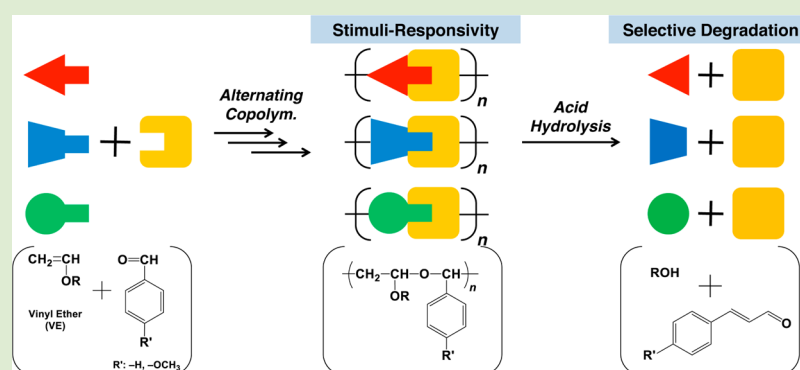


Efficient Design for Stimuli-Responsive Polymers with Quantitative Acid-Degradability: Specifically Designed Alternating Controlled Cationic Copolymerization and Facile Complete Degradation

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S Supporting Information



ABSTRACT: Specifically designed alternating cationic copolymerization produced well-defined thermo- or pH-responsive polymers with complete acid-degradability. For example, a thermosensitive alternating copolymer with acid-labile acetal linkages in the main chain was obtained from the controlled cationic copolymerization of *p*-methoxybenzaldehyde (pMeOBzA) and a vinyl ether (VE) with an oxyethylene side chain. The resulting copolymer exhibited a sharp thermosensitive phase transition in water. The same strategy but using different VEs with esters and benzaldehyde (BzA) yielded pH-responsive copolymers with nearly alternating sequences and narrow molecular weight distributions (MWDs). The alternately arranged acetal bonds in the copolymers allowed complete facile and rapid degradation under acidic conditions, which selectively produced low-molecular-weight compounds ($\text{MW} \sim 1-2 \times 10^2$).

Stimuli responsiveness of a polymer chain can be divided into two categories: reversible property changes as epitomized by thermoresponsive polymers and irreversible transitions, such as degradation. Independently, these two research areas have been explored extensively. In particular, recent progress in precision polymerization techniques has enhanced the development of various well-defined stimuli-responsive polymers whose properties and shapes change in response to external stimuli.¹⁻³ Stimuli-triggered degradable polymers, the specific segments and/or linkages of which are cleaved, have also attracted growing interest for use in various applications, such as drug release, sensors, and lithography.⁴⁻⁶ Combining these two types of stimuli-responsiveness, that is, property change and degradability, is expected to lead to the development of unprecedented intelligent materials. For instance, the selective degradation of polymers would enable a drastic change in the properties of polymer-coated surfaces as well as the facile removal of functional template polymers. Block or star-shaped degradable polymers would form completely different self-assemblies or surface patterns depending on the sequence of the stimuli. Furthermore, it is of pivotal

importance to design the monomer sequences for controlling the polymer properties.⁷

