Macromolecules **1997,** *30,* 27−31

Living Cationic Isomerization Polymerization of β-Pinene. 2. Synthesis of Block and Random Copolymers with Styrene or *p*-Methylstyrene

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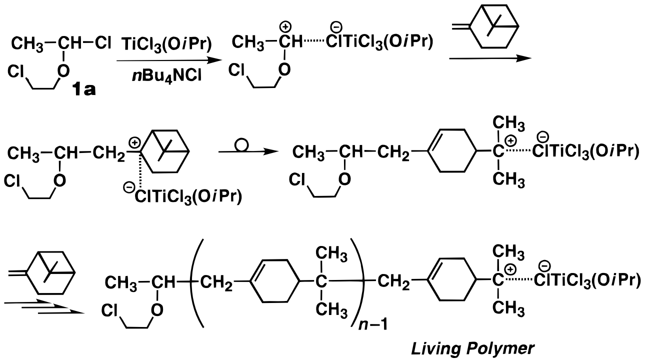
Received July 23, 1996; Revised Manuscript Received October 29, 1996[⊗]

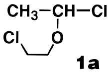
ABSTRACT: Block copolymers of β-pinene with styrene (St) or *p*-methylstyrene (*p*MeSt) were prepared by the sequential living cationic polymerizations initiated with the HCl adducts of styrene (**1b**: HCl−St) or 2-chloroethyl vinyl ether (**1a**: HCl−CEVE), respectively, in the presence of isopropoxytitanium trichloride [$\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$] and tetra-*n*-butylammonium chloride ($n\mathrm{Bu_4NCl}$) in $\mathrm{CH_2Cl_2}$ at −40 °C. As for the β-pinene−St pair, both AB and BA block copolymers ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \sim 1.3$) were obtained by this method. With *p*MeSt, the addition of β-pinene to the living *p*MeSt polymers gave block copolymers with narrow molecular weight distributions (MWDs) ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \sim 1.2$), whereas the reverse order of addition led to block copolymers with broad MWDs ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \sim 1.9$). In the polymerization of a mixture of β-pinene and St, the former was consumed faster to give tapered copolymers. In contrast, β-pinene and *p*MeSt were copolymerized nearly at the same rate to give random or statistical copolymers.

Introduction

A bicyclic aliphatic monomer abundantly found in natural turpentine, β-pinene, readily undergoes cationic polymerization to give polymers that contain six-membered rings as repeat units.[2−5] The unique backbone structure originates from the isomerization of the initially bicyclic growing end into the open-chain tertiary cation structurally similar to the *tert*-butyl cation. Despite such a mechanistic complexity, we have recently developed living cationic polymerization of β-pinene with the use of combinations of the hydrogen chloride adduct (**1a**) of 2-chloroethyl vinyl ether (CEVE) as initiator and isopropoxytitanium chloride [$\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$] as activator in the presence of tetra-*n*-butylammonium chloride ($n\mathrm{Bu_4NCl}$) (Scheme 1).[6]

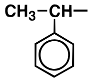
Scheme 1





$\mathrm{CH_3{-}CH{-}Cl}$ (with $\mathrm{OCH_2CH_2Cl}$ below)

1a



1b

This work was to extend this finding to the controlled synthesis of β-pinene-based block and random copolymers with styrene (St) or *p*-methylstyrene (*p*MeSt). Although the homopolymer has already been commercialized as resins, few are known for β-pinene copolymers. According to a recent report,[3] the monomer undergoes azeotropic copolymerization with isobutene, but its block copolymers have not been obtained yet.

Recently, we have also found that St can be polymerized into living polymers with the HCl adduct of styrene [**1b** (HCl−St): $\mathrm{CH_3CH(Ph)Cl}$]/$\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$/$n\mathrm{Bu_4NCl}$ initiating system.[7] These findings for β-pinene[6] and St[7] suggest that block copolymerizations of the two monomers would be possible with the $\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$-based systems, because the components of the initiating systems are quite similar, although the order of sequential monomer addition and other reaction conditions should be carefully chosen for the synthesis of well-controlled block copolymers.[8] Along with the block copolymerizations, we examined polymerizations of mixtures of β-pinene and styrenes to elucidate their reactivity and to synthesize random and living copolymers.

Results and Discussion

1. Living Polymerization of St and *p*MeSt with $\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$. Prior to block copolymerizations of β-pinene and the styrenes, homopolymerizations of the latter monomers were investigated with the HCl adduct of CEVE or St (**1a** or **1b**, respectively) in conjunction with $\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$ and $n\mathrm{Bu_4NCl}$ in $\mathrm{CH_2Cl_2}$ at −40 °C.

