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Synthesis of Methyl Vinyl Ether–Styrene Block Copolymers by the Sequential Living Cationic Polymerization[1]

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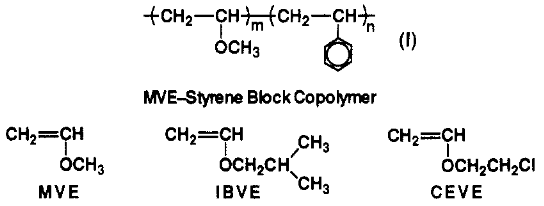
ABSTRACT: AB block copolymers of methyl vinyl ether (MVE) and styrene were synthesized by the sequential living cationic polymerization. The first-stage polymerization was with MVE and was initiated in methylene chloride solvent at −78 °C with the adduct [1; $CH_3CH(O\textit{i}Bu)Cl$] of hydrogen chloride and isobutyl vinyl ether (IBVE) as an initiator in conjunction with tin tetrachloride ($SnCl_4$; a Lewis acid activator) and tetra-*n*-butylammonium chloride ($n\mathrm{Bu_4NCl}$; an added salt). To the solutions of the resultant living poly(MVE) at −78 °C (conversion ~ 100%) were sequentially added styrene and a mixture of $SnCl_4$ and the salt. Under these conditions, the added styrene remained virtually intact, but upon warming the solution to −15 °C a smooth and quantitative second-stage polymerization ensued to give the target MVE–styrene block copolymers with narrow molecular weight distributions in high yield (>80 wt %). When solution-cast from toluene, the isolated block copolymers (typically, MVE/styrene = 21/33 in DP_n by ^1H NMR) gave nonsticky, transparent, homogeneous films that completely differed from the corresponding cast products from homopolymers of MVE and styrene as well as from their blends. Similar AB block copolymers were also prepared from 2-chloroethyl vinyl ether and styrene. The key to these successful block copolymerizations is the development of an initiating system ($1/SnCl_4$ with added $n\mathrm{Bu_4NCl}$) that induces living cationic polymerizations of both styrene and MVE and the other vinyl ethers, along with the judicious adjustment of the polymerization conditions for each of the comonomers.

Introduction

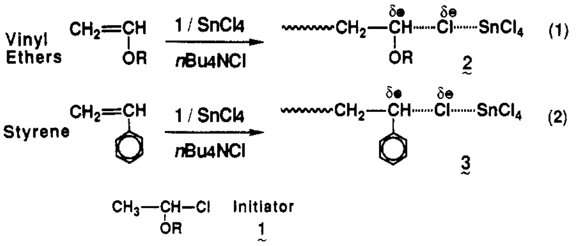
Homopolymer mixtures or blends of methyl vinyl ether (MVE) and styrene are known to undergo an interesting phase separation, called the lower critical solution temperature phenomenon,[3] and have been eliciting intensive and extensive studies in polymer physics.[4] It is therefore a natural consequence that not a few polymer physicists and chemists consider connecting these homopolymer segments via a covalent linkage, or the synthesis of block copolymers of MVE and styrene (Chart 1), to be an important subject of research. Because MVE can be polymerized primarily by cationic polymerization alone, the most promising synthetic tool to obtain this particular block copolymer should be a sequential living cationic polymerization of both monomers, but, however straightforward it seems to be, the MVE–styrene block copolymerization has been difficult and none have been reported thus far.

The difficulty in the synthesis of MVE–styrene and related block copolymers stems from an inherent problem in cationic polymerization; namely, the cross propagation among structurally different monomers, such as vinyl ethers and styrenes, often encounters frequent side reactions among which cross chain transfer is most serious. Another problem more specific for vinyl ether–styrene combinations is that, although living cationic polymerizations have been developed for a number of vinyl monomers,[5] including MVE[6,7] and styrene,[8,9] the large difference in reactivity between these monomers (e.g., vinyl ethers > styrene derivatives) usually renders the initiating systems and the optimum reaction conditions totally different and thereby virtually inapplicable to the monomer pair. Thus only a limited number of block copolymers of vinyl ethers have been obtained (e.g., with *p*-alkoxystyrenes,[10,11] *p*-methylstyrene,[1,12] and isobutylene[13,14]), and blocking efficiency is still low for the latter two comonomers.[12-14]

Chart 1



Despite these unfavorable backgrounds, specifically for MVE and styrene, we have recently found that a single common initiating styrene can permit living cationic polymerizations of these different monomers. Namely, both alkyl vinyl ethers[15] and styrene[16] (eqs 1 and 2, respectively) are polymerized into well-defined living polymers with the adduct (1; initiator) of hydrogen chloride and a vinyl ether, in conjunction with tin tetrachloride ($SnCl_4$; activator) in the presence of tetra-*n*-butylammonium chloride ($n\mathrm{Bu_4NCl}$) in methylene chloride (CH_2Cl_2) solvent below 0 °C.[17] Relative to the synthesis of MVE–styrene block copolymers, it is especially important that the vinyl ether adduct 1, coupled with $SnCl_4$, is capable of initiating living styrene polymerization (eq 2), although the carbocation derived from $1/SnCl_4$[17] would considerably differ from that of styrene (see species 3, eq 2).[18] This fact implies that the vinyl ether-type growing end (2; eq 1) might initiate living polymerization of styrene to give vinyl ether–styrene block copolymers such as polymer I.