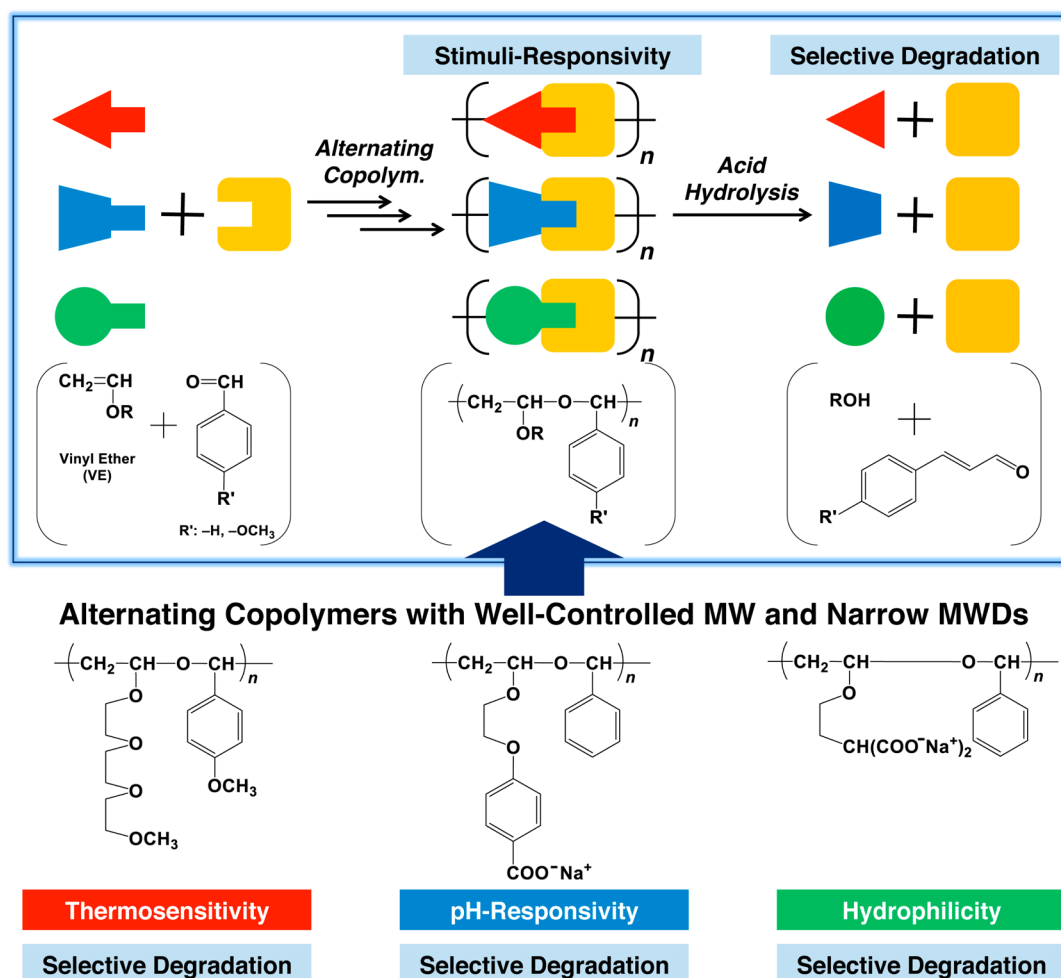
Recently, efforts have been channeled into producing stimuli-responsive polymers with degradable moieties, especially with poly(ethylene glycol) analogues. For example, Lutz et al. reported the synthesis of thermosensitive and biocompatible terpolymers with labile main-chain esters by atom transfer radical terpolymerization, which were hydrolyzed into short oligomers.⁸ Alternating ring-opening copolymerizations of succinic anhydride and functional epoxide monomers with ethylene glycol units were achieved by Hao et al., which yielded degradable and thermosensitive polymers.⁹ Wang et al. reported that poly(carbonate ether)s synthesized via copolymerization of carbon dioxide and ethylene oxide with an appropriate monomer ratio exhibited thermosensitivity in water.¹⁰ Lynd et al. reported the incorporation of degradable methylene ethylene oxide repeat units within a poly(ethylene

Received: November 2, 2013

Accepted: December 26, 2013

Published: December 30, 2013

Scheme 1. Design Basics: Essential Structures for Degradable Stimuli-Responsive Polymers by Controlled Cationic Copolymerization of VEs Containing Functional Groups and BzAs

Table 1. Cationic Copolymerization of TGMVE with BzAs^a

entry	BzAs	time	conv. of TGMVE ^b (%)	$M_n \times 10^{-3}$ ^c	M_w/M_n ^c	polymer/cyclic trimer ^d	cont. of BzAs ^e (%)
1	BzA	30 min	98	13.4	1.31	90/10	9
2	pMeOBzA	7 min	38	10.6	1.26	90/10	47
3		2 h	91	32.1	1.29	98/2	48

^a[TGMVE]₀ = 0.60 (for entry 1) or 0.80 M (for entries 2 and 3), [BzA]₀ = 0.60 (for entry 1) or 1.6 M (for entries 2 and 3), [EtSO₃H]₀ = 4.0 mM, [GaCl₃]₀ = 4.0 mM, [1,4-dioxane] = 1.0 M, [DTBP] = 2.0 mM, in toluene at -78 °C. ^bCalculated based on residual monomers using the peak of DTBP as a standard in ¹H NMR spectra in acetone-*d*₆. ^cDetermined by GPC in CHCl₃, polystyrene calibration. ^dCalculated by comparing the integral area of polymer and oligomer peaks in GPC profiles. ^eDetermined by ¹H NMR in acetone-*d*₆.

oxide) backbone.¹¹ Various postpolymerization approaches were also utilized to prepare dual responsive polymers.^{12–15} However, the precision synthesis of polymers with dual responsiveness has not been fully explored because of limited molecular design approaches. In particular, no studies have been reported on polymer systems with high sensitivity and quantitative degradability into low-molecular-weight compounds (rather than short polymer chains) that could be simply removed under reduced pressure or heating.

