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Well-Defined Alternating Copolymers of Benzaldehydes with Vinyl Ethers: Precision Synthesis by Cationic Copolymerization and Quantitative Degradation to Cinnamaldehydes

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Introduction. Aromatic aldehydes are difficult to polymerize cationically,[1-3] and there have only been a few isolated copolymerization studies with styrene or isoprene,[2,4] not with more reactive monomers, such as vinyl ethers (VEs).[2] Recently, we have demonstrated that various Lewis acids in conjunction with Lewis bases were effective for inducing living cationic polymerizations of various monomers, some of which could not be polymerized in a living fashion with different types of initiating systems.[5-7] This progress in initiating systems even permitted controlled copolymerization of benzaldehyde (BzA) with isobutyl vinyl ether (IBVE).[8] Copolymers of 25−30% BzA units with narrow molecular weight distributions (MWDs) were obtained using $GaCl_3$ in the presence of an added base at low temperature.

One feature of the copolymerization was that no BzA−BzA linkages were produced in the reaction. Consequently, there are three elemental reactions for propagation: the crossover reaction from the BzA growing end and the homopropagation and crossover from the IBVE active center. The relative reactivity of the self-propagation and crossover reactions determines the sequence distribution of the two monomers in the polymer chain. If a more reactive BzA derivative (BzAs) than BzA is combined with IBVE, or a less reactive VE than IBVE is copolymerized with BzA [e.g., *p*-methoxyBzA (*p*MeOBzA) with IBVE, BzA with 2-chloroethyl VE (CEVE)], then even alternating copolymerization would proceed. An alternating copolymer of a BzAs with a VE is attractive as a degradable polymer because easily degradable acetal linkages are regularly located in the main chain.[9] In addition, the high content of glassy BzA units in the backbone is expected to yield materials with higher glass transition temperature (T_g) and rigidity.

In the present study, therefore, cationic copolymerization of various BzAs with VEs was examined using $GaCl_3$ in the presence of an added base. As a result, we found that alternating copolymers with low polydispersity could be obtained from cationic copolymerization of *p*MeOBzA with IBVE and BzA with CEVE using an ethanesulfonic acid ($EtSO_3H$)/$GaCl_3$ initiating system with 1,4-dioxane. Acid hydrolysis of the copolymers yielded nearly all single low-molecular-weight compounds.

Results and Discussion. *Copolymerization of BzAs with VEs Using $EtSO_3H/GaCl_3$ Initiating System.* Cationic copolymerization of BzAs with VEs was conducted with the $EtSO_3H/GaCl_3$ initiating system (an initiator/a catalyst) in the presence of 1,4-dioxane as an added Lewis base in toluene at −78 °C. Under these conditions, controlled copolymerization of BzA with IBVE proceeded (Table1, entry 1).[8] Copolymers with alternating structures are expected under appropriate monomer combinations, as mentioned in the Introduction. Therefore, as monomer combinations in the copolymerization, *p*MeOBzA with IBVE and BzA with CEVE were selected.

Controlled Copolymerization. First, copolymerization of *p*MeOBzA with IBVE was examined. The polymerization proceeded smoothly, and IBVE and *p*MeOBzA conversions reached about 70 and 67% in 1 h, respectively. Product polymers were colorless brittle film or somewhat hard gummy substance and were soluble in various organic solvents. Gel permeation chromatograph (GPC) profiles of the products showed an existence of long-lived growing species and a strong UV absorption at 254 nm corresponding to the refractive index (RI) counterpart, which indicated that the polymers contained *p*MeOBzA uniformly over the entire molecular weight region. The amount of a cyclic trimer side product decreased dramatically compared with that produced in the BzA−IBVE copolymerization (Table 1, entry 1).[8] However, GPC profiles of the product polymers exhibited tailing with progression of the polymerization. The M_n of product polymers leveled off around 12 000. No linear relationship between the M_n values and aldehyde conversion for polymerization was observed, and the MWDs of the polymers were relatively broad (M_w/M_n 1.20 to 1.35). These results suggested that side reactions, such as a transfer reaction, occurred. Therefore, the copolymerization was conducted under higher monomer concentration in the presence of 2,6-di-*tert*-butylpyridine (DTBP) to minimize side reactions by eliminated protons.[10] In this case, higher M_n polymers with narrower MWDs were produced, and the M_n increased in direct proportion to aldehyde conversion for polymerization (Figure 1A).[11] GPC profiles of products polymers showed the presence of a long-lived growing species (Figure 1B).