On the basis of these findings, the objective of this study was to synthesize MVE–styrene AB block copolymers by

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Scheme 1. Synthesis of MVE–Styrene Block Copolymers by Sequential Living Cationic Polymerization

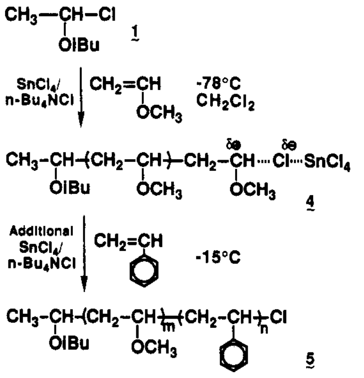

Table 1. Cationic Homopolymerization of Methyl Vinyl Ether with 1/SnCl$_4$[a]

	-15 °C				-78 °C			
time, min	2	5	10	20	20	30	60	>150
convn, %	26	49	75	94	50	65	82	~100

[a] Reaction conditions: [MVE]$_0$ = 0.50 M; [1]$_0$ = [SnCl$_4$]$_0$ = [nBu$_4$NCl]$_0$ = 10.0 mM; in CH$_2$Cl$_2$ solvent.

the sequential living cationic polymerization initiated with the 1/SnCl$_4$ initiating system (Scheme 1), which is applicable in common to both monomers in the presence of added nBu$_4$NCl salt in CH$_2$Cl$_2$.[15,16] Efforts were directed toward optimizing reaction conditions for the first-phase MVE polymerization and the subsequent propagation of styrene from the MVE growing end (4). Similar two-stage syntheses of block copolymers of styrene were examined with isobutyl and 2-chloroethyl vinyl ethers (IBVE and CEVE, respectively).

Results and Discussion

1. Living Cationic Polymerization of MVE. As the basis of the MVE–styrene block copolymerization (Scheme 1), optimum reaction conditions were first established for the first-stage living cationic polymerization of MVE with the 1/SnCl$_4$ system, which has yet to be examined. Thus MVE was polymerized with 1/SnCl$_4$ (R = isobutyl) in CH$_2$Cl$_2$ in the presence of nBu$_4$NCl at -15 and -78 °C under conditions similar to those for IBVE reported by us.[15] The typical reagent concentrations were as follows: [MVE]$_0$ = 0.50 M; [1]$_0$, = [SnCl$_4$]$_0$ = [nBu$_4$NCl]$_0$ = 10.0 mM. The polymerizations proceeded smoothly without any induction to be completed within 30 and 150 min at -15 and -78 °C, respectively; the relevant conversion data are summarized in Table 1.

As shown in the molecular weight distribution (MWD) curves in Figure 1, it soon turned out that a low polymerization temperature is needed to obtain well-defined living polymers from MVE, although mononmer consumption was quantitative at both -15 and -78 °C. The MWDs were much narrower at -78 °C, where the polydispersity ratios ($\bar{M}_w/\bar{M}_n$) are well below 1.1 (1.04–1.07), whereas those for -15 °C are indeed narrow at the beginning of the polymerization but clearly broaden and show tailings as conversion increases.

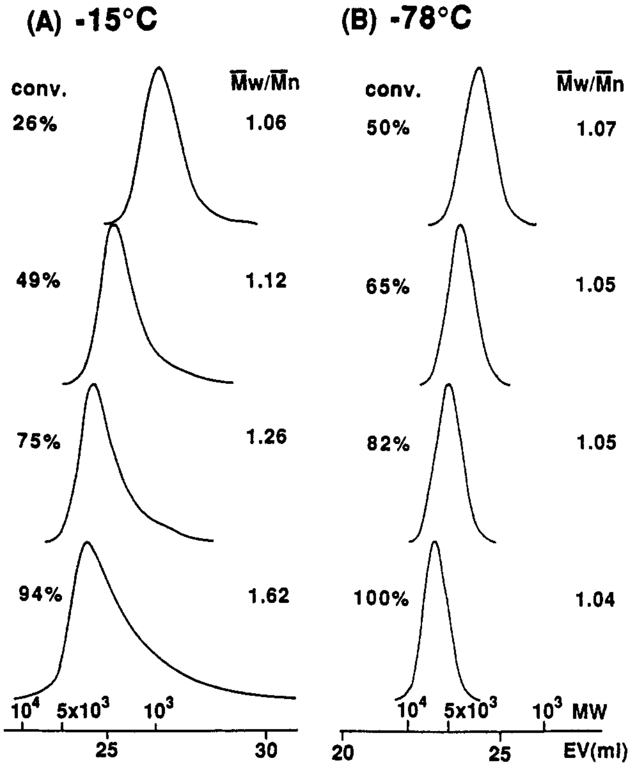

Figure 1. MWD of poly(MVE) obtained in the polymerization with 1/SnCl$_4$ in the presence of nBu$_4$NCl in CH$_2$Cl$_2$ solvent at -15 (A) and -78 °C (B): [MVE]$_0$ = 0.50 M; [1]$_0$ = [SnCl$_4$]$_0$ = [nBu$_4$NCl]$_0$ = 10.0 mM. Conversions and polydispersity ratios are as indicated.