As reported previously,[7] the **1b**/$\mathrm{TiCl_3(O}\mathit{i}\mathrm{Pr)}$/$n\mathrm{Bu_4NCl}$ system induced smooth polymerization of styrene (open circles in Figure 1) to give living polymers with narrow molecular weight distributions ($\bar{M}_\mathrm{w}/\bar{M}_\mathrm{n} \sim 1.1$), where the number-average molecular weights ($\bar{M}_\mathrm{n}$) of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values assuming

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[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.

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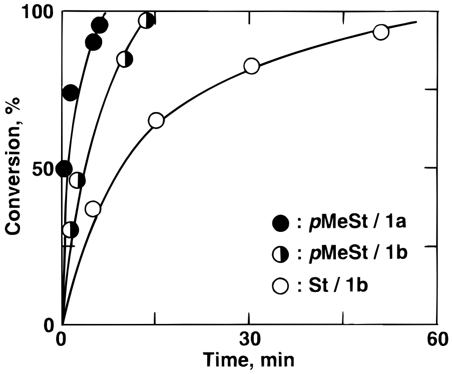


Figure 1. Polymerization of St with **1b** (○) and *p*MeSt with **1a** (●) and **1b** (◑) in conjunction with $TiCl_3(OiPr)$ and nBu$_4$NCl in CH_2Cl_2 at −40 °C: $[M]_0 = 1.0$ M; $[\mathbf{1a}]_0 = [\mathbf{1b}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM (for St), 30 mM (for *p*MeSt); $[nBu_4NCl]_0 = 10$ mM.

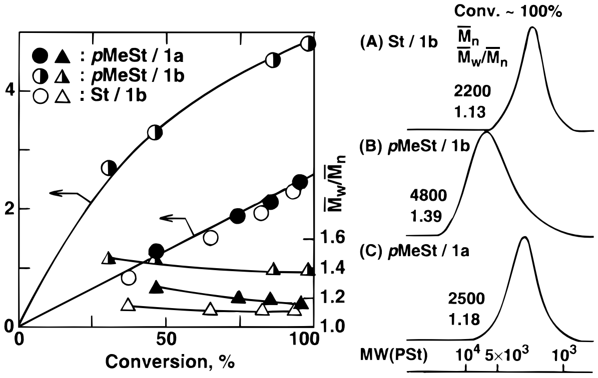


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(St) and poly(*p*MeSt) obtained in the same experiments as for Figure 1: St/**1b** (○, △, A); *p*MeSt/**1b** (◑, ▲, B); *p*MeSt/**1a** (●, ▲, C). Conversion for MWDs ~ 100%.

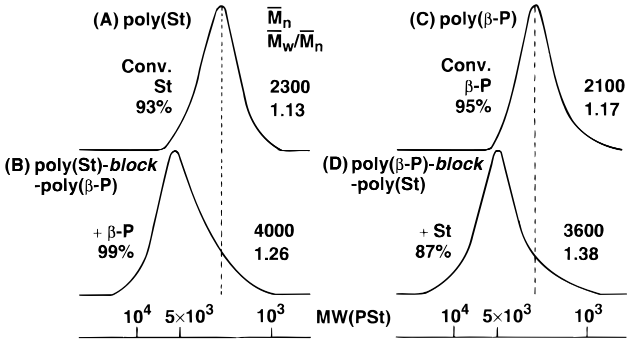
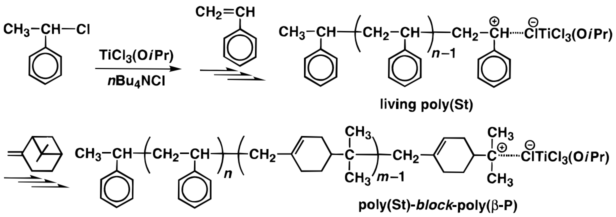


Figure 3. MWD curves of poly(St) (A), poly(β-pinene) (C), and the polymers obtained after the addition of β-pinene (B) and St (D) to samples A and C, respectively, with **1b**/$TiCl_3(OiPr)$/nBu$_4$NCl in CH_2Cl_2 at −40 °C. (A and B) $[St]_0 = 0.50$ M; $[\mathbf{1b}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 10$ mM; $[\beta\text{-pinene}]_{add} = 0.50$ M. (C and D) $[\beta\text{-pinene}]_0 = 0.50$ M; $[\mathbf{1b}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 10$ mM; $[St]_{add} = 0.50$ M.

that one molecule of the initiator generates one polymer chain (open circles in Figure 2).