Next, we examined copolymerization of BzA with CEVE. BzA conversion reached 86% in 48 h. Product polymers exhibited a similar form and solubility to those of products from *p*MeOBzA-IBVE copolymerization. The M_n of the product polymers increased in direct proportion to aldehyde conversion for polymerization (Figure 1A). The MWDs of the products were narrow, and long-lived growing species were observed by GPC profiles of the products (Table 1, entry 3; Figure 1A,C). The amount of cyclic trimer side product was less than the BzA-IBVE copolymerization (Figure 1C). The profiles also showed a strong UV absorption at 254 nm corresponding to the RI counterpart over the entire molecular weight region, which indicated that the polymers contained BzA.

Alternating Structure. In all ^1H NMR spectra of the products, some resonances were observed that were not present in those of the VE homopolymer (Figure 2). Broad resonance around 6.5 to 7.5 ppm was observed, assignable to the aromatic protons of the BzAs. In addition, other broad resonance around 3.6 to 4.8 ppm was assigned to two methine proton resonance from the VE−BzAs sequences. (In the case of copolymers of *p*MeOBzA and IBVE, methyl proton resonance of the methoxy group overlapped the

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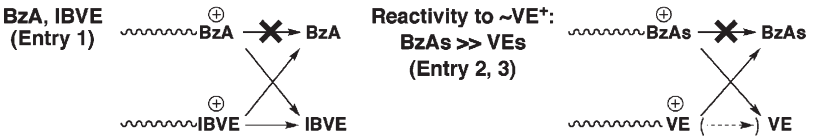
Table 1. Cationic Copolymerization of Benzaldehydes (BzAs) with Vinyl Ethers (VEs) Using the $EtSO_3H/GaCl_3$ Initiating System[a]



entry	monomer combination[b]	time	conv. (%)	M_n[c]	M_w/M_n[c]	aldehyde content (%)	polymer/oligomer
1	BzA-IBVE	1 h	72	14 400	1.12	27	63/37
2	*p*MeOBzA-IBVE	1 h	68	11 000	1.33	47	91/9
3	BzA-CEVE	24 h	70	16 300	1.12	47	91/9

[a] $[BzAs]_0$ = 0.6 M, $[VE]_0$ = 0.6 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, in toluene at −78 °C. [b] *p*MeOBzA: *p*-methoxyBzA; IBVE: isobutyl VE; CEVE: 2-chloroethyl VE. [c] M_n: number-average molecular weight; M_w/M_n: polydispersity ratio (weight-average molecular weight/number-average molecular weight), by gel permeation chromatography (polystyrene calibration).