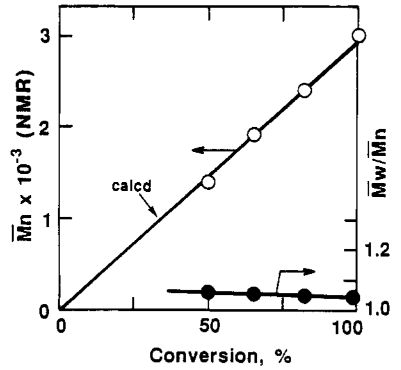

Figure 2. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(MVE) obtained with 1/SnCl$_4$ in the presence of nBu$_4$NCl in CH$_2$Cl$_2$ at -78 °C as a function of MVE conversion (cf. Figure 1B): [MVE]$_0$ = 0.50 M; [1]$_0$ = [SnCl$_4$]$_0$ = [nBu$_4$NCl]$_0$ = 10.0 mM. $\bar{M}_n$ by ^{1}H NMR spectroscopy (see text). The diagonal solid line shows the calculated $\bar{M}_n$ assuming the formation of one living polymer chain per initiator 1.

Accordingly, at -78 °C the number-average molecular weights ($\bar{M}_n$) of the polymers, determined by ^{1}H NMR,[19] are directly proportional to MVE conversion and close to the calculated values based on the assumption that one polymer chain is formed per initiator 1 (Figure 2). By contrast, the molecular weights for -15 °C were about half those for -78 °C at the same conversion and increased only slightly as the reaction proceeded.

All these results indicate that the 1/SnCl$_4$-initiated polymerization of MVE is living at -78 °C, which is in contrast to the fact that the same initiating system can give living polymers from IBVE even at higher temperatures (0 or -15 °C) and otherwise under similar conditions.[15] The difference is most likely attributed to the lower stability of the MVE growing carbocation, which may undergo chain-transfer reactions at -15 °C. Similar effects of polymerization temperature on vinyl ether polymerizations have recently been reported.[14]

2. Synthesis of MVE–Styrene Block Copolymers. Polymerization of Styrene from Living Poly(MVE). Following the optimization of the living polymerization conditions for MVE, styrene was polymerized from the living growing poly(MVE) (4) obtained with 1/$SnCl_4$ in the presence of $n$$Bu_4NCl$ at −78 °C (Scheme 1). Thus, when the first-stage MVE polymerization reached above 95% conversion in 20 min ($[MVE]_0$ = 0.20 M; $[1]_0$ = $[SnCl_4]_0$ = $[nBu_4NCl]_0$ = 10.0 mM), styrene was added to the unquenched reaction mixture at the same temperature [MVE/styrene/1 (living end) = 20/45/1 mole ratio]. However, the added monomer was hardly consumed, evidently due to the lower reactivity of styrene.

To accelerate the second-stage reaction, an additional amount of $SnCl_4$ was added to this quiescent mixture, where $[SnCl_4]$ is now ca. 100 mM. Immediately after the $SnCl_4$ addition, white precipitates, which are apparently complexes of the tin chloride with MVE monomer and polymers, appeared.[7,13] At the higher $SnCl_4$ concentration, polymerization of styrene was still virtually absent, and upon raising the temperature to −15 °C, a small part of styrene was indeed consumed (by gas chromatography), but the reaction mixture soon exhibited an intense color change from light yellow through green to dark purple. As already reported by us,[20,21] the coloration is due to the decomposition of the growing poly(MVE) end (4) via β-hydrogen abstraction, which is obviously caused by the high concentration of $SnCl_4$ that facilitates the ionization of 4 and in turn its decay process.[21] It is therefore unsuitable to polymerize styrene from the living poly(MVE) simply at an increased $SnCl_4$ concentration, where the problems are the very low consumption of styrene, the precipitation of the added $SnCl_4$, and, most seriously, the Lewis acid-assisted deactivation of the growing end 4.

These problems were finally circumvented in the following way (Scheme 1). Instead of adding $SnCl_4$ alone, its mixture with $n$$Bu_4NCl$ in CH_2Cl_2 was added with vigorous magnetic stirring to the living poly(MVE)/styrene solution at −78 °C, where $[SnCl_4]$ = 92 mM and $[nBu_4NCl]$ = 33 mM. The use of an additional feed of the salt along with $SnCl_4$ was intended to solubilize the Lewis acid effectively and also to suppress the deactivation of the living end 4, while keeping the $SnCl_4$ concentration still high enough to accelerate styrene polymerization.

Although styrene was still hardly polymerized at −78 °C under these conditions, raising the temperature to −15 °C now induced an efficient polymerization of the added styrene [conversions: 44% (3 h); 82% (5 h)]. Throughout the second-stage reaction, the solutions were colorless, transparent, and homogeneous or free from precipitates, in sharp contrast to the heterogeneous mixtures where $SnCl_4$ was added without premixing with the salt.

As Figure 3 shows, the living homopolymer of MVE with a very narrow MWD (Figure 3A) disappeared during the styrene polymerization, and the block copolymerization products appeared as new and still narrow distributions of higher molecular weights (Figure 3B,C). In addition to these main products, a small amount of a secondary product was seen in the lower molecular weight region. The molecular weights of the main products increased as styrene conversion increased, suggesting a successful propagation of a polystyrene segment from the poly(MVE) end.

