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Alternating-Like Cationic Copolymerization of Styrene Derivatives and Benzaldehyde: Precise Synthesis of Selectively Degradable Copoly(styrenes)

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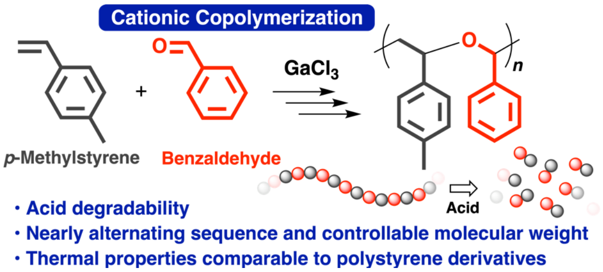


Abstract

Cationic copolymerizations of styrene derivatives and benzaldehyde (BzA) were systematically investigated for the purpose of both achieving living alternating copolymerization and creating “degradable polystyrene derivatives”. As a result of the optimization of reaction conditions, the copolymerization of *p*-methylstyrene (pMeSt) and BzA was demonstrated to proceed in a living manner with $GaCl_3$ as a catalyst in the presence of tetrahydropyran, yielding a copolymer with a nearly alternating sequence and a controllable molecular weight. *sec*-Benzylic ether structures were generated in the main chain of the copolymer due to the crossover reactions between the monomers; hence, the copolymer was degraded into low-molecular-weight compounds under acidic conditions. In addition, the copolymer exhibited a glass transition temperature and degradation temperature that were comparable to those of the pMeSt homopolymer.

Introduction

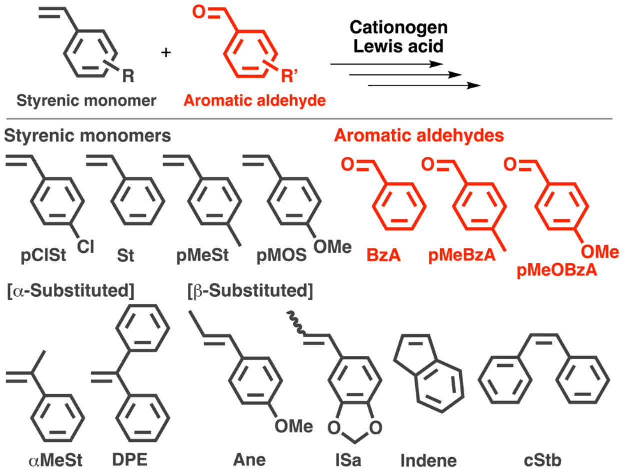
Aldehydes with appropriate structures can be polymerized via the cationic or anionic addition reactions of carbonyl groups.[1–5] A representative example is the polymerization of formaldehyde into polyoxymethylene, which is an industrially important engineering plastic.[5] Aliphatic aldehydes such as acetaldehyde are also homopolymerizable, although the polymerization reaction needs to be conducted at low temperature due to the low ceiling temperature (T_c).[1–4] However, aromatic aldehydes are generally nonhomopolymerizable although special types such as *o*-phthalaldehyde are homopolymerizable[6–9]. For example, benzaldehyde (BzA) has an extremely low T_c, which was estimated to be approximately –160 °C.[8]

An effective strategy to obtain polymers from aromatic aldehydes is copolymerization with vinyl monomers. In the 1960s, cationic copolymerization of styrene (St) and BzA was reported to proceed with BF_3OEt_2 as a Lewis acid catalyst.[10–14] The monomer reactivity ratios of St and BzA were determined to be both less than 1, suggesting that the crossover reactions were more frequent than the homopropagation reactions. However, the obtained copolymers were analyzed by elemental analysis and infrared spectroscopy; hence, it was unclear whether the crossover reactions truly occurred.

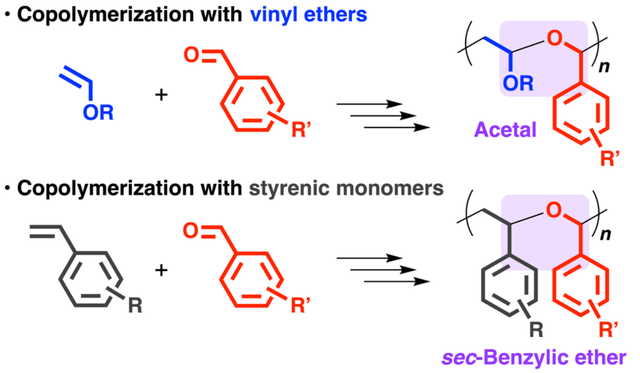
We have previously reported that vinyl ethers (VEs) function as effective comonomers in cationic alternating copolymerization with aromatic aldehydes.[15,16] The use of a suitable Lewis acid catalyst is of particular importance for copolymerization. Specifically, copolymers were obtained with $GaCl_3$, whereas a cyclic trimer consisting of one VE and two aldehyde units was exclusively produced when $EtAlCl_2$ was used. Moreover, the alternating copolymerization was demonstrated to proceed in a living manner when elaborately designed initiating systems were employed. For example, the copolymerization of 2-chloroethyl VE and BzA proceeded in a controlled manner with $GaCl_3$ in conjunction with $EtSO_3H$ as a protonogen in the presence of 1,4-dioxane in toluene at –78 °C, yielding an alternating copolymer with an M_n value of 16×10^3 and M_w/M_n value of 1.1.[16] The obtained copolymers had acetal moieties, which were derived from the crossover reaction from VE to aromatic aldehyde, in the main chains; hence, the copolymers exhibited acid degradability. The cationic copolymerization of VEs and aromatic aldehydes has been subsequently developed in various directions, such as the synthesis of copolymers with naturally occurring conjugated aldehydes,[17] stimuli-responsive alternating copolymers with functional VEs,[18] and the control of the cleavable positions via the sequential addition of aldehyde monomers during the living polymerization of VEs.[19]