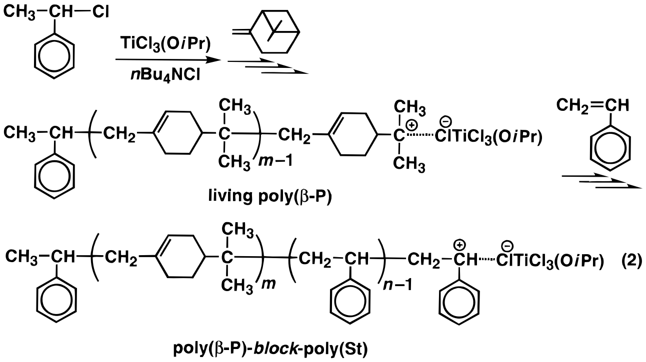
Under similar conditions but with use of a smaller amount of $TiCl_3(OiPr)$ (30 mM for St vs 100 mM for *p*MeSt), the latter undergoes still faster polymerization (filled and half-filled circles in Figure 1) due to its higher cationic reactivity. The reaction with **1a** is faster than with **1b**. The $\bar{M}_n$ of the poly(*p*MeSt) obtained with **1b** is higher than the calculated value (half-filled circles in Figure 2), and the MWDs were broader. This is due to slow initiation from **1b**, where the reactivity of the C−Cl terminal is lower than that of the polymer terminal derived from *p*MeSt. In contrast, the polymers obtained with **1a** had narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.1$) and the $\bar{M}_n$ increased in direct proportion to monomer conversion (filled circles in Figure 2). This indicates that **1a** serves as an efficient initiator for living *p*MeSt polymerization due to the higher reactivity of its C−Cl bond derived from a vinyl ether.[9] Thus, living cationic polymerizations of St and *p*MeSt were feasible with the $TiCl_3(OiPr)$-based initiating systems with appropriate initiators; **1b** for St and **1a** for *p*MeSt.

2. Block Copolymerization of β-Pinene with Styrenes. (a) Block Copolymerization. With the **1b**/$TiCl_3(OiPr)$/nBu$_4$NCl system, sequential block copolymerizations between β-pinene and St were examined in CH_2Cl_2 at −40 °C. On addition into the living poly(St) solution (Figure 3A; conversion = 93%), β-pinene polymerized smoothly (99% for 60 min). The MWD of the products stayed narrow ($\bar{M}_w/\bar{M}_n = 1.26$) and shifted toward higher molecular weight (Figure 3B), indicative of the formation of BA block copolymers of St and β-pinene (eq 1); herein and in the following text, we denote β-pinene as monomer A and the styrene monomers as B.



(1)

In the reverse order of addition where St was added into living poly(β-pinene) (Figure 3C; conversion = 95%), it was consumed, though the rate was much slower than that in the homopolymerization under similar conditions (87% for 6 h in the sequential polymerization whereas 93% for 50 min in the homopolymerization). This is probably due to the complexation of $TiCl_3(OiPr)$ by the in-chain endo-olefins in the preformed poly(β-pinene), which decreases the effective concentration of $TiCl_3(OiPr)$ available for the activation of the chlorine-bearing polymer terminal. The MWD curve was fairly narrow and shifted toward higher molecular weight (Figure 3D; $\bar{M}_w/\bar{M}_n = 1.38$), indicating the formation of AB block copolymers of β-pinene and St as well (eq 2).



(2)

The efficient blocking in both AB and BA orders is ascribed to similar reactivity of the C−Cl bonds in the ∼∼∼CH(Ph)−Cl and ∼∼∼$C(CH_3)_2$−Cl, derived from the two monomers, as suggested by similar solvolysis rate constants of the C−Cl bonds in their model compounds, $CH_3CH(Ph)$−Cl and $CH_3C(CH_3)_2$−Cl.[10]

The block copolymerizations between β-pinene and *p*MeSt were then examined with **1a** as initiator. In the first-stage polymerization of *p*MeSt, for example, a smaller amount of $TiCl_3(OiPr)$ (30 mM) was used in