Characterization of MVE–Styrene Block Copolymers. The block copolymerization products (e.g., Figure 3B,C) were then fractionated by preparative size-exclusion chromatography (SEC) into the main product (with an increased molecular weight) and the minor fraction. Figure 4 shows the ^1H NMR spectra of the two parts from the product obtained at a styrene conversion of 82% (MVE conversion = 100%; Figure 3C).

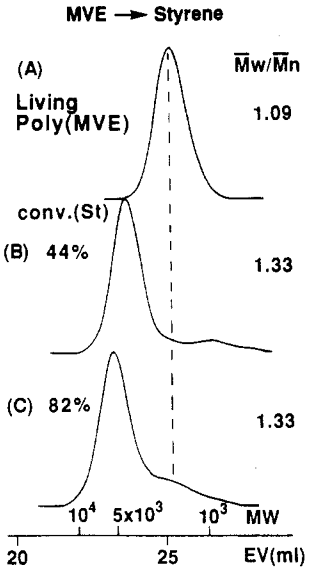

Figure 3. Block copolymerization of styrene from living poly(MVE) (Scheme 1) followed by size-exclusion chromatography. (A) Starting living poly(MVE): time = 20 min; conversion = 98%; $[MVE]_0$ = 0.20 M (20 equiv to 1); $[1]_0$ = $[SnCl_4]_0$ = $[nBu_4NCl]_0$ = 10.0 mM. (B and C) block copolymerization products: styrene conversion (time after its addition) = (B) 44% (2 h) and (C) 82% (5 h). Polymerization conditions: (second stage) $[styrene]_0$ = 0.38 M (45 equiv to 1 (living end)), $[SnCl_4]$ = 92 mM, $[nBu_4NCl]$ = 33 mM. Note that the total volume of the reaction mixtures increases from 5.0 mL (first stage) to 6.0 mL (second stage) due to the mixing of additional amounts of $SnCl_4$ and $n$$Bu_4NCl$; see the Experimental Section. $\bar{M}_w/\bar{M}_n$ values are for the unfractionated entire products.

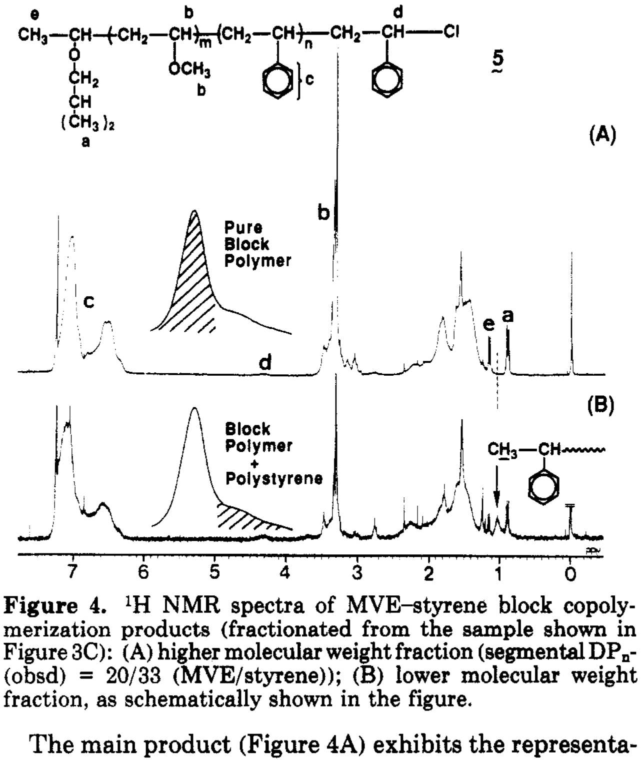

Figure 4. ^1H NMR spectra of MVE–styrene block copolymerization products (fractionated from the sample shown in Figure 3C): (A) higher molecular weight fraction (segmental DP_n(obsd) = 20/33 (MVE/styrene)); (B) lower molecular weight fraction, as schematically shown in the figure.

The main product (Figure 4A) exhibits the representative signals of poly(MVE) (peak b) and polystyrene (peak c) chains, and the spectrum is very similar to those of homopolymer mixtures. In addition, it shows end-group signals: peaks a and e (the pendant methyl of the isobutyl group and the α-end methyl from the IBVE adduct 1[15]) and peak d (the ω-end methine at the benzyl chloride-type terminal of the polystyrene segment[8b,16]). The integrated peak intensities of these terminal resonances, relative to those of the main chains, give the degrees of polymerization (DP_n) of the MVE and the styrene seg-

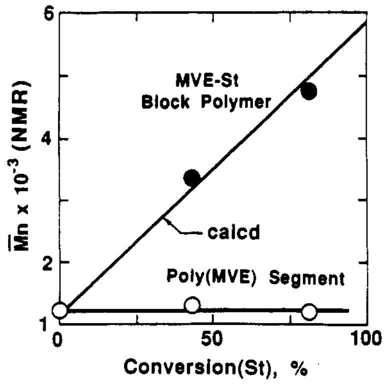

Figure 5. Molecular weights $\bar{M}_n$ of MVE–styrene block polymers **5** (filled circles) and their poly(MVE) segments (open circles) as a funtion of styrene conversion; see the caption of Figure 3 for reaction conditions. $\bar{M}_n$ was determined by ^{1}H NMR; see Figure 4 and the relevant text. The diagonal solid line indicates the calculated $\bar{M}_n$ for **5** based on the assumption that one living poly(MVE) chain as well as the block polymer is formed per initiator **1**.

ments (e.g., ratios b/a and c/a, respectively).