On the basis of this background, we have reinvestigated the cationic copolymerization of St derivatives and BzA (Scheme 1) for the purpose of both achieving living alternating copolymerization and creating "degradable polystyrene derivatives". Designing reaction conditions based on those effective for the controlled copolymerization of VEs and aromatic aldehydes potentially leads to the living alternating copolymerization of St derivatives and BzA. In addition, unlike an acetal moiety resulting from VE and BzA, a *sec*-benzylic ether structure is generated via the crossover reaction from St derivatives to BzA (Scheme 2). Therefore, alternating copolymers of St derivatives and BzA contain an oxygen atom instead of one of the two methylene groups in the repeating units. Such structures are expected to exert both properties comparable to polystyrene derivatives and acid degradability. As a result of systematic investigation, the cationic copolymerization of *p*-methylstyrene (pMeSt) and BzA was found to proceed in a living manner to yield a copolymer with nearly alternating sequences and controllable molecular weights (MWs). In addition, the copolymer was successfully degraded under acidic conditions due to the cleavage of the *sec*-benzylic ether moieties in the main chain. Copolymerizations of various α- and β-substituted St derivatives and BzA were also investigated.

Scheme 1. Cationic Copolymerization of Various Styrenic Monomers and Aromatic Aldehydes (Top), and Monomers Used in This Study (Bottom).



Scheme 2. Cationic Alternating Copolymerization of Vinyl Monomers and Aromatic Aldehydes



Results and discussion

Cationic copolymerization of styrenic monomers and BzA

Cationic copolymerization of St and BzA was reported over 50 years ago;[10–11] however, structural analysis was based on elemental analysis and infrared spectroscopy. To examine the copolymerization product in detail by NMR, we first conducted the cationic copolymerization of St and BzA under conditions similar to those adopted in the past study. The copolymerization with BF_3OEt_2 as a catalyst in toluene at 0 °C proceeded to yield a polymer with an M_n of 3.8×10^3 in 2 h (entry 1 in Table

1; Figure S1). ^{1}H NMR analysis of the product indicated that the crossover reactions between St and BzA most likely occurred to generate *sec*-benzylic ether moieties in the main chain, along with homopropagation of St. However, the occurrence of side reactions was also detected by the detailed analysis. Specifically, a cyclic trimer consisting of one St and two BzA was produced as a side product, as in the case of the copolymerizations of VEs and BzA derivatives (Figure S2). In addition, Friedel–Crafts reactions of the propagating chain with toluene (Scheme S1A) likely occurred, as determined by 2D NMR analysis (Figures S3–S6). Similar Friedel–Crafts reactions also potentially occur with the aromatic rings of monomers or copolymer side groups; however, the occurrence of such reactions could not be detected by NMR analysis. Moreover, the MWs of the copolymers decreased as the polymerization time increased (entry 1 in Table 1), suggesting that the *sec*-benzylic ether moieties in the main chain were cleaved by BF_3OEt_2 during the copolymerization (Scheme S1B).

Table 1. Cationic Copolymerization of Styrenic Monomers and Aromatic Aldehydes under Various Conditions [a]

entry	styrenic	aldehyde	Lewis acid	temp (ºC)	time	conv. (%)		M_n $\times 10^{-3}$ [b]	M_w/M_n [b]	aldehyde content (%) [c]	polymer/cyclic trimer ratio[d]
						styrenic	aldehyde				
1	St	BzA	BF_3OEt_2	0	2 h	53	37	3.8	1.81	40	88/12
					4 h	63	45	2.0	2.51	35	88/12
					8 h	99	76	1.6	2.48	35	90/10
					16 h	99	78	0.9	2.17	35	89/11
2	St	BzA	$GaCl_3$	–78	15 min	9	6	1.5	1.68	44	99/1
3	pClSt	BzA	$GaCl_3$	–78	30 min	5	8	0.9	1.48	40	99/1
4	pMeSt	BzA	$GaCl_3$	–78	10 min	27	24	8.1	1.69	42	99/1
5	pMOS	BzA	$GaCl_3$	–78	10 min	79	2	37.0	2.60	0	–
6	pMOS	pMeOBzA	$GaCl_3$	–78	10 min	84	0	14.5	1.64	0	–