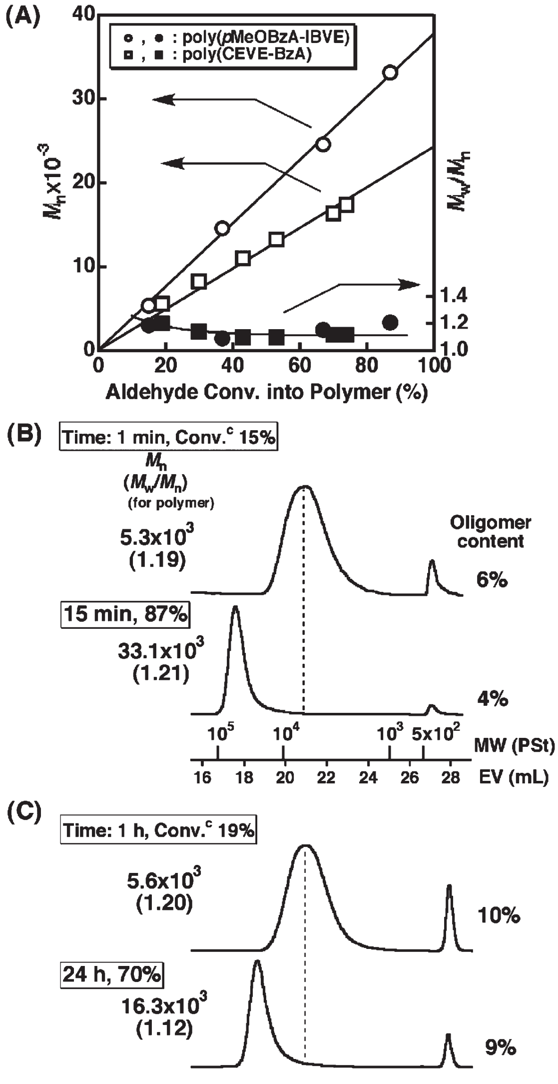


Figure 1. (A) M_n and M_w/M_n of products obtained by copolymerization of *p*-methoxybenzaldehyde (*p*MeOBzA) with isobutyl vinyl ether (IBVE)[a] and benzaldehyde (BzA) with 2-chloroethyl vinyl ether (CEVE)[b], (B) molecular weight distribution (MWD) curves of products by copolymerization of *p*MeOBzA with IBVE[a], and (C) MWD curves of products by copolymerization of BzA with CEVE[b]. (All M_n and M_w/M_n values are for main peaks.) (Polymerization conditions: [a]$[p\text{MeOBzA}]_0$ = 0.8 M, $[IBVE]_0$ = 2.0 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, [2,6-di-*tert*-butylpyridine (DTBP)] = 2.0 mM, in toluene at −78 °C; [b]$[BzA]_0$ = 0.6 M, $[CEVE]_0$ = 0.6 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, in toluene at −78 °C: [c]aldehyde conversion into polymer).

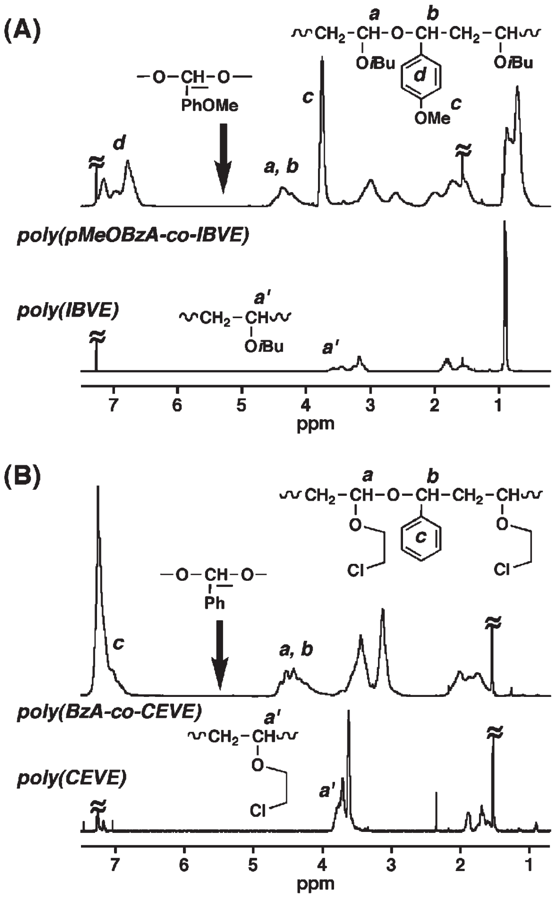


Figure 2. ^1H NMR spectra (300.04 MHz, $CDCl_3$, 30 °C) of (A) poly[*p*-methoxybenzaldehyde (*p*MeOBzA)-*co*-isobutyl vinyl ether (IBVE)][a] and (B) poly[benzaldehyde (BzA)-*co*-2-chloroethyl vinyl ether (CEVE)][b] obtained by $EtSO_3H/GaCl_3$ initiating system (polymerization conditions: [a]$[p\text{MeOBzA}]_0$ = 0.8 M, $[IBVE]_0$ = 2.0 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, [2,6-di-*tert*-butylpyridine (DTBP)] = 2.0 mM, in toluene at −78 °C; [b]$[BzA]_0$ = 0.6 M, $[CEVE]_0$ = 0.6 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, in toluene at −78 °C).

methine resonance.) If the copolymers have BzAs−BzAs sequences, then the peaks stemming from the acetal methine protons adjacent to the aromatic ring would be observed. The acetal methine resonance of model compounds anisaldehyde dimethylacetal and benzaldehyde dimethylacetal appear at 5.3 and 5.4 ppm in the ^1H NMR spectra, respectively. However, there were no peaks in the 4.8 to 6.0 ppm range in the ^1H NMR spectra of the product copolymers, indicating the lack of BzAs−BzAs linkages.[12] Meanwhile, the product copolymers contained 45−48% BzAs units based on the resonance integral ratio of the acetal methine