We recently achieved precision synthesis of alternating degradable polymers of a conjugated aldehyde and an alkyl vinyl ether¹⁶ in which acid-labile acetal linkages were arranged at regular intervals based on base-assisting living cationic polymerization.¹⁷ The resulting copolymers were completely degraded into low-molecular-weight compounds. The base-

assisting polymerization system is also generally tolerant toward various polar functional monomers and leads to the selective synthesis of a series of well-defined stimuli-responsive poly-[vinyl ethers (VEs)] as well as hydrophilic poly(VEs) with ionizable functional groups.³ The second great wave of progress, in terms of precision synthesis in cationic polymerization, has created new momentum for the establishment of novel stimuli-responsive polymers that exhibit a multifaceted nature based on poly(VE) platforms.

In this study, we examined the viability of the precision synthesis of novel types of dual responsive polymers using the base-assisting controlled cationic polymerization of conjugated aldehydes and VEs with various functional groups (Scheme 1). To incorporate stimuli-responsive functionalities into the copolymers, we used *tri*-ethylene glycol methyl VE

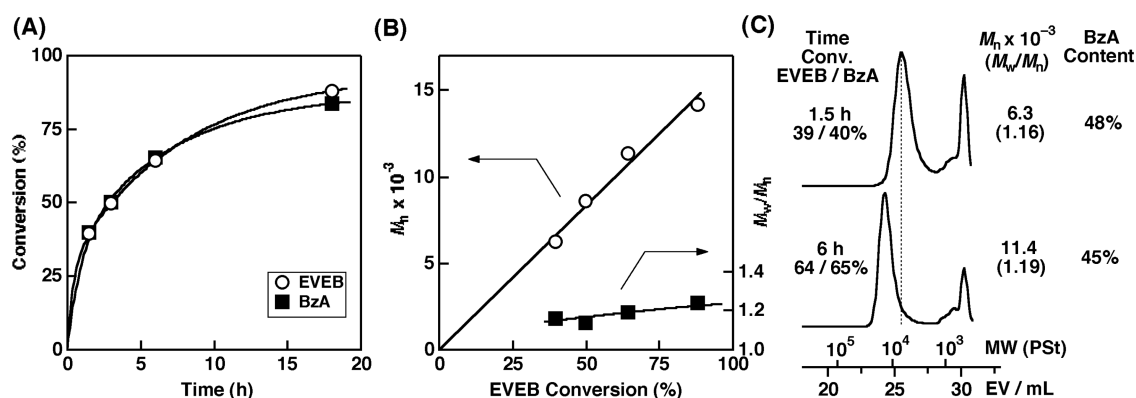


Figure 1. (A) Time–conversion curves of EVEB and BzA, (B) M_n and M_w/M_n for the obtained polymers, and (C) MWD curves for the copolymerization of EVEB with BzA using the $\text{EtSO}_3\text{H}/\text{GaCl}_3$ initiating system in the presence of THF at -78°C : $[\text{EVEB}]_0 = 0.40\text{ M}$, $[\text{BzA}]_0 = 0.40\text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 4.0\text{ mM}$, $[\text{GaCl}_3]_0 = 4.0\text{ mM}$, $[\text{THF}] = 10\text{ mM}$, in toluene/ CH_2Cl_2 (10/9 v/v).

(TGMVE),¹⁸ which is a thermosensitive polymer, and ester-containing ethyl 4-[2-(vinylxy)ethoxy]benzoate (EVEB)¹⁹ and diethyl [2-(vinylxy)ethyl]malonate (VOEM),²⁰ which are precursors for polycarboxylic acids. The copolymerization of these monomers with an aromatic aldehyde yielded nearly alternating copolymers with low polydispersity. The final products were water-soluble and exhibited sensitive stimuli (temperature or pH)-responsive behaviors in water. Furthermore, these nearly alternating copolymers were completely degraded into low-molecular-weight compounds.