[a] For entry 1: $[St]_0 = 1.6$ M, $[BzA]_0 = 1.6$ M, $[BF_3OEt_2]_0 = 1.7 \times 10^2$ mM (5 mol%) in toluene. For entries 2–6: $[\text{styrenic monomer}]_0 = 0.60$ M, $[\text{aromatic aldehyde}]_0 = 0.60$ M, $[\text{IBVE–HCl}]_0 = 4.0$ mM, $[GaCl_3]_0 = 4.0$ mM, [1,4-dioxane] = 1.0 M, in toluene/dichloromethane (7/3 v/v for entries 2–4 or 9/1 v/v for entries 5 and 6). See Figures S1 and S7 for the MWD curves. [b] Determined by GPC (polystyrene standards). For a polymer peak. [c] Content in polymer. Determined by ^{1}H NMR. [d] The ratio of pMeSt units incorporated into polymer/cyclic trimer. Determined by ^{1}H NMR.

To explore suitable reaction conditions for controlled cationic copolymerization of St and BzA, $GaCl_3$ was used as a Lewis acid catalyst in conjunction with the adduct of isobutyl vinyl ether with HCl (IBVE–HCl) as a cationogen in the presence of 1,4-dioxane as a weak Lewis base at –78 °C, based on our previous finding of suitable conditions for the controlled copolymerization of VEs and aromatic aldehydes.[16] At the same time, *p*-substituted St derivatives with different reactivities were examined in copolymerization with BzA. The copolymerization of St and BzA resulted in a copolymer with a BzA content of 44% (entry 2 in Table 1). However, monomer conversion was low when the reaction was quenched at a reaction time of 15 min. A similar result was obtained when *p*-chlorostyrene (pClSt), which is less reactive than St, was used instead of St (entry 3). In contrast, the copolymerization proceeded faster to yield a copolymer with a higher MW when pMeSt, which is more reactive than St, was used (entry 4). The BzA content in the copolymer was comparable to the St and pClSt counterparts. The use of *p*-methoxystyrene (pMOS), which is more reactive than pMeSt, resulted in the generation of a pMOS homopolymer (entry 5). pMOS was exclusively consumed even when *p*-methoxybenzaldehyde (pMeOBzA), a more reactive aldehyde than BzA (an aromatic aldehyde with an electron-donating group is more reactive than BzA in cationic copolymerization[16]), was used instead of BzA (entry 6). From these results, pMeSt and BzA were employed as monomers to optimize the reaction conditions.

Optimization of the cationic copolymerization of pMeSt and BzA

The copolymerization of pMeSt and BzA with $GaCl_3$ in the presence of 1,4-dioxane was conducted over a longer reaction time (entry 1 in Table 2). A decrease in the MWs of the products with the increase in the reaction time was not observed, unlike the copolymerization of St and BzA with BF_3OEt_2 (vide infra); however, the polymerization likely ceased at monomer conversion of 30–40%. To optimize the reaction conditions, we focused on 1,4-dioxane, which was used as a weak Lewis base that moderates the activity of $GaCl_3$ and/or stabilizes the propagating carbocations via the acid-base interaction. The use of tetrahydropyran (THP; $pK_b = 4.83$; conjugate acid $pK_a = -2.79$),[20,21] which is more basic than 1,4-dioxane ($pK_b = 5.85$; conjugate acid $pK_a = -3.22$),[20,21] instead of 1,4-dioxane and at a lower concentration was found to be effective for the smooth consumption of monomers (entry 2). Moreover, the M_n values of the copolymers increased with increasing monomer conversion, indicating that living propagating species were generated. Tetrahydrofuran (THF; $pK_b = 4.22$; conjugate acid $pK_a = -2.08$),[20,21] which is a stronger Lewis base than 1,4-dioxane and THP, was not suitable for the copolymerization (entry 3).

Table 2. Cationic Copolymerization of pMeSt and BzA under Various Conditions [a]

entry	solvent (v/v) [b]	additive	time	conv. (%)		$M_n \times 10^{-3}$ [c]	M_w/M_n [c]	BzA content (%) [d]
				pMeSt	BzA			
1	tol/DCM (9/1)	1,4-dioxane	30 min	33	31	9.6	1.67	44
			1.5 h	37	34	10.5	1.65	–
2	tol/DCM (9/1)	THP	30 min	15	12	6.2	1.53	44
			4 h	57	51	10.9	1.61	43
3	tol/DCM (9/1)	THF	4 h	0	0	–	–	–
4	DCM	THP	4 h	43	30	8.3	1.58	37
5	MCHx/DCM (8/2)	THP	10 min	23	24	9.8	1.42	42
			90 min	84	70	19.8	1.49	42

[a] $[\text{pMeSt}]_0 = 0.60$ M, $[\text{BzA}]_0 = 0.60$ M, $[\text{IBVE–HCl}]_0 = 4.0$ mM, $[GaCl_3]_0 = 4.0$ mM, [additive] = 0.10 (for THP and THF) or 1.0 M (for 1,4-dioxane) at –78 ºC. [b] tol: toluene. DCM: dichloromethane. MCHx: methylcyclohexane. [c] Determined by GPC (polystyrene standards). For a polymer peak. [d] Determined by ^{1}H NMR.