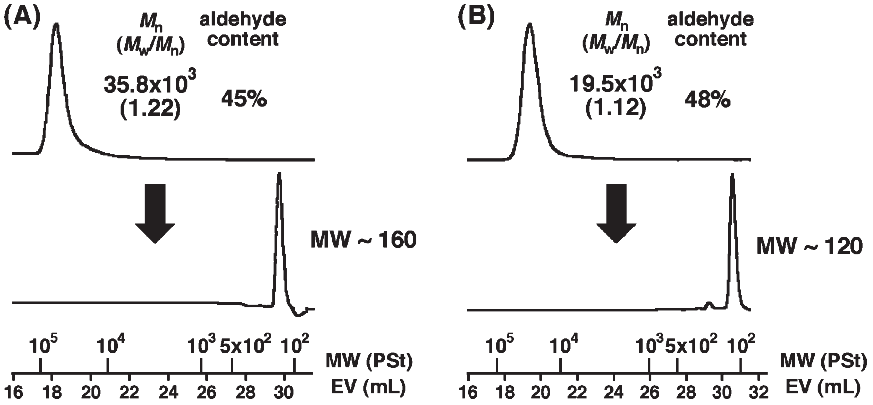


Figure 3. Molecular weight distribution curves of copolymer (upper, isolated) and hydrolysis products (lower): (A) poly[*p*-methoxybenzaldehyde-(*p*MeOBzA)-*co*-isobutyl vinyl ether(IBVE)] and (B) poly[benzaldehyde (BzA)-*co*-2-chloroethyl vinyl ether (CEVE)] (hydrolysis conditions: 0.5 N aqueous HCl-tetrahydrofuran (THF) at 30 °C for 2 h).

peak and other peaks. These results indicated that the product copolymers had nearly alternating structures.[13] Therefore, controlled alternating copolymerization proceeded with these monomer combinations.

Preliminary study on physical properties of the resulting alternating copolymers showed that the BzA-containing copolymers differ in T_g from vinyl ether polymers. The T_g of poly(*p*MeOBzA-*co*-IBVE) was 33 °C, and that of poly(BzA-*co*-CEVE) was 31 °C.[14] They are higher than that of a random copolymer poly(BzA-*co*-IBVE) (T_g = 6 °C)[8] and those of vinyl ethers (for example, T_g of poly(IBVE) is −20 °C).[15] In addition, these alternating copolymers could form a free-standing film in contrast with poly(alkyl vinyl ethers).

Facile and Selective Degradation into Single Small Compounds. With the resulting copolymers of *p*MeOBzA with IBVE and BzA with CEVE, the acetal linkages susceptible to acids are located at nearly regular intervals because of the alternating structure. Therefore, relatively mild acidic conditions would allow hydrolysis of the copolymers.

Tetrahydrofuran (THF)−HCl aqueous solution was added to a THF solution of poly(*p*MeOBzA-*co*-IBVE) or poly(BzA-*co*-CEVE) to initiate acid hydrolysis, with the reaction maintained at 30 °C for 2 h. From GPC profiles of the hydrolysis products, the reactions of both copolymers yielded a nearly single low-molecular-weight compound (Figure 3). The ^{1}H NMR spectra of the products indicated that cinnamaldehyde (CinA) and *p*-methoxyCinA were the products obtained from poly(BzA-*co*-CEVE) and poly(*p*MeOBzA-*co*-IBVE), respectively (Supporting Information).[16] These compounds, which were derived from one BzAs unit and one VE unit, also support alternating sequences of the copolymers. Meanwhile, there were almost no other peaks in the ^{1}H NMR spectra of both hydrolysis products, showing that the acid hydrolysis yielded degradation products with high selectivity. We also examined acid hydrolysis of poly(BzA-*co*-IBVE) (M_n 30600, M_w/M_n 1.08, BzA content 25%), a random copolymer, to compare with the alternating copolymer. Acid hydrolysis also proceeded, as confirmed by GPC profiles of the products (Supporting Information). However, compounds with various molecular weights (M_n 100−4500) were obtained. These results showed that selective acid degradation required an alternating structure.