Alternating cationic copolymerization of aldehydes and VEs containing various functional groups:

The cationic copolymerization of TGMVE with benzaldehyde (BzA) was first performed using the $\text{EtSO}_3\text{H}/\text{GaCl}_3$ initiating system in toluene at -78°C in the presence of 1,4-dioxane as an added base and a small amount of 2,6-di-*tert*-butylpyridine (DTBP) as a proton trap (Table 1, entry 1). These conditions are appropriate for the controlled alternating copolymerization of conjugated aldehydes with alkyl VEs.^{16,21} In 30 min, the conversion of BzA reached a plateau at approximately 28%, whereas TGMVE reached 98%, to produce random copolymers ($M_n = 13.4 \times 10^3$, $M_w/M_n = 1.31$). After the removal of a small amount of cyclic trimer²² by dialysis against methanol, the aldehyde content of the main product was determined to be as low as 9% using ^1H NMR spectroscopy. To increase the aldehyde content in the polymers and produce alternating copolymers, a more reactive aldehyde, *p*-methoxybenzaldehyde (pMeOBzA),²³ was used for the copolymerization with a larger aldehyde feed ratio ($[\text{TGMVE}]_0/[\text{pMeOBzA}]_0 = 1:2$) under similar conditions (Table 1, entries 2 and 3).¹⁶ The polymerization was initiated without an induction period and almost equimolar amounts of TGMVE and pMeOBzA were consumed, to produce polymers in 2 h (the conversion for TGMVE: 91%; $M_n = 32.1 \times 10^3$, $M_w/M_n = 1.29$).²² The molecular weight distribution (MWD) curve of the obtained polymers shifted to higher molecular weight region with increasing monomer conversion, which is indicative of the presence of long-lived species. In the ^1H NMR spectra of the copolymers, there were broad peaks around 3.8–4.8 ppm assignable to the two methine protons from the TGMVE–pMeOBzA sequences (Figure S1 in the Supporting Information). On the other hand, there were no signals resulting from aldehyde–aldehyde linkages in the 4.8–6.0 ppm range, which corresponded to the previous report.²⁴ The aldehyde content of the copolymers was 47–48% as

determined by ^1H NMR. Furthermore, the copolymers completely degraded under acidic conditions to produce low-molecular-weight compounds, which will be demonstrated in the “Complete degradation of the alternating copolymers” paragraph, as opposed to oligomers. Thus, these results indicated that a nearly alternating copolymer with controlled MW and a narrow MWD was successfully prepared.

To produce pH-responsive alternating copolymers with carboxy groups, the cationic copolymerization using an ester-containing VE (EVEB) was examined. Because EVEB exhibited less reactivity compared with TGMVE and alkyl VEs, less reactive BzA was employed as a comonomer instead of pMeOBzA. First, the copolymerization was conducted using the $\text{EtSO}_3\text{H}/\text{GaCl}_3$ initiating system in the presence of THF as an added base in toluene at -30°C ($[\text{EVEB}]_0 = 0.40\text{ M}$, $[\text{BzA}]_0 = 0.40\text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 4.0\text{ mM}$, $[\text{GaCl}_3]_0 = 4.0\text{ mM}$, $[\text{THF}] = 10\text{ mM}$), because the EVEB solution in toluene became quite viscous at a low temperature, -78°C . Although the conversion of EVEB reached 100% in 100 min, that of BzA reached a plateau at around 40% conversion. This result suggests that the VE homopolymerization preferentially proceeds under these conditions, and lowering the polymerization temperature would be crucial to incorporation of BzA into the polymers, which is consistent with the previous report.²¹ Thus, a toluene/ CH_2Cl_2 (10/9 v/v) mixture was used as the polymerization medium to carry out the copolymerization at -78°C . The copolymerization was performed using the $\text{EtSO}_3\text{H}/\text{GaCl}_3$ initiating system in the presence of THF as an added base. Although the reaction mixture was heterogeneous at the initial stage of copolymerization at -78°C , the mixture gradually became transparent with reaction time, and both monomers were smoothly consumed at similar rates, as shown in Figure 1A. The M_n s of the polymers determined using GPC measurements increased in direct proportion to EVEB conversion (Figure 1B).²⁵ Furthermore, the copolymers had narrow MWDs ($M_w/M_n \leq 1.2$; Figure 1C). Their ^1H NMR spectra revealed that the copolymers had 45–48% of the aldehyde with no aldehyde–aldehyde linkages,²⁶ which indicated that the resulting copolymers consisted of nearly alternating structures (Figures 1C and S2). In addition to the kinetic and spectral evidence, the alternating structure was also supported by complete degradability of the copolymers under acidic conditions (see below). Thus, the mixture of toluene/ CH_2Cl_2 proved to be an effective reaction medium for the controlled copolymerization of EVEB and BzA, which yielded