Subsequently, other solvents were used instead of toluene to avoid the Friedel–Crafts reaction of the propagating carbocation with toluene, which was observed in the copolymerization of St and BzA with BF_3OEt_2 (vide infra). The copolymerization in dichloromethane yielded a copolymer with an MW comparable to those obtained in toluene/dichloromethane (9/1 v/v); however, the BzA content in the copolymer was smaller (entry 4 in Table 2). In contrast, copolymerization in methylcyclohexane/dichloromethane (8/2 v/v) was demonstrated to be very suitable for controlled copolymerization (entry 5). Higher monomer conversion was attained at a shorter reaction time than the reaction in toluene/dichloromethane (9/1 v/v). Furthermore, the product had a higher MW and a comparable BzA content compared to the product obtained in toluene/dichloromethane (9/1 v/v). Therefore, the copolymerization under the optimized conditions was examined in detail, which is explained in the subsequent paragraphs. Other cationogens (2-chloro-2,4,4-trimethylpentene (TMPCl), 1-phenylethyl chloride (St-HCl), and α,α-dimethylbenzyl chloride (Cumyl-Cl)) and other Lewis acids ($EtAlCl_2$, $SnCl_4$, and $FeCl_3$) were also examined (Tables S1 and S2); however, the use of IBVE–HCl and $GaCl_3$ was superior to the others in terms of activity and polymerization controllability.

The reaction conditions optimized for pMeSt and BzA were also suited for the copolymerization of pMeSt and *p*-methylbenzaldehyde (entry 3 in Table S3). However, unsatisfactory results were obtained in the copolymerizations of pClSt or St with BzA (entries 1 and 2 in Table S3). Reaction conditions need to be elaborately tuned depending on the reactivities of monomers.

Figure 1 shows the details of the copolymerization of pMeSt and BzA under the optimized conditions. Both monomers were smoothly consumed with an increase in the reaction time, as shown in Figure 1A. The molecular weight distribution (MWD) curve of the product shifted to the higher-MW region as monomer conversion increased (Figure 1C). In addition, the M_n values of the products increased along with the values calculated from monomer conversion and the amounts of feeded monomer and cationogen (Figure 1B). These results demonstrate that well-controlled polymerization proceeded and side reactions, such as chain transfer reactions, did not occur during the copolymerization.

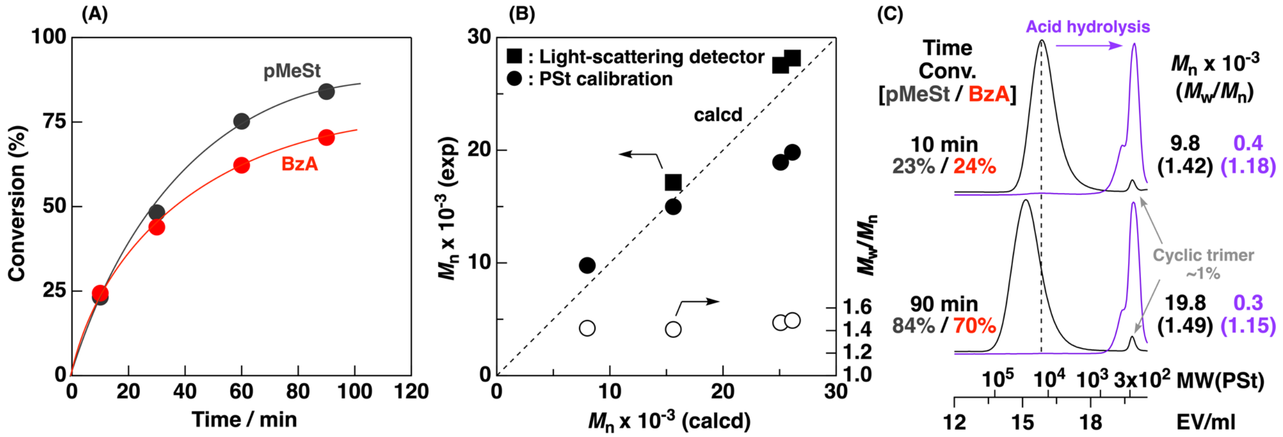


Figure 1. (A) Time-conversion curves of the copolymerization of pMeSt and BzA, (B) M_n and M_w/M_n values, and (C) MWD curves of the obtained polymers. Polymerization conditions: $[pMeSt]_0 = 0.60$ M, $[BzA]_0 = 0.60$ M, $[IBVE–HCl]_0 = 4.0$ mM, $[GaCl_3]_0 = 4.0$ mM, [THP] = 0.10 M, in methylcyclohexane/dichloromethane (8/2 v/v) at –78 °C. Hydrolysis conditions: 0.50 M trifluoroacetic acid in dichloromethane at r.t. for 3 h, 2.0 wt%. The data correspond to entry 5 in Table 2.

