ACS Macro Letters
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α-Substituent Effect on *o*-Vinylbenzaldehyde Cyclopolymerization

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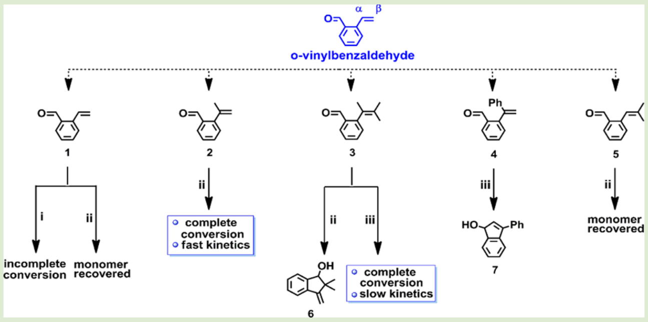
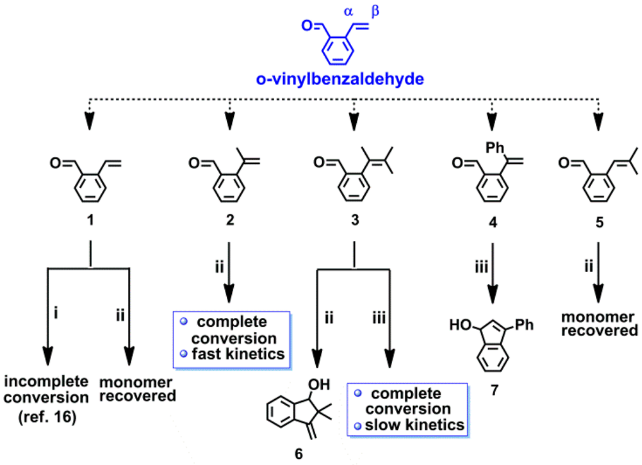
Supporting Information



ABSTRACT: The cationic cyclopolymerization of *o*-vinylbenzaldehydes initiated by boron trifluoride is described. Unlike the incomplete conversion of *o*-vinylbenzaldehyde (**1**) at 0 °C, α-methyl-substituted monomers (**2**) and (**3**) undergo cyclopolymerizations with complete conversions at −78 °C. On the other hand, α-phenyl-substituted monomer (**4**) generated indenyl alcohol (**7**) when subjected to cationic polymerization conditions. The proposed mechanism for *o*-(α-methyl)vinylbenzaldehyde polymerization explains the importance of reaction temperature for polymer formation. Resulting amorphous poly(*o*-(α-methyl)vinylbenzaldehyde (**10**) exhibited good thermal stability (T_{onset} = 340 °C) with a T_g of 153 °C. Polymer (**10**) is a brittle and glassy plastic with a storage modulus (E') of 3 × 10^8 Pa and elongation at break of ∼3%.

Unexpected polymerization behavior of diallyl quaternary ammonium salts reported by Butler and co-workers led to the discovery of cyclopolymerization.[1,2] Highly cyclized polymers from difunctional monomers, mostly 1,6-dienes, were synthesized through this polymerization route.[3] In addition to functionally symmetrical aliphatic diene[4] and dialdehyde[5−7] monomers, cyclopolymerization of *o*-divinylbenzene[8,9] and *o*-phthalaldehyde[10−14] were investigated to yield soluble and high molecular weight polymers for both anionic and cationic initiation modes. One of the research programs in our group targets development of polymers that are more stable than polyphthalaldehydes for controlled release applications.[15] To this end, we were interested in cyclopolymerization of *o*-vinylbenzaldehyde (**1**) and its derivatives. However, cationic initiation of functionally unsymmetrical *o*-vinylbenzaldehyde with $BF_3 \cdot OEt_2$ generates low molecular weight (DP = 20−30) polymers with incomplete conversion of vinyl and aldehyde groups.[16] Here we show how a small change in the monomer results in clean and high yielding polymerizations to generate high molecular weight (i.e., as high as 60 kDa, DP = 400) polymers with complete conversions. Primary structure determination, elucidation of polymerization mechanism, and thermomechanical characterization of this new polymer are reported. Our results demonstrate the importance of substituents at α and β positions of monomer (**1**) on cyclopolymerization (Scheme 1). An alkyl group at the α position is necessary to promote complete conversion of monomer (**1**) at −78 °C. On the other hand, branching at the β position affects the cyclopolymerization kinetics. We anticipate these findings will provide a starting point for preparation of novel cyclopolymers from easily accessible monomers.