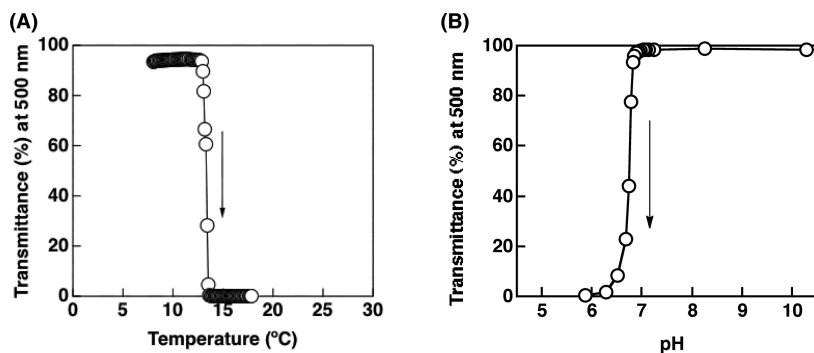


Figure 2. (A) Thermosensitive behaviors of poly(TGMVE-*alt*-pMeOBzA) [$M_n(\text{GPC}) = 33.9 \times 10^3$, $M_w/M_n = 1.27$, aldehyde content = 48%] in water: 1.0 wt % aqueous solution, heating rate: 1 °C/min. (B) pH-responsive behaviors of poly(VEB-*alt*-BzA) [precursor polymer: $M_n(\text{GPC}) = 8.6 \times 10^3$, $M_w/M_n = 1.14$, aldehyde content = 45%] in water: 0.5 wt % aqueous solution, $[\text{NaCl}]_0 = 0.1 \text{ M}$, at 30 °C.

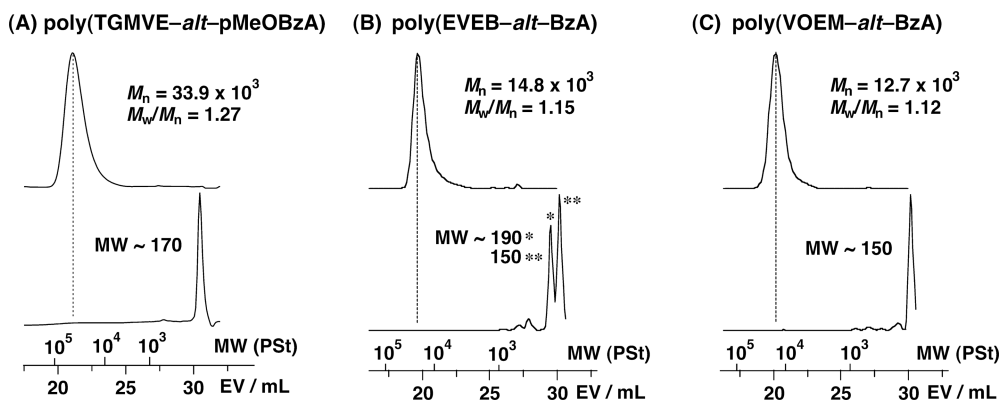


Figure 3. MWD curves of original polymers (upper) and hydrolysis products (lower) for (A) poly(TGMVE-*alt*-pMeOBzA), (B) poly(EVEB-*alt*-BzA), and (C) poly(VOEM-*alt*-BzA) [hydrolysis conditions: 0.50 M aqueous HCl-1,2-dimethoxyethane (for A) or HCl-THF (for B and C) at 30 °C for 2 (for A) or 4 h (for B and C); 0.5 wt % (for A) or 0.3 wt % (for B and C) polymer solution]; aldehyde contents of the original copolymer: (A) 48, (B) 42, and (C) 46%.

nearly alternating copolymers with ester pendants, although our previous results showed that the copolymerizations of BzAs and alkyl VEs in CH_2Cl_2 produced only VE homopolymers.²¹ The slow formation of EVEB-EVEB linkages facilitated the alternating propagation reactions between BzA and EVEB because the homopolymerization of EVEB under similar conditions proceeded much more slowly than copolymerization.