The ^{1}H NMR spectrum of the copolymer (Figure 2A) exhibited peaks assigned to the *sec*-benzylic ether moieties resulting from the crossover reactions between pMeSt and BzA at 3–4 ppm (peaks 2 and 6; see also Figure S8 for ^{13}C NMR). From the integral ratios of peaks of the *sec*-benzylic ether moieties and aromatic rings, the BzA content in the copolymer was calculated to be 43%. Therefore, the copolymer most likely had pMeSt and BzA units in a nearly alternating order in the main chain.

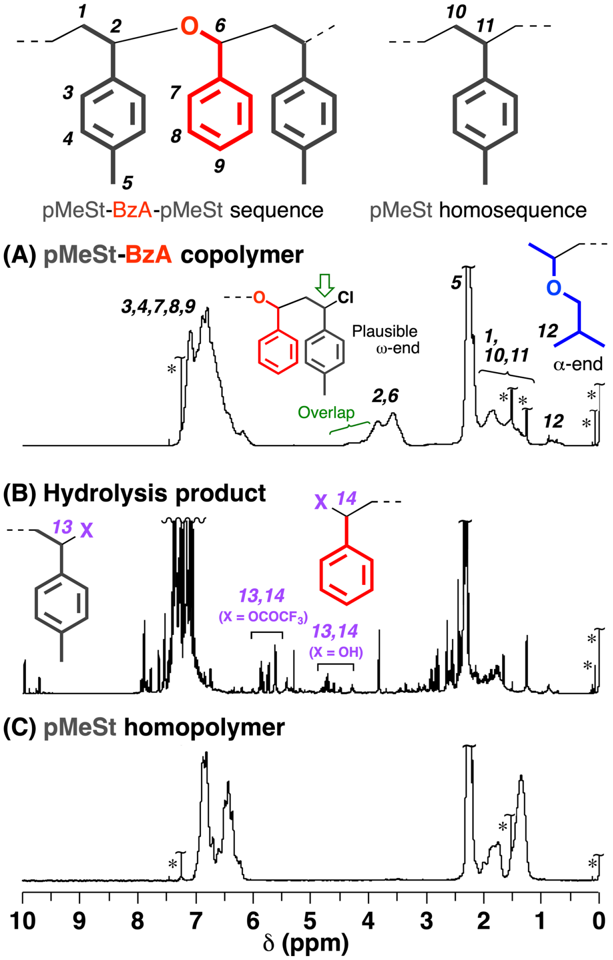
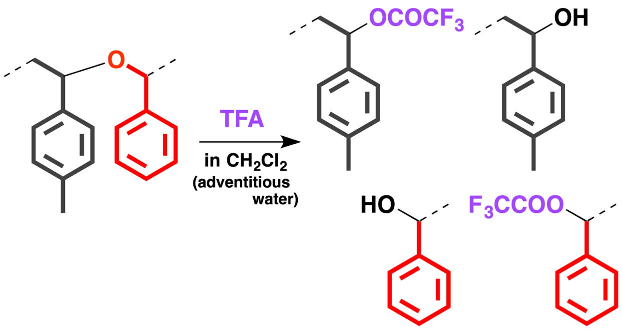


Figure 2. ^{1}H NMR spectra of (A) the copolymerization product of pMeSt and BzA (the sample in Figure 1 (30 min); after purification by reprecipitation from methanol), (B) acid hydrolysis product of the copolymer, and (C) pMeSt homopolymer (synthesized by $Ph_3CB(C_6F_5)_4$). * $CHCl_3$, water, vaseline, grease, or TMS.

Successful copolymerization via frequent crossover reactions was also confirmed by acid hydrolysis of the copolymer. After reaction with trifluoroacetic acid (TFA, 0.50 M) in dichloromethane at room temperature for 3 h, the copolymer was degraded due to the cleavage of the *sec*-benzylic ether moieties (Scheme 3), resulting in low-MW compounds with an M_n of 0.3—0.4 × 10^3, as shown in Figure 1C (see also Figures S9 and S10 for the ^{19}F NMR and electrospray ionization mass spectrometry (ESI-MS) spectra, respectively, of the hydrolysis product). Peaks were not observed in the high-MW region in the MWD curves of the hydrolysis products (Figure 1C), indicating that neither pMeSt homopolymers nor long homosequences of pMeSt existed in the copolymerization products.

Scheme 3. Acid Hydrolysis of Copolymers via Cleavage of *sec*-Benzylic Ether Moieties



To confirm the livingness of the copolymerization, a monomer-addition experiment was conducted under the optimized conditions. When pMeSt and BzA conversion reached 92% and 78%, respectively, in the first-stage copolymerization, a fresh portion of the monomers was added into the reaction solution. After the addition, the copolymerization smoothly proceeded again (Figure 3A) to yield a polymer with a higher MW and unimodal MWD (Figure 3C). The M_n values of the products increased linearly even after the addition (Figure 3B) although the MWD became broader as the copolymerization proceeded.[22,23] These results indicate that the copolymerization of pMeSt and BzA proceeded in a living manner.