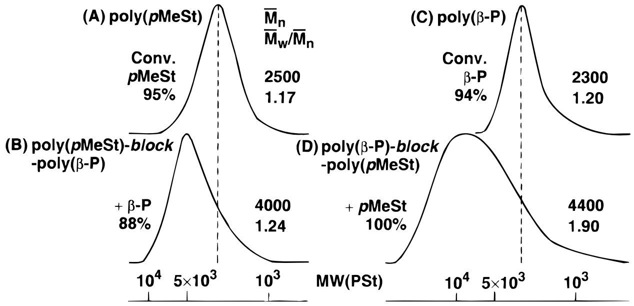


Figure 4. MWD curves of poly(*p*MeSt) (A), poly(*β*-pinene) (C), and the polymers obtained after the addition of *β*-pinene (B) and *p*MeSt (D) to samples A and C, respectively, with **1a**/TiCl$_3$(O*i*Pr)/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40 °C. (A and B) [*p*MeSt]$_0$ = 0.50 M; [**1a**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 30 mM (for A), 100 mM (for B); [*n*Bu$_4$NCl]$_0$ = 10 mM; [*β*-pinene]$_{add}$ = 0.50 M. (C and D): [*β*-pinene]$_0$ = 0.50 M; [**1a**]$_0$ = 20 mM; [TiCl$_3$(O*i*Pr)]$_0$ = 100 mM; [*n*Bu$_4$NCl]$_0$ = 10 mM; [*p*MeSt]$_{add}$ = 0.50 M.

accordance to the high reactivity of *p*MeSt, and to the resulting living ends was added an additional amount of the titanium compound upon addition of the second monomer, *β*-pinene, so that the total concentration of TiCl$_3$(O*i*Pr) became 100 mM. The added feed was polymerized smoothly (88% for 120 min) to give BA block copolymers whose MWDs shifted toward higher molecular weight and remained narrow (Figure 4B).

For the reverse order of monomer addition (from *β*-pinene to *p*MeSt; Figure 4D), the second-stage polymerization occurred smoothly (100% for 15 min), but the products gave broader MWDs ($\overline{M}_w/\overline{M}_n$ = 1.90), in contrast to the BA block copolymers (Figure 4B). The broadening in MWD suggests slow initiation from the living poly(*β*-pinene) terminal or the higher reactivity of the terminal [∼∼∼CH(*p*MePh)−Cl] derived from *p*MeSt compared with that from *β*-pinene [∼∼∼C(CH$_3$)$_2$−Cl].

(b) ^{1}H NMR Analysis of the Block Copolymers. The structures of the block copolymers were then analyzed by ^{1}H NMR spectroscopy. Figure 5A shows the ^{1}H NMR spectrum of the AB block copolymers of *β*-pinene and St. There appeared the methine proton (*i*) of the C−Cl terminal of poly(St) at 4.5 ppm besides the characteristic signals of the two repeat units (*e*, the endo-olefin in the isomerized *β*-pinene unit; *c*, the phenyl group in the St unit). As expected, the initiator fragment (CH$_3$CHPh−) could not be observed separately. The number-average degrees of polymerization ($\overline{DP}_n$) of *β*-pinene and St segments can be obtained from the peak intensity ratio of *e*/*i* and *c*/5*i*, respectively. The values were 24 for *β*-pinene and 21 for St, which were in good agreement with the calculated values ([M]$_0$/[**1a**]$_0$ × conversion), 25 for *β*-pinene and 22 for St, respectively (Table 1).

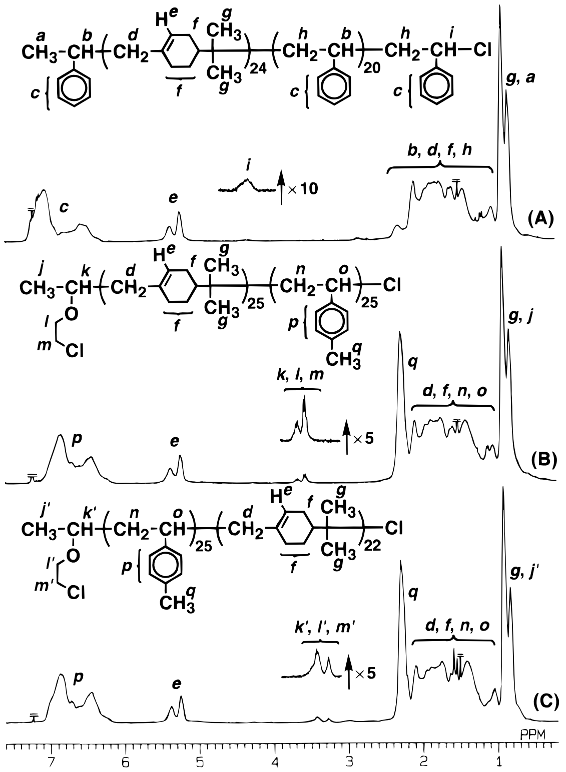


Figure 5. ^{1}H NMR spectra of poly(*β*-pinene)-*block*-poly(St) (A), poly(*β*-pinene)-*block*-poly(*p*MeSt) (B), and poly(*p*MeSt)-*block*-poly(*β*-pinene) (C). All samples were obtained in the same experiments as for Figures 3 and 4.