The observed segmental DP$_n$'s were in good agreement with the calculated values based on the initial feed ratios of initiator **1** to MVE and styrene and on their conversions; e.g., MVE/styrene: calcd 20.36; obsd 21/33 ($\bar{M}_n$ = 4800); at conversions MVE/styrene = 100/82% (the sample shown in Figure 3C and Figure 4A). Similar results were also obtained with the other samples. From these DP$_n$ data, the total $\bar{M}_n$ of the main products, as well as the segmental $\bar{M}_n$ of their poly(MVE) parts, were determined and plotted against styrene conversion in Figure 5. Starting from the value for the homopoly(MVE) precursor, the total $\bar{M}_n$ (filled circles) increases in proportion to conversion and, as indicated above, in good agreement with the calculated value (solid line). Equally important, the $\bar{M}_n$ of the poly(MVE) segment (open circles) remains virtually unchanged and the same as that of the precursor homopolymer (shown on the ordinate) throughout the second-stage polymerization. These results show the formation of block polymers **5** via the smooth growth of styrene from the living poly(MVE) **4** where the newly generated styrene growing end is also of a long lifetime.

Spectrum B, Figure 4, is for the lower molecular weight fraction of the product (Figure 3C). It shows the same sets of resonances as does the main product (Figure 4A), except for an additional signal at ca. 1 ppm, which is assignable to the α-end methyl of polystyrene (as indicated in the figure) initiated by a proton.[8b,16] Therefore, the minor fraction is most likely a mixture of MVE–styrene block copolymer **5** (with a short polystyrene segment) and styrene homopolymer. The latter might result from a minor chain transfer during the styrene polymerization. It should be emphasized, however, that the amount of the minor fraction is small, indicating a high blocking efficiency from the living poly(MVE) **4** to styrene. Equally important, the α-end methyl signal of polystyrene ($\sim$1 ppm) is totally absent in the spectrum of the main product (Figure 4A; as indicated by the dashed line), further showing that it is a pure block copolymer without homopolystyrene.

All these spectral analyses and the DP$_n$/$\bar{M}_n$ data, summarized in Figures 3–5, demonstrate the formation of MVE–styrene block copolymers (**5**) according to the reaction sequence and procedures shown in Scheme 1.

Solution-Cast Films and Solubility Characteristics. Further evidence for the formation of MVE–styrene block copolymers **5** was obtained by analysis of their appearance and solubility characteristics (Table 2). The block copolymerization products of two compositions (MVE/styrene = 20/18 and 20/33 in segment DP$_n$; fractionated by SEC) were cast from toluene solutions (ca. 10 w/v %), and the appearances of the resulting products were compared with the corresponding homopolymers and their blends having nearly the same chain lengths (DP$_n$ = 50 for each).

The block copolymerization products gave nonsticky, smooth, transparent, homogeneous solid films that completely differ in appearance from the corresponding homopolymers of MVE (sticky, opaque, viscous liquid) and styrene (white powder), as well as from their blend (1:1 w/w; sticky, lightly opaque, apparently heterogeneous semisolid or highly viscous liquid). These visual observations show the absence of macroscopic phase separation of the mutually incompatible MVE and styrene segments in the solution-cast film of the block copolymerization products.

As also shown in Table 2, the two block copolymer samples have solubility characteristics intermediate between the two homopolymers. For example, they are soluble in ethanol (a nonsolvent of polystyrene), insoluble in water (a good solvent of poly(MVE)), and soluble in toluene (a good solvent for both homopolymers). These physical analyses thus demonstrate also the formation of true block copolymers of MVE and styrene.

3. Synthesis of CEVE–Styrene Block Copolymers. By adopting a similar method (cf. Scheme 1), block copolymerizations were studied for styrene with two vinyl ethers, IBVE and CEVE. For both pairs, as with MVE, the vinyl ethers were polymerized first in a living fashion with the **1**/SnCl$_4$ system in the presence of *n*Bu$_4$NCl at −78 °C in CH$_2$Cl$_2$ solvent, and styrene was added subsequently to the solutions of the resulting living poly(vinyl ethers), followed by the addition of an SnCl$_4$/salt mixture and raising the temperature to −15 °C. The typical reaction conditions are compiled in the caption of Figure 6, which compares the MWDs of the precursor living polymers and representative products.

In the first-stage polymerizations, both IBVE and CEVE gave living polymers with very narrow MWDs (Figure 6A,C; conversion > 95%). Styrene was added to these solutions, and upon subsequent addition of an SnCl$_4$/*n*Bu$_4$NCl mixture and warming, the second-stage polymerizations immediately ensued at −15 °C.