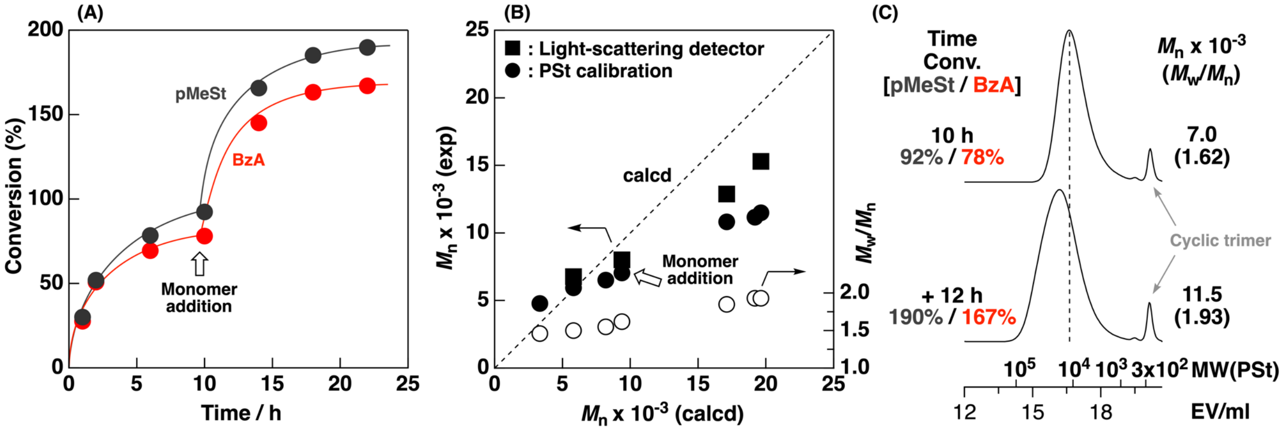
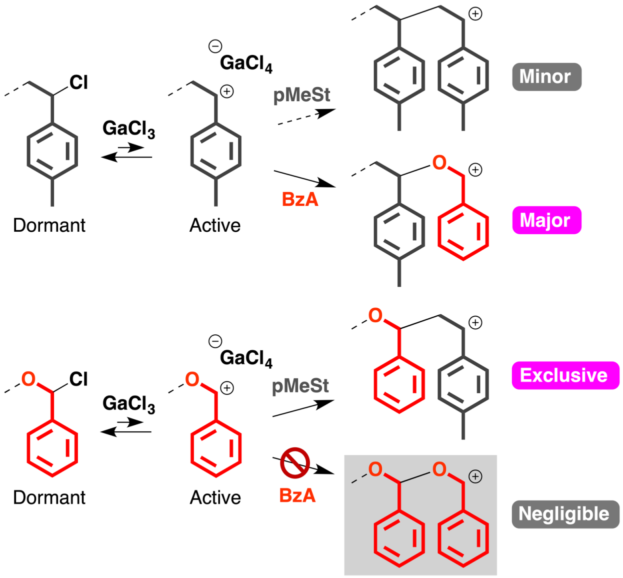


Figure 3. Monomer-addition experiment: (A) Time-conversion curves; (B) M_n determined by GPC

(circle; polystyrene standards, square; light-scattering detector) and M_w/M_n values; and (C) MWD curves of the obtained polymers. Polymerization conditions: $[\text{pMeSt}]_0 = [\text{pMeSt}]_{\text{added}} = 0.20$ M, $[\text{BzA}]_0 = [\text{BzA}]_{\text{added}} = 0.20$ M, $[\text{IBVE–HCl}]_0 = 4.0$ mM, $[\text{GaCl}_3]_0 = 6.0$ mM, [THP] = 0.10 M, in methylcyclohexane/dichloromethane (8/2 v/v) at –78 °C.

Both the higher reactivity of BzA than that of pMeSt and the nonhomopolymerizability of BzA are most likely responsible for the generation of copolymers with nearly alternating sequences (Scheme 4). The pMeSt-derived carbocation preferentially reacts with a BzA monomer rather than a pMeSt monomer, although pMeSt possesses homopolymerizability. The BzA-derived carbocation exclusively reacts with pMeSt. BzA–BzA homosequences are not produced, which is consistent with the very low ceiling temperature of BzA.[8] Such preferential occurrences of the crossover reactions compared to the homopropagation reactions result in nearly alternating sequences of pMeSt and BzA. The monomer reactivity ratios were determined to be 0.42 and ~0 for pMeSt and BzA, respectively, by the Kelen–Tüdõs method[24,25] (Figure 4), which is consistent with the nearly alternating sequences.

Scheme 4. Possible Mechanisms of Controlled Cationic Alternating Copolymerization of pMeSt and BzA.[a]



[a] Counteranions are omitted in some structures.