Table 1. Block Copolymers of *β*-Pinene and Styrene or *p*-Methylstyrene

	sequential $\overline{DP}_n$	
	obsd	calcd
β-pinene → St	24/21	25/22
β-pinene → *p*MeSt	22/25	22/25
*p*MeSt → *β*-pinene	30/28	25/25

Parts B and C of Figure 5, respectively, show the ^{1}H NMR spectra of the AB and BA block copolymers of *β*-pinene and *p*MeSt. Both spectra exhibit all key absorptions of the *β*-pinene (*d*−*g*) and *p*MeSt (*n*−*q*) repeat units and the chloroethyl group derived from the initiator (*k*−*m* and *k*′−*m*′) at the α-end. There are almost no remarkable differences in their main chain absorptions. However, the methine and methylene protons at the α-end group absorb more upfield with the BA block copolymers (*k*′−*m*′ in Figure 3C) than with the AB block (*k*−*m* in Figure 3B), probably due to the effects of aromatic rings in the adjacent *p*MeSt unit in the former. This means that **1a** efficiently initiates polymerization of both monomers. The $\overline{DP}_n$ values of *β*-pinene and *p*MeSt units were determined from the peak intensity ratio of 5*e*/(*k* + *l* + *m*) and 5*p*/4(*k*′ + *l*′ + *m*′), respectively. The observed values were in agreement with the calculated values from the gas-chromatographic monomer conversions, as shown in Table 1.

These results indicate that block copolymers of *β*-pinene with St and *p*MeSt can be prepared with **1b** and **1a**, respectively, in conjunction with TiCl$_3$(O*i*Pr) and *n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40 °C. These are the first examples of the synthesis of block copolymers of *β*-pinene.

3. Copolymerization of *β*-Pinene and Styrenes. (a) Copolymerization. For possible random copolymerization of *β*-pinene and styrene monomers, their equimolar mixtures were polymerized with **1b**/TiCl$_3$(O*i*Pr)/*n*Bu$_4$NCl in CH$_2$Cl$_2$ at −40 °C. With the *β*-pinene−styrene pair (Figure 6), monomer consumption was slower for St than for *β*-pinene (for example, 18% St and 64% *β*-pinene for 15 min), although the rate difference is smaller in their homopolymerizations. *β*-Pinene, a monomer with a strained ring, is cationically more reactive than St, as suggested by the higher reactivity of isobutene relative to St.[10] The reactivity of the C−Cl terminal derived from *β*-pinene is not so reactive, as mentioned above, and the polymerization from this C−Cl bond is not so fast. Furthermore, the endo-olefin in the poly(*β*-pinene) segments complexes with TiCl$_3$(O*i*Pr). These factors may facilitate relatively selective homopropagation of *β*-pinene during the early stages of the copolymerization and thereby lead to tapered block copolymers.

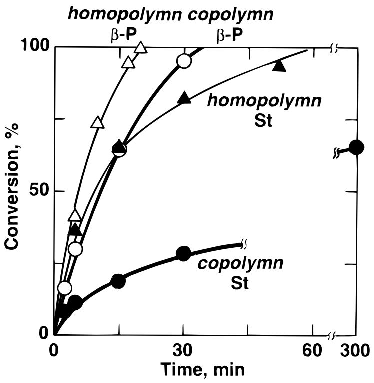


Figure 6. Copolymerizations of β-pinene (○) and St (●), and the homopolymerizations of β-pinene (△) and St (▲) with **1b**/$TiCl_3(OiPr)/nBu_4NCl$ in CH_2Cl_2 at −40 °C: $[\beta\text{-pinene}]_0 = [St]_0 = 0.50$ M; $[\mathbf{1b}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 10$ mM.