As mentioned above, alternating copolymers of BzAs with VEs were degradable under relatively mild acidic conditions, yielding CinAs almost exclusively, although they were stable around neutral pH and under basic conditions. These copolymers with the interesting characters would be suitable for photoresistant and adhesive materials. In addition, our preliminary work demonstrated that copolymerization of CinA with VEs were achieved. It will be reported elsewhere.

Conclusions. We have demonstrated that the controlled cationic copolymerization of *p*MeOBzA with IBVE and BzA with CEVE can be achieved using the $EtSO_3H/GaCl_3$ initiating system in the presence of 1,4-dioxane. The copolymerization was mediated by a long-lived growing species, yielding copolymers with narrow MWDs. The product copolymers contained ~50% BzAs units (45−48%) and no BzAs−BzAs linkages, and hence the product copolymers had nearly alternating structures. In addition, selective acid hydrolysis of the copolymers was achieved with aqueous HCl. The facile hydrolysis process yielded CinAs, which were also polymerizable aldehydes as single low-molecular-weight compounds due to regular intervals of acid-degradable acetal linkages in the main chain.

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Supporting Information Available: Experimental details, ^{1}H NMR and ^{13}C NMR spectra, IR spectra, MWD curves, and calibration curves. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Aso, C.; Tagami, S.; Kunitake, T. *J. Polym. Sci., Part A* **1969**, *7*, 497–511.
(2) Aso, C.; Tagami, S.; Kunitake, T. *Kobunshi Kagaku* **1966**, *23*, 63–68.
(3) Aso, C.; Tagami, S.; Kunitake, T. *Polym. J.* **1970**, *1*, 395–402.
(4) Tagami, S.; Aso, C. *Kobunshi Kagaku* **1970**, *27*, 922–928.
(5) Aoshima, S.; Yoshida, T.; Kanazawa, A.; Kanaoka, S. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 1801–1813.
(6) Kanazawa, A.; Kanaoka, S.; Aoshima, S. *Macromolecules* **2009**, *42*, 3965–3972.
(7) Aoshima, S.; Kanaoka, S. *Chem. Rev.* **2009**, *109*, 5245–5287.
(8) Ishido, Y.; Aburaki, R.; Kanaoka, S.; Aoshima, S. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, *48*, in press.
(9) Hashimoto, T.; Ishizuka, K.; Umehara, A.; Kodaira, T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4053–4064.
(10) Kennedy, J. P.; Chou, R. T. *J. Macromol. Sci., Chem.* **1982**, *A18*, 3–10.
(11) Copolymerization of *p*MeOBzA with IBVE under conditions similar to those of Table 1 except for the presence of DTBP was also conducted (polymerization conditions: $[p\text{MeOBzA}]_0$ = 0.6 M, $[\text{IBVE}]_0$ = 0.6 M, $[EtSO_3H]_0$ = 4.0 mM, $[GaCl_3]_0$ = 4.0 mM, [1,4-dioxane] = 1.0 M, [DTBP] = 2.0 mM, in toluene at −78 °C). In this case, no linear relationship between the M_n values and aldehyde

conversion for polymerization were observed, mostly because of chain transfer. For well-controlled reaction, higher monomer concentration for efficient propagation reaction was required.

(12) Homopolymerizaion of BzA has never been achieved under similar conditions. This is most likely due to its very low ceiling temperature, which was estimated to be −160 °C on the basis of a calculation study.[1]

(13) IR spectra of poly(IBVE) and poly(*p*MeOBzA-*co*-IBVE) are shown in the Supporting Information. In the IR spectrum of the copolymer, a new C-O-C stretching band (1038 cm^{-1}) appears, in addition to C-O-C counterparts (1085 and 1109 cm^{-1}) for the IBVE side groups. These results also support the fact that BzAs were successfully incorporated into the product copolymers.

(14) Poly(*p*MeOBzA-*co*-IBVE): M_n = 34 500, $M_\mathrm{w}/M_\mathrm{n}$ = 1.33, BzAs content = 45%; poly(BzA-*co*-CEVE): M_n = 13800, $M_\mathrm{w}/M_\mathrm{n}$ = 1.10, BzA content = 47%.

(15) Lal, J.; Trick, G. S. *J. Polym. Sci., Part A* **1964**, *2*, 4559–4572.

(16) In this hydrolysis reaction, alcohols derived from side chains of VE units were also generated (Supporting Information), which were removed during the purification process of hydrolysis products.