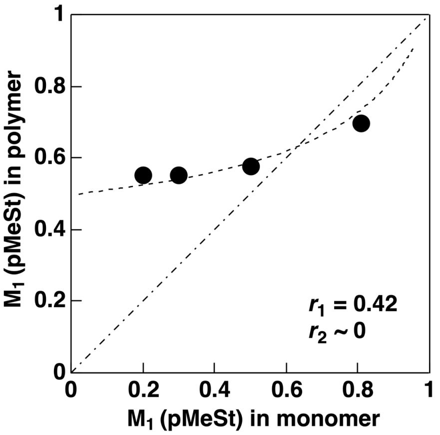


Figure 4. Copolymer compositions for the cationic copolymerizations of pMeSt and BzA (broken curve: the curve was drawn using the *r* values obtained by the Kelen–Tüdõs method; dashed-dotted line: azeotropic line). See Table S4 for the polymerization data and Figure S11 for the Kelen–Tüdõs plot.

The livingness of the copolymerization is likely derived from an appropriate dormant–active equilibrium (Scheme 4) constructed with $GaCl_3$ in the presence of THP at –78 °C. The carbon–chlorine bonds formed at the pMeSt- and BzA-derived propagating ends are cleaved by catalysis of $GaCl_3$ to generate carbocations that undergo propagation reactions. Subsequently, the carbocations are transformed into dormant species again by the reaction with a $GaCl_4^-$ counteranion. Suitable rates of the activation and deactivation cycles are achieved through the moderation of the Lewis acidity of $GaCl_3$ by the interaction with THP, which contributes to the even propagation of all the propagating chains. Side reactions are also potentially suppressed through the interaction between the propagating carbocation and THP. During copolymerization, the pMeSt-derived carbon–chlorine end is likely dominant compared to the BzA-derived carbon–chlorine end because the former is less frequently activated due to the lower stability of the pMeSt-derived carbocation than the BzA-derived carbocation, the latter of which is stabilized by conjugation with not only the aromatic ring but also the alkoxy group. The pMeSt-derived carbon–chlorine end probably remained after quenching the copolymerization, although it was difficult to confirm the existence of the carbon–chlorine moieties by ^{1}H NMR due to the overlap with the peaks of the *sec*-benzylic ether moieties.

Thermal properties of the pMeSt–BzA copolymer

The pMeSt–BzA copolymer was demonstrated to exhibit thermal properties comparable to those of the pMeSt homopolymer. Differential scanning calorimetry (DSC) analysis of the copolymer detected a glass-transition temperature (T_g) of 86 °C, which was a slightly lower value than the T_g of a pMeSt homopolymer (109 ºC) with a comparable MW (Figure 5A). In addition, the 5% weight loss temperature (T_{d5}) was 311 °C, as determined by thermogravimetric analysis (TGA) (Figure 5B). The TGA result suggests that the pMeSt–BzA copolymer has a relatively high thermal stability, although the T_{d5} is slightly lower than that of the pMeSt homopolymer (T_{d5} = 353 ºC). The slight differences in the thermal properties between the pMeSt–BzA copolymer and the pMeSt homopolymer are derived from the carbon–oxygen bonds, which are more flexible than the carbon–carbon bonds, in the main chain of the copolymer. However, the pMeSt–BzA copolymer has the potential to become a promising material as an acid-catalyzed degradable polystyrene derivative (Figure 1C).