Furthermore, we examined the cationic copolymerization of a malonate-containing VE (VOEM) with BzA under similar conditions ($[\text{VOEM}]_0 = 0.40 \text{ M}$, $[\text{BzA}]_0 = 0.40 \text{ M}$, $[\text{EtSO}_3\text{H}]_0 = 4.0 \text{ mM}$, $[\text{GaCl}_3]_0 = 4.0 \text{ mM}$, $[\text{THF}] = 10 \text{ mM}$, in toluene at $-78 \text{ }^\circ\text{C}$) to investigate the versatility of this system for polar-functional VEs. To achieve the living cationic homopolymerization of VOEM in the base-assisting system, the appropriate combination of a Lewis acid and an added base was indispensable; TiCl_4 and $\text{Et}_{1.5}\text{AlCl}_{1.5}$ yielded only chain transfer reactions.²⁰ The copolymerization using GaCl_3 in conjunction with THF proceeded smoothly for 25 h and yielded a well-defined copolymer ($M_n = 15.7 \times 10^3$, $M_w/M_n = 1.20$; Figure S3).²⁵ The aldehyde content determined by ^1H NMR was 46%, indicating that a nearly alternating copolymer was successfully prepared (Figure S4). Thus, the optimal conditions permitted controlled alternating copolymerization of BzA even with polar functional monomers. Subsequent deprotection of the pendant malonate groups under basic conditions quantitatively yielded a water-soluble copolymer with dicarboxy groups, poly{[2-

(vinyl)oxy)ethylmalonic acid]-*alt*-BzA} [poly(VOEMA-*alt*-pMeOBzA)].

Stimuli-responsive behaviors of alternating copolymers with functional groups:

Thermosensitive behaviors of poly(TGMVE-*alt*-pMeOBzA)s in water: The solubility of poly(TGMVE-*alt*-pMeOBzA)s in water was tested at various temperatures. A homopolymer of TGMVE undergoes a lower critical solution temperature (LCST)-type phase separation in water at approximately 86 °C.¹⁸ The turbidity of a 1.0 wt % aqueous solution of the copolymer with an aldehyde content of 48% [$M_n(\text{GPC}) = 33.9 \times 10^3$, $M_w/M_n = 1.27$] was measured with increasing temperature (1.0 °C/min). Upon increasing the solution temperature, the copolymer exhibited a sharp phase separation at 13.3 °C (Figure 2A), with complete transition within 1 °C as well as that for the TGMVE homopolymer. These results indicate that the incorporation of pMeOBzA units into copolymers decreases the temperature of phase separation (T_{ps}) as much as about 73 °C and the alternating sequences may result in sharp response. Furthermore, this turbidity change was reversible with temperature.

pH-Responsive behaviors of poly(VEB-*alt*-BzA) in water:

The solubility transition dependency on pH was examined using the carboxy-containing polymers [poly(VEB-*alt*-BzA)s] that were obtained by the deprotection of poly(EVEB-*alt*-BzA)s under basic conditions. A VEB homopolymer exhibited pH-responsive solubility transitions in water at pH 6.5, and the solution was transparent at high pH but rapidly became opaque

at low pH.¹⁹ The pH-responsive behavior of the copolymer poly(VEB-*alt*-BzA) [precursor polymer: $M_n(\text{GPC}) = 8.6 \times 10^3$, $M_w/M_n = 1.14$, aldehyde content = 45%] was examined. Upon decreasing the solution pH, the copolymer exhibited a sharp solubility transition near pH 6.7 in water (Figure 2B), the critical pH of which was slightly higher than that for the VEB homopolymer. The sharp solubility transition was almost completed within pH 0.1 as well as the case of the VEB homopolymer. Furthermore, the aqueous solution reverted to its transparent state at high pH. The acetal linkages in the copolymers remained intact under all pH conditions examined.