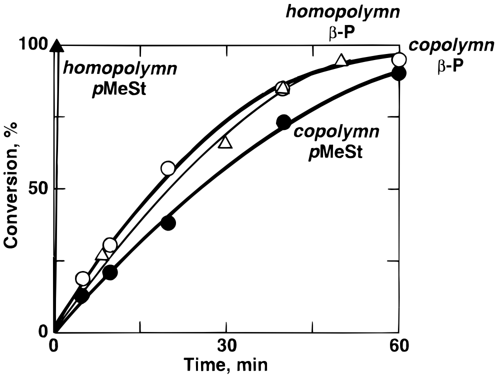


Figure 7. Copolymerizations of β-pinene (○) and *p*MeSt (●), and the homopolymerizations of β-pinene (△) and *p*MeSt (▲) with **1a**/$TiCl_3(OiPr)/nBu_4NCl$ in CH_2Cl_2 at −40 °C: $[\beta\text{-pinene}]_0 = [p\text{MeSt}]_0 = 0.50$ M; $[\mathbf{1a}]_0 = 20$ mM; $[TiCl_3(OiPr)]_0 = 100$ mM; $[nBu_4NCl]_0 = 10$ mM.

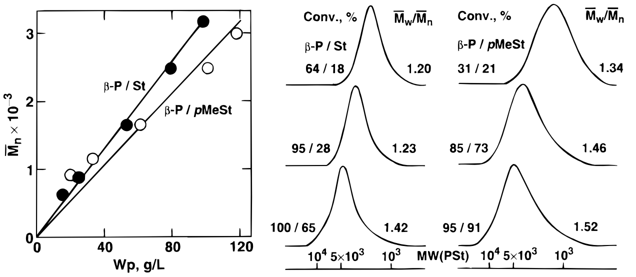


Figure 8. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of the copolymers of β-pinene with St (●) and with *p*MeSt (○) obtained in the same experiments as for Figures 6 and 7, respectively.

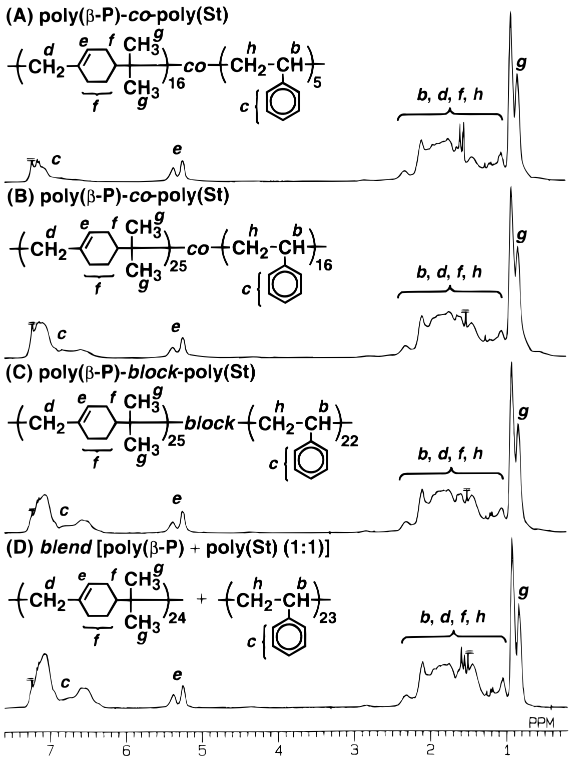


Figure 9. ^{1}H NMR spectra: (A and B) copolymers of β-pinene and St, conversion for β-pinene/St = 64/18 (A), 100/65 (B); (C) poly(β-pinene)-*block*-poly(St), conversion for β-pinene/St = 100/87, sample D in Figure 3; (D) blend of poly (β-pinene) ($\overline{DP}_n$ = 24) and poly(St) ($\overline{DP}_n$ = 23), β-pinene/St = 1/1 (repeat units ratio).