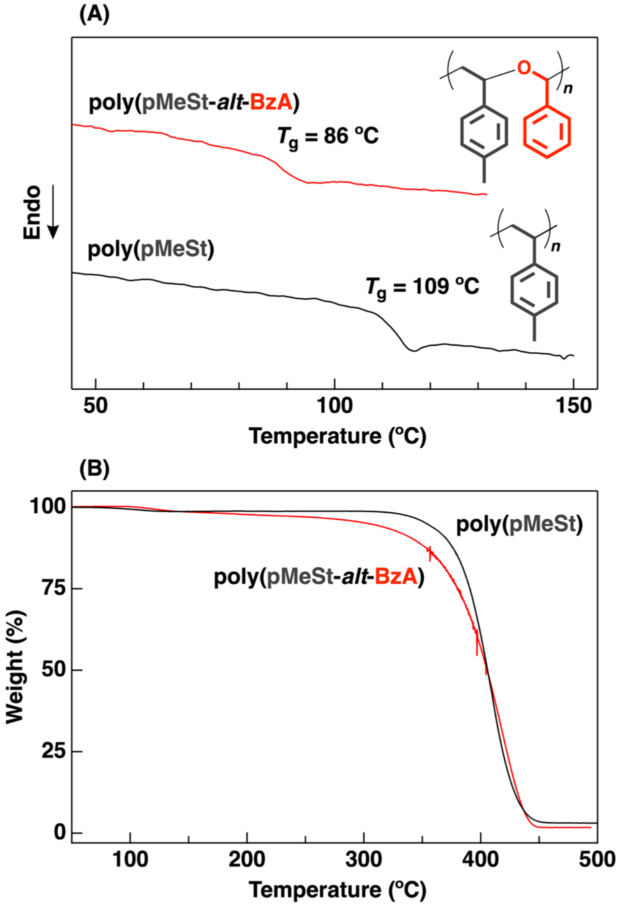


Figure 5. (A) DSC thermograms and (B) TGA analysis of poly(pMeSt-*alt*-BzA) (the sample in Figure 1 (30 min); M_n(GPC, polystyrene calibration) = 15.0 × 10^3, M_n(GPC, light-scattering detector) = 17.1 × 10^3) and poly(pMeSt) (obtained under the conditions reported in reference 26; M_n(GPC, polystyrene calibration) = 17.2 × 10^3). DSC: second heating scan, heating rate = 10 °C/min. TGA: heating rate = 10 °C/min.

α- or β-substituted St derivatives

α- or β-substituted St derivatives[27,28] were subjected to copolymerization with BzA because the substituents on the vinyl group were expected to reduce the frequency of the homopropagation and instead promote the crossover reactions with BzA. Indeed, various α- or β-substituted St derivatives were demonstrated to undergo frequent crossover reactions in cationic copolymerization with *o*-phthalaldehyde in our recent study.[29] However, all the α- or β-substituted St derivatives employed in this study were ineffective for copolymerization (Table 3 and Figures S12–S16) under these conditions. In the case of α-methylstyrene (αMeSt), an αMeSt homopolymer and a cyclic trimer consisting of one αMeSt and two BzA units were obtained (entry 1 in Table 3). A polymer was not obtained from 1,1-diphenylethylene (DPE), and a cyclic trimer was exclusively obtained (entry 2). *trans*-Anethole (Ane) and indene, which are very effective comonomers for copolymerization with *o*-phthalaldehyde, were negligibly incorporated into polymer chains in the reaction with BzA (entries 3 and 5). Isosafrole (ISa) mainly yielded a cyclic trimer (entry 5). *cis*-Stilbene (cStb) was not consumed in the reaction (entry 6). The cyclization reaction was likely promoted at the BzA–St derivative–BzA^+ propagating end due to the steric effect associated with the α- or β-substituent in the cases of αMeSt, DPE, Ane, and ISa (Scheme S2).

Table 3. Cationic Copolymerization of Various α or β-Substituted St Derivatives and BzA[a]

entry	St deriv.	time	conv. (%)		$M_n \times 10^{-3}$ [b]	M_w/M_n [b]	BzA content in polymer (%)[c]	polymer/cyclic trimer ratio[d]
			St deriv.	BzA				
1	αMeSt	30 min	13	27	2.0[e] (0.2[f])	1.39[e] (1.02[f])	0	45/55
2	DPE	120 h	11	19	0.3	1.03	–	–
3	Ane	24 h	74	40	3.9[e] (0.3[f])	2.56[e] (1.02[f])	0	92/8
4	ISa	24 h	2	4	0.3	1.35	–	–
5	indene	1 h	35	8	3.6	1.79	4	>99/<1
6	cStb	96 h	0	0	–	–	–	–

[a] [St derivative]$_0$ = 0.60 M, [BzA]$_0$ = 0.60 M, [IBVE–HCl]$_0$ = 4.0 mM, [$GaCl_3$]$_0$ = 4.0 mM, [THP] = 0.10 M in methylcyclohexane/dichloromethane (8/2 v/v) at –78 ºC. See Figures S12–S16 for the MWD curve, ^1H NMR spectra, and ESI-MS spectra. [b] Determined by GPC (polystyrene standards). [c] Determined by ^1H NMR. [d] The ratio of St derivative units incorporated into polymer/cyclic trimer. Determined by ^1H NMR. [e] For a polymer peak. [f] For an oligomer peak.

Conclusion

In conclusion, the cationic copolymerization of pMeSt and BzA proceeded via frequent crossover reactions in a living manner with an initiating system consisting of IBVE–HCl, $GaCl_3$, and THP, yielding copolymers with nearly alternating sequences and controllable MWs. The obtained copolymers could be degraded under acidic conditions due to the cleavage of the *sec*-benzylic ether moieties in the main chain. Moreover, the copolymers exhibited thermal properties comparable to those of the pMeSt homopolymer. The use of St or pClSt, which are less reactive than pMeSt, resulted in inefficient copolymerization. The reaction conditions need to be tuned to achieve controlled copolymerization of these St derivatives and BzA. In addition, α- or β-substituted St derivatives were not efficiently incorporated into polymer chains, and instead, cyclic trimers were obtained in most cases in copolymerization with BzA. The results obtained in this study contribute to the design and synthesis of "degradable polystyrene derivatives" with well-defined structures via the controlled cationic copolymerization of St derivatives and BzA derivatives. Optimization of the reaction conditions for copolymerization using various St derivatives is required to widen the scope of the obtainable copolymers.

Associated Content

Supporting Information

Experimental section, polymerization data, and NMR and ESI-MS spectra of polymerization products.

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Notes

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