In the IBVE–styrene system, however, the solution of the living poly(IBVE) (DP$_n$ = 20) and styrene turned brown as soon as it was warmed to −15 °C, indicating that the living poly(IBVE) was partly deactivated via β-proton elimination[20,21] even in the presence of an additional amount of *n*Bu$_4$NCl. The product at 32% styrene conversion showed a bimodal MWD (Figure 6B) consisting of a relatively narrow population of higher molecular weights and a considerable amount of a lower molecular weight fraction eluting at nearly the same position as does the starting poly(IBVE) (Figure 6A). Although with the bimodal MWD, ^{1}H NMR structural analysis also indicated that the product was a mixtur of an IBVE–styrene block copolymer, homopoly(IBVE), and possibly homopolystyrene.

In sharp contrast, the polymerization of styrene from the living poly(CEVE) (DP$_n$ = 30; Figure 6C) proceeded homogeneously without any coloration and precipitation. Contrary to the MVE–styrene system (see above), these disturbing phenomena were also absent when a second feed of SnCl$_4$ was added without premixing with *n*Bu$_4$NCl, indicating that the living poly(CEVE) does not decay both at −78 and −15 °C even in the presence of a relatively

Table 2. Appearance and Solubility Characteristics of MVE–Styrene Block Copolymers

polymer	$\overline{DP}_n$ MVE/styrene ▭ ▬		appearance	solubility (5 w/v %, rt)[a] H$_2$O (0 °C)	EtOH	toluene
▭	50/0		sticky, opaque	○	○	○
▭▬	20/18	} block	nonsticky, transparent	×	○	○
▭▬▬	20/33		nonsticky, transparent	×	△	○
▬	0/50		white powder	×	×	○
▭ ▬ }	blend (1:1)		sticky, lightly opaque			

[a] ○: soluble. △: turbid. ×: insoluble.

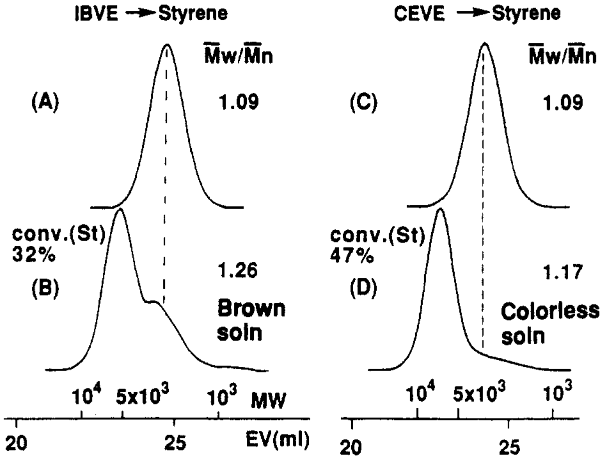

Figure 6. IBVE- and CEVE–styrene block copolymerizations followed by size-exclusion chromatography. (A) Starting living poly(IBVE): time = 40 min; conversion = 98%; [IBVE]$_0$ = 0.20 M (20 equiv to 1); [1]$_0$ = 10.0 mM; [SnCl$_4$]$_0$ = 5.0 mM; [nBu$_4$NCl]$_0$ = 7.0 mM. (B) IBVE–styrene block copolymerization products from sample A: styrene conversion = 32%; time = 3 h (after its addition); [styrene]$_0$ = 0.33 M (40 equiv to 1 (living end)), [SnCl$_4$] = 85 mM, [nBu$_4$NCl] = 27 mM. (C) Starting living poly(CEVE): time = 40 min; conversion = 98%; [CEVE]$_0$ = 0.30 M (30 equiv to 1); [1]$_0$ = [SnCl$_4$]$_0$ = [nBu$_4$NCl]$_0$ = 10.0 mM. (D) CEVE–styrene block copolymerization products from sample C: styrene conversion = 47%; time = 3 h (after its addition); [styrene]$_0$ = 0.50 M (60 equiv to 1 (living end)), [SnCl$_4$] = 92 mM, [nBu$_4$NCl] = 33 mM. Note that the total volume of reaction mixtures increases from 5.0 mL (first stage) to 6.0 mL (second stage) due to the mixing of additional amounts of SnCl$_4$ and nBu$_4$NCl; see the Experimental Section.

high concentration of the Lewis acid. In a typical experiment, styrene conversions were as follows: 10% (1 h), 47% (3 h), 67% (5 h); CEVE/styrene/1 (living end) = 30/60/1; see the caption for Figure 6C,D.

The products showed narrow MWDs without tailings in the lower molecular weight region; a typical example (styrene conversion = 47%) is given in Figure 6D. ^{1}H NMR analysis of the products (Figure 7) confirmed the formation of CEVE–styrene block copolymer 6, as indicated by the key resonances of both segments (peak b and c for CEVE and styrene, respectively), the initiator residue (α-end peaks a and e), and the ω-end methine of the polystyrene segment (peak d), as well as by the absence of an α-methyl of homopolystyrene that would appear at ca. 1 ppm.[8b,16]

As with the MVE–styrene counterpart, the peak intensity ratios, b/a and c/a, gave DP$_n$'s of CEVE and styrene segments, respectively (Figure 8). The observed segmental DP$_n$'s agreed well with the calculated values; e.g., CEVE/styrene (% conversions): obsd 29/34, calcd 30/28 (100/47%); obsd 28/41, calcd 30/40 (100/67%). The DP$_n$ of the styrene segment increased in proportion to conversion (filled circles), while that of the CEVE segment remained nearly the same as with the starting homopoly(CEVE) (open circles). Therefore, the styrene polymerization from the living poly(CEVE) is also living to give CEVE–styrene block copolymers 6, structurally similar to the MVE-based counterpart 5 (Scheme 1).