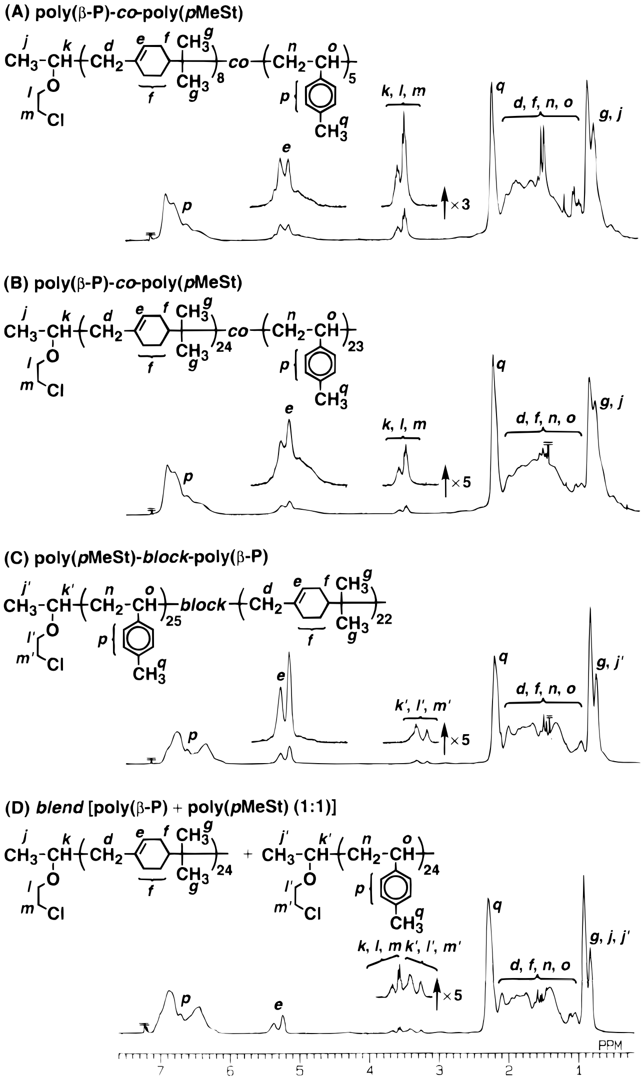
In contrast, similar copolymerizations of β-pinene and *p*MeSt led to parallel consumption of both monomers (Figure 7), suggesting the occurrence of random copolymerization.

Figure 8 plots the $\bar{M}_n$ of the polymers thus obtained against the total yield. In both copolymerizations with St and *p*MeSt, the $\bar{M}_n$ increased in direct proportion to the yield, and the MWDs were unimodal throughout the reactions. The broadening in MWD is attributable to the difference in cross propagation rates. These results suggest the formation of long-lived copolymers. Depending on the reactivity differences of each monomer pair, the β-pinene/St copolymers were tapered and blocky, whereas the β-pinene/*p*MeSt were random or statistical, as will be shown in the next section.

(b) ^{1}H NMR Analysis of the Copolymers. The structures of the copolymers were then examined by ^{1}H NMR spectroscopy. Figure 9A shows the spectrum for the copolymer of β-pinene and St obtained at the middle stage of the polymerization (conversion: β-pinene, 64%; St, 18%). The shape of the phenyl absorptions (*c*) of the styrene unit was quite different from those for the block copolymers (Figure 9C) and a blend of poly(St) and poly(β-pinene) (Figure 9D). This means that styrene is copolymerized with β-pinene to give St−β-pinene heterosequences that in turn give the characteristic phenyl signals. In contrast, the signal of the β-pinene unit (*e*) is similar to that in the homopoly(β-pinene) segments, though not exactly the same. In the spectrum of the copolymer obtained at the later stage (β-pinene, 100%; St, 65%; Figure 9B), the shape of the phenyl protons became similar to that in the homopolystyrene segments. These results indicate that copolymerizations of β-pinene and St generate tapered block copolymers where the content of β-pinene is higher near the α-end and lower near the ω-end.

Parts A and B of Figure 10, respectively, show the ^{1}H NMR spectra of the copolymers of β-pinene and *p*MeSt obtained at an early (31% for β-pinene and 21% for *p*MeSt) and a later (95% for β-pinene and 91% for *p*MeSt) stage of the polymerizations. Not only the phenyl absorptions (*p*) of the styrene unit but also the endo-olefin signals (*e*) of the β-pinene unit were quite different in shape from those in the block copolymers (Figure 10C) and a blend of the two homopolymers (Figure 10D). These indicate that the homosequence of each unit is short and that copolymerizations of β-pinene and *p*MeSt generate random copolymers.

Interestingly, the spectra of the random copolymers (Figure 10A,B) exhibit only one type of the initiator fragment (*k*−*m*) that is adjacent to a β-pinene unit, but no signals of the other type of the initiator fragment (*k*′−*m*′) adjacent to a *p*MeSt unit. Note that these α-end signals are clearly separated in the spectrum for the


(A) poly(β-P)-*co*-poly(*p*MeSt)

(B) poly(β-P)-*co*-poly(*p*MeSt)

(C) poly(*p*MeSt)-*block*-poly(β-P)

(D) *blend* [poly(β-P) + poly(*p*MeSt) (1:1)]