Scheme 1. Substituent Effects on *o*-Vinylbenzaldehyde Polymerization[a]



[a]Reagents and conditions: (i) $BF_3 \cdot OEt_2$ (5 mol %), CH_2Cl_2, 0 °C, 1 h; then precipitate with excess MeOH at 0 °C; (ii) $BF_3 \cdot OEt_2$ (5 mol %), CH_2Cl_2, −78 °C, 1 h; then precipitate with excess MeOH at −78 °C; (iii) $BF_3 \cdot OEt_2$ (5 mol %), CH_2Cl_2, −78 °C, 4 h; then precipitate with excess MeOH at −78 °C. Monomers designed for this work: *o*-vinylbenzaldehyde (**1**), *o*-(α-methyl)vinylbenzaldehyde (**2**), *o*-(α-methyl-β-dimethyl)vinylbenzaldehyde (**3**), *o*-(α-phenyl)-vinylbenzaldehyde (**4**), and *o*-(β-dimethyl)vinylbenzaldehyde (**5**).

Cationic polymerization of monomer (**1**) with 5 mol % of $BF_3 \cdot OEt_2$ at 0 °C for 1 h in CH_2Cl_2 formed low molecular

Received: September 20, 2013
Accepted: September 27, 2013
Published: October 3, 2013

dx.doi.org/10.1021/mz4004908 | *ACS Macro Lett.* 2013, 2, 935−938

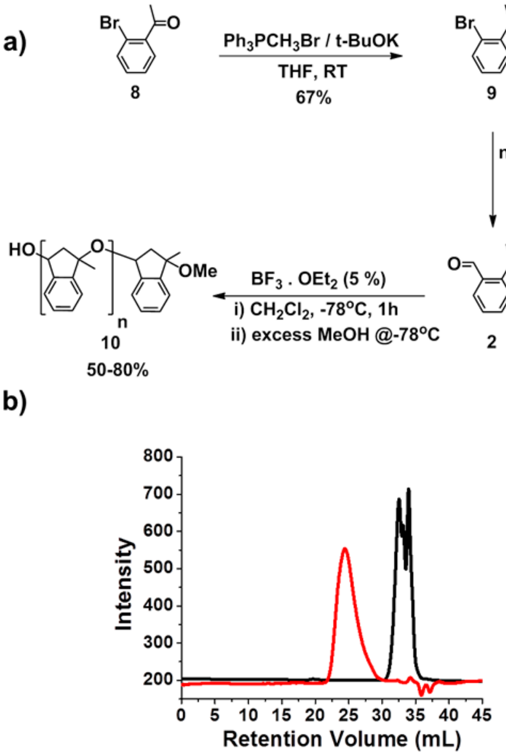


Figure 1. (a) Cyclopolymerization scheme for *o*-(*α*-methyl)-vinylbenzaldehyde (**2**) and (b) GPC analysis of quenched (red trace)/unquenched (black trace) samples with prechilled (−78 °C) MeOH.

weight polymer (M_n = 2100 Da, DP = 16, GPC measurement against polystyrene standards) with low yields (30−40%). Consistent with previous findings,[16] both ^{1}H NMR and IR analyses (Supporting Information (SI), Figures 3 and 6) indicated the existence of pendent aldehyde groups on the polymer backbone. To achieve better control in cationic polymerization of *o*-vinylbenzaldehyde (**1**), the reaction temperature was set to −78 °C and unreacted monomer was collected after 1 h (SI, Figure 7). The lack of a clean polymerization for the monomer (**1**) at 0 °C presumably originates from the formation of a relatively unstable secondary carbocation.

To improve the stability of the carbocationic intermediate and thus improve the likelihood of propagation, we modified the monomer structure by incorporating a methyl at the *α* position. As shown in Figure 1, *o*-(*α*-methyl)vinylbenzaldehyde (**2**) was synthesized from commercially available 2-bromoacetophenone (**8**) in two steps. Previously applied polymerization conditions (5 mol % BF$_3$·OEt$_2$ in CH$_2$Cl$_2$ at 0 °C for 1 h) for *o*-vinylbenzaldehyde (**1**) were followed, but no polymer was collected.

Interestingly, polymer formation was only observed when the reaction temperature was set to −78 °C and the polymerization mixture was quickly precipitated with excess MeOH at −78 °C (Figure 1b, GPC traces). ^{1}H and ^{13}C NMR spectroscopy analysis of precipitated material confirmed polymer formation (Figure 2). Soluble and high molecular weight polymers (i.e., as high as 60 kDa, DP = 400) with yields 50−80% are prepared in an hour with these conditions. Both indanyl- and dihydrobenzofuran-based repeating unit structures are consistent with the observed NMR. To elucidate the nature of the repeating unit, the tertiary carbocation intermediate was trapped with 2 equiv of Et$_3$SiH in the presence of BF$_3$·OEt$_2$.[17,18] However, fast cyclization and propagation kinetics of monomer (**2**) prevented efficient hydride termination. Instead, we trapped the cationic intermediate of *o*-(*α*-methyl-*β*-dimethyl)vinylbenzaldehyde (**3**) both with Et$_3$SiH and Et$_3$SiD to form 2,2,3-trimethyl-2,3-dihydro-1*H*-inden-1-ol (**20**) and 2,2,3-trimethyl-2-hydro-3-deuterio-1*H*-inden-1-ol (**21**), respectively (SI, Figure 9). Isolation of products **20** and **21** suggested the indanyl repeating