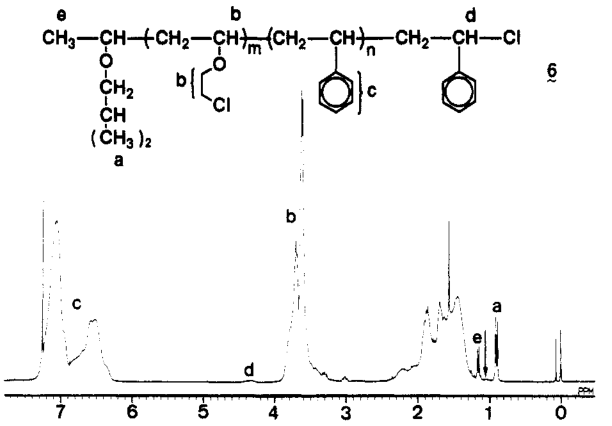

Figure 7. ^{1}H NMR spectrum of CEVE–styrene block copolymerization products (6) [DP$_n$(obsd) = 28/41 (CEVE/styrene)]; the unfractionated sample shown in Figure 6D]. The arrow at ca. 1 ppm indicates the signal position expected for the α-end methyl of proton-initiated polystyrene.

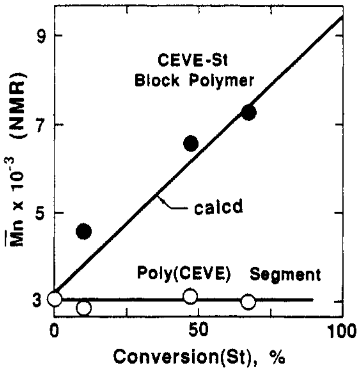

Figure 8. Molecular weights $\bar{M}_n$ of CEVE–styrene block polymers 6 (filled circles) and their poly(CEVE) segments (open circles) as a function of styrene conversion; see the caption of Figure 6 (C and D) for reaction conditions. $\bar{M}_n$ was determined by ^{1}H NMR; see Figure 7 and the relevent text. The diagonal solid line indicates the calculated $\bar{M}_n$ for 6 based on the assumption that one living poly(CEVE) chain as well as the block polymer is formed per initiator 1.

Thus, with styrene, MVE and CEVE lead to well-defined AB block copolymers, whereas IBVE does not, via the sequential living cationic polymerizations with the 1/$SnCl_4$ system (cf. Scheme 1). Separate experiments[22] showed that the overall polymerization rates of these vinyl ethers under the block copolymerization conditions are in the order IBVE > MVE > CEVE ≫ styrene, and, therefore, vinyl ethers much more reactive than styrene such as IBVE are not suited for the efficient cross-propagation of less reactive styrene from their living ends.

Also important, these block copolymerizations should apparently be carried out from a more reactive to a less reactive comonomer (e.g., from MVE to styrene). Specifically for the MVE–styrene pair, for example, the reverse order of monomer addition (from styrene to MVE) did not give well-defined AB block copolymers but instead resulted in rapid deactivation of the MVE growing end due to a very high concentration of $SnCl_4$ needed for the first-stage styrene polymerization. In this regard, our vinyl ethers–styrene systems differ from Kennedy's similar systems where MVE[13] and IBVE[14] are polymerized from poly(isobutylene) growing ends.

4. Concluding Remarks. This study has shown for the first time that MVE–styrene block copolymers (**5**) can be synthesized by the sequential living cationic polymerization from MVE to styrene with the 1/$SnCl_4$/$n$$Bu_4NCl$ system (Scheme 1). Similar block copolymers (**6**; Figure 7) can also be prepared for the CEVE–styrene pair. The critical factors for these syntheses include (i) the development of the 1/$SnCl_4$ initiating system, which is applicable in common to vinyl ethers and styrene under similar conditions (with $n$$Bu_4NCl$ in CH_2Cl_2 below −15 °C) and (ii) the judicious adjustment of polymerization conditions in each stage so as to be best suited for both comonomers, such as the vinyl ether polymerizations at −78 °C and the addition of an $SnCl_4$/$n$$Bu_4NCl$ mixture prior to the second-stage polymerization of styrene at −15 °C.

Although we must admit the segment lengths of our MVE–styrene block copolymers (**5**) should be increased for extensive studies of phase separation behavior, etc., which is now under our investigation, it is important from the synthetic viewpoint that an efficient cross-propagation from the living poly(MVE) (**4**) to styrene and its undisturbed growth are possible under selected conditions to permit control in segment lengths and compositions. Even from the physical viewpoint, the currently available samples with relatively short segment lengths should be of interest as compatibilizers for homopolymer blends of MVE and styrene, which would alter their phase separation and other physical properties.