Complete degradation of the alternating copolymers:

We investigated the acid-degradability of the stimuli-responsive copolymers as well. Acid hydrolysis reactions of the obtained copolymers were performed under mild conditions (0.50 M aqueous HCl–THF at 30 °C for 2 or 4 h).¹⁶ Because of the acid-labile acetal linkages in the main chains, the nearly alternating copolymers prepared in this study were successfully degraded. In the GPC profiles, the original polymer peaks disappeared quantitatively after acid treatment, and new peaks appeared at MW regions near $1\text{--}2 \times 10^2$ (Figure 3). ¹H NMR analyses revealed that the hydrolysis products from the poly(TGMVE-*alt*-pMeOBzA) and poly(VOEM-*alt*-BzA) were *p*-methoxycinnamaldehyde and cinnamaldehyde (cinnamic aldehyde), respectively (Figures S5 and S7).¹⁶ For poly(EVEB-*alt*-BzA), two main peaks appeared in the low-molecular-weight region of the GPC profile of the hydrolysis products (MW $\sim 1\text{--}2 \times 10^2$). One peak was assigned to cinnamaldehyde and the other peak was assigned to ethyl 4-(2-hydroxyethoxy)benzoate, an alcohol derived from the EVEB pendant group, which could not be removed after the workup procedures due to its solubility in water (Figure S6). These results indicated that acid-hydrolysis successfully yielded the low-molecular-weight compounds described in Scheme 1.

The carboxy-containing polymer [poly(VEB-*alt*-BzA)] obtained after deprotection was also successfully degraded into low-molecular-weight compounds under acidic conditions (0.50 M aqueous HCl-methanol at 30 °C for 3 h). ¹H NMR analysis of the products in D₂O before and after acid treatments confirmed that the broad peaks derived from the polymers transformed into the sharp peaks of the lower-molecular-weight compound, 4-(2-hydroxyethyl)benzoic acid (Figure S8). Furthermore, the broad peaks derived from the main chains of the polymers at approximately 1.5–5.0 ppm completely disappeared after hydrolysis. Thus, poly(VEB-*alt*-BzA) was determined to be successfully acid-hydrolyzed into low-molecular-weight compounds. These results demonstrate that unique pH-responsive copolymers with complete acid-degradability were precisely synthesized by the alternating copolymerization of BzA and VE containing ester groups.

In summary, we have successfully prepared stimuli-responsive alternating copolymers with acid-degradability using the base-assisting controlled cationic copolymerization of BzAs and VEs with functional groups. The cationic copolymerization of *p*-methoxyBzA and VE with oxyethylene side chains under optimal conditions produced nearly alternating copolymers with acid-labile acetal linkages in the main chains. The copolymers exhibited sharp thermosensitive behaviors in water. pH-responsive copolymers with nearly alternating sequences and narrow MWDs were precisely synthesized from BzA and ester-containing VEs. Furthermore, these copolymers completely degraded under acidic conditions

to produce low-molecular-weight compounds. These novel types of dual responsive polymers that exhibited both unique sensitivity and complete degradability are highly promising candidates for intelligent functional materials.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental procedures, NMR spectra of the polymers, and hydrolysis products and GPC curves. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported in part by Grant-in-Aid for Scientific Research on Innovative Areas of “Fusion Materials: Creative Development of Materials and Exploration of Their Function through Molecular Control” (No. 2206) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).

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(22) Our group has previously reported that the cationic copolymerization of conjugated aldehydes and VEs is accompanied by cyclic oligomer formation with two aldehydes and one VE as a side reaction.²¹ The ratio of the oligomers in these polymerization systems depends heavily on the combination of comonomers (1–56%).^{16,21} In contrast, the present system of TGMVE with BzAs produced less cyclic oligomers (2–10%).

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(24) Acetal methine proton signal of a model compound, anisaldehyde dimethylacetal, appears at 5.3 ppm. Homopolymerization of BzAs has never achieved under similar conditions,²¹ which would be due to its low ceiling temperatures.

(25) The concentration of oligomers produced in the copolymerization reactions using EVEB or VOEM was larger than the concentration produced using TGMVE, which might be related to the presence of polar functional groups.

(26) Acetal methine proton signal of a model compound, benzaldehyde dimethylacetal, appears at 5.4 ppm.