Figure 10. ^{1}H NMR spectra: (A and B) copolymers of β-pinene and *p*MeSt, conversion for β-pinene/*p*MeSt = 31/21 (A), 95/91 (B); (C) poly(*p*MeSt)-*block*-poly(β-pinene), conversion for β-pinene/*p*MeSt = 88/100, sample B in Figure 4; (D) blend of poly(β-pinene) ($\overline{\mathrm{DP}}_n$ = 24) and poly(*p*MeSt) ($\overline{\mathrm{DP}}_n$ = 24), β-pinene/*p*MeSt = 1/1 (repeat units ratio).

polymer blend (Figure 10D), both components of which had been obtained with the same initiator (**1a**). This means that the initiating cationic species from **1a** almost selectively adds to β-pinene and then induces random copolymerizations.

From these and other results, it can be concluded that the reactivity order is β-pinene ≥ *p*MeSt ≫ St for the monomers but ~~~CH(*p*MePh)−Cl ≫ ~~~CH(Ph)−Cl ≈ ~~~C(CH$_3$)$_2$−Cl for the terminal C−Cl bonds. These two factors may affect the efficiency in the block copolymerizations and the copolymer sequences (tapered vs random) between β-pinene and the two styrenes.

Experimental Section

Materials. (−)-β-Pinene (Wako Chemicals; purity >97%) was distilled twice under reduced pressure over calcium hydride before use. Styrene (Wako Chemicals; purity >98%), *p*-methylstyrene (Tokyo Kasei; purity >95%), and 2-chloroethyl vinyl ether (Nisso Maruzen Chemical; purity >99%) were washed with 10% aqueous sodium hydroxide and then water, dried overnight with anhydrous sodium sulfate, and distilled twice under reduced pressure over calcium hydride before use. 1-Phenylethyl chloride (**1b**; Wako Chemicals; purity >97%) was distilled twice under reduced pressure. *n*Bu$_4$NCl (Tokyo Kasei; purity >98%) was used as received. CH$_2$Cl$_2$ was doubly distilled over phosphorus pentoxide and then over calcium hydride before use. *n*-Hexane (the solvent for **1a**) and chlorobenzene (an internal standard for gas chromatography) were doubly distilled over calcium hydride before use.

Isopropoxytitanium chloride [TiCl$_3$(O*i*Pr)][7,11] and adduct **1a**[9] were prepared and purified as already reported.

Polymerization Procedures. Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. A typical example for the BA (*p*MeSt → β-pinene) block copolymerization is given below. The reaction was initiated by sequentially adding, via dry syringes, a solution of **1a** (in *n*-hexane; 0.50 mL) and a mixture of TiCl$_3$(O*i*Pr) and *n*Bu$_4$NCl (in CH$_2$Cl$_2$; 1.0 mL) into a solution (3.5 mL) of *p*MeSt (0.17 mL) and chlorobenzene (0.20 mL) in CH$_2$Cl$_2$ at −40 °C. The reaction was run for 7 min, where *p*MeSt conversion reached 95%. β-Pinene (0.20 mL) was then added to the preformed living poly(*p*MeSt) solution. The reaction was quenched with prechilled methanol (2 mL) after predetermined intervals. Monomer conversions of the styrene monomers were determined from the concentrations of the residual monomers measured by gas chromatography with chlorobenzene as internal standard. For β-pinene, the gas-chromatographic conversion is higher than the polymer yield by gravimetry, because isomerization of the residual β-pinene monomer occurred in the GC columns. Thus, the gravimetric conversion was used for β-pinene.

The quenched reaction mixture was diluted with toluene (25 mL) and washed sequentially with 2% hydrochloric acid, aqueous 1% sodium hydroxide solution, and water to remove titanium-containing residues. The organic layer was evaporated to dryness under reduced pressure and dried in vacuo at 40 °C for 5 h to give the product polymers.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios 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 JASCO PU-980 precision pump and a JASCO 830-RI refractive index detector. The columns were calibrated against 10 standard polystyrene samples $\bar{M}_n$ = 800−300 000; $\bar{M}_w/\bar{M}_n$ = 1.03−1.10) as well as styrene oligomers (tetramer, trimer, and dimer). ^{1}H NMR spectra of the polymers were recorded in CDCl$_3$ at room temperature on a JEOL JNM-GSX270 spectrometer (270.7 MHz). Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

Acknowledgment. J.L. is grateful to the Japan Society of the Promotion of Science for the Dissertation Ph.D. Fellowship (1994−96), which allowed him to stay at Kyoto University.

References and Notes

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MA9610976