18 g, 1.50 mmol) and *o*-dichlorobenzene (0.04 mL) in CH_3CN (2.18 mL). The total volume of the reaction mixture was 3.0 mL. After stirring at –40 °C, the polymerization was terminated by the addition of prechilled methanol (1 mL) containing a small amount of ammonia. Monomer conversion was determined from the concentration of the residual monomer as measured by ^{1}H NMR with *o*-dichlorobenzene as an internal standard (96% in 6 h). The quenched reaction mixture was diluted with ethyl acetate and then washed with aqueous HCl, aqueous $NaHCO_3$, and water. The organic layer was concentrated to dryness under reduced pressure and vacuum-dried to give the product polymer (M_n = 15800, M_w/M_n = 1.15). The obtained polymer was further purified by precipitation into a mixture of *n*-hexane and toluene (1/1) to remove residual monomer.

Measurements

^{1}H and ^{119}Sn NMR spectra were recorded on a JEOL ECS-400 spectrometer operating at 400 and 149 MHz for ^{1}H and ^{119}Sn, respectively. The main parameters for the ^{119}Sn NMR experiments were as follows: spectral width = 3000 ppm, pulse width = 5.0 μs (45°), pulse delay = 3.0 s, data points = 65536, number of transients = 1600, and complete decoupling from ^{1}H. Me_4Sn (0 ppm as a singlet) dissolved in acetone-d_6 in a capillary was used as an external standard. The number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the product polymers were determined by SEC in DMF containing 100 mM LiCl at 40 °C on two hydrophilic polymer gel columns [Tosoh α-M (7.8 mm i.d. × 30 cm) + Tosoh α-3000 (7.8 mm i.d. × 30 cm); flow rate 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against standard polystyrene samples (Agilent Technologies; M_p = 580-3053000, M_w/M_n = 1.02-1.23). The MALLS analysis was performed in THF on a DAWN HELEOS photometer (Wyatt Technology; 1 ~ 633 nm). The refractive index increments were measured in THF at 40 °C on an Optilab rEX (Wyatt Technology; 1 ~ 633 nm). The calibration factor (*f*) was determined by the ratio of M_n(SEC) and M_n(MALLS) of the poly(pHOS) obtained with pMOS–HCl/$SnCl_4$/*n*-Bu_4NCl. The MALDI-TOF-MS spectrum was measured on a Shimadzu AXIMA-CFR Plus mass spectrometer (linear mode) with dithranol as the ionizing matrix and sodium trifluoroacetate as the ion source.

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