Experimental Section

Materials. MVE (Tokyo Kasei, purity > 99%), commercially obtained in a small gas cylinder, was passed through a series of two columns packed with potassium hydroxide and calcium hydride in this order and was condensed at −78 °C just before use into a graduated glass tube equipped with a three-way stopcock and baked under dry nitrogen, where the liquefied monomer was diluted with CH_2Cl_2 into a stock monomer solution at a known concentration (0.2–1.0 M). Commercial styrene, bromobenzene, and n-octane (both internal standards for gas chromatography (GC)) were washed with an aqueous 10% sodium hydroxide solution and then water, dried overnight with anhydrous magnesium sulfate (for styrene only) or calcium chloride, and distilled twice over calcium hydride under reduced pressure: purity > 99.5% by GC. $SnCl_4$ from a commercial source (Wako Chemical, guaranteed reagent) was distilled twice over phosphorus pentoxide under reduced pressure. These four purified liquids were stored in brown ampules under dry nitrogen. $n$$Bu_4NCl$ (Tokyo Kasei, purity > 99%) was used as commercially supplied after drying in vacuo. The initiator 1 [$CH_3CH(OR)Cl$; R = isobutyl] was prepared by electrophilic addition of hydrogen chloride to IBVE in n-hexane, as reported previously.[15] CH_2Cl_2 (polymerization solvent) and n-hexane (solvent for 1) were washed with an aqueous 10% sodium hydroxide solution and then deionized water, dried overnight with calcium chloride, and distilled twice over calcium hydride into a flask equipped with a three-way stopcock and containing 3-Å molecular sieves.

Procedures. Sequential living cationic polymerizations were carried out under dry nitrogen in a round-bottomed 30-mL flask equipped with a three-way stopcock and a magnetic stirring bar. All reagents were transferred via dried syringes through a three-way stopcock against a dry nitrogen stream. A typical example of the MVE–styrene block copolymerization was as follows (Scheme 1): To a cooled MVE solution (0.25 M, 4.0 mL) in CH_2Cl_2 at −78 °C were added with vigorous stirring a solution of initiator 1 (100 mM, 0.50 mL; in n-hexane) and then a solution of $SnCl_4$ and $n$$Bu_4NCl$ (100 mM each, 0.50 mL; in CH_2Cl_2). The polymerization mixture was thus 5.0 mL in volume where $[MVE]_0$ = 0.20 M (20 equiv to the initiator); $[1]_0 = [SnCl_4]_0 = [n\text{Bu}_4\text{NCl}]_0$ = 10.0 mM. After 20 min one of the runs was quenched with prechilled ammoniacal methanol (2.5 mL) to find that MVE conversion was 98% by gravimetry of the products (see below for polymer recovery procedures).

To another solution of the living poly(MVE) (**4**), prepared under the identical conditions and kept unquenched at −78 °C, were added a solution of styrene (4.5 M, 0.50 mL; in CH_3Cl_2) containing bromobenzene (0.08 mL; internal standard for GC) and then a solution of $SnCl_4$ and $n$$Bu_4NCl$ (1 M and 300 mM, respectively; 0.50 mL; in CH_2Cl_2). For the latter solution, special care was taken to add it slowly and dropwise with vigorous magnetic stirring. Thus, the reaction mixture of this second-stage polymerization was then 6.0 mL in total volume where $[\text{styrene}]_0$ = 0.38 M (45 equiv to 1 or the living end **4**); $[SnCl_4]$ = 92 mM; $[n\text{Bu}_4\text{NCl}]$ = 33 mM. The styrene polymerization was quenched after 5 h; conversion was 82% by GC; see also Figures 3–5 for detailed results.

The CEVE- and IBVE–styrene block copolymerizations were carried out similarly, except that vinyl ether conversions in the first stage were determined by GC with n-octane as the internal standard. The reagent concerntrations and other reaction conditions are shown in the caption of Figure 6. The corresponding homopolymerizations of styrene and vinyl ethers were also carried out similarly to the first-stage reaction described for the MVE–styrene block copolymers.

The quenched reaction solutions were diluted with toluene (30 mL) and washed sequentially with 2% hydrochloric acid and deionized water (both below 10 °C) to remove the tin-containing residues, evaporated to dryness under reduced pressure, and vacuum dried overnight to give the product polymers.

Measurements and Analysis. The MWDs of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-802, K-803, and K-804) connected to a precision pump (Jasco 880-PU) and refractive and ultraviolet detectors (Jasco 830-RI and 875-UV, respectively). The $\bar{M}_w/\bar{M}_n$ ratios were determined from the SEC curves on the basis of a polystyrene carlibration (molecular weight range: 10^2–3×10^5; calibrated against 10 standard samples). Preparative SEC for sample isolation was performed on a Shodex H-2003 polystyrene gel column connected to the same chromatography system as for analytical SEC.

^1H NMR spectra (270 MHz) were recorded at 30 °C in deuterated chloroform on a JEOL GSX-270 spectrometer. Chemical shifts were determined relative to the signal of the residual CH_2Cl_2 (5.32 ppm) in the deuterated solvent.

Samples for visual inspection of the block copolymers and blends (Table 1) were prepared from toluene solutions of the polymers (ca. 20 w/v %) by casting onto glass vials and slowly drying at 25 °C for 3 days. Solubility characteristics were analyzed with ca. 5 wt % solutions at 25 °C.

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(19) The $\bar{M}_n$ of poly(MVE) was determined by 270-MHz ^{1}H NMR spectroscopy from the peak intensity ratio of the pendant methyl and the main-chain methine (2.9–3.8 ppm) of the main chain to the α-end methyl (0.9 ppm) derived from the initiator 1; see Figure 4 and the relevant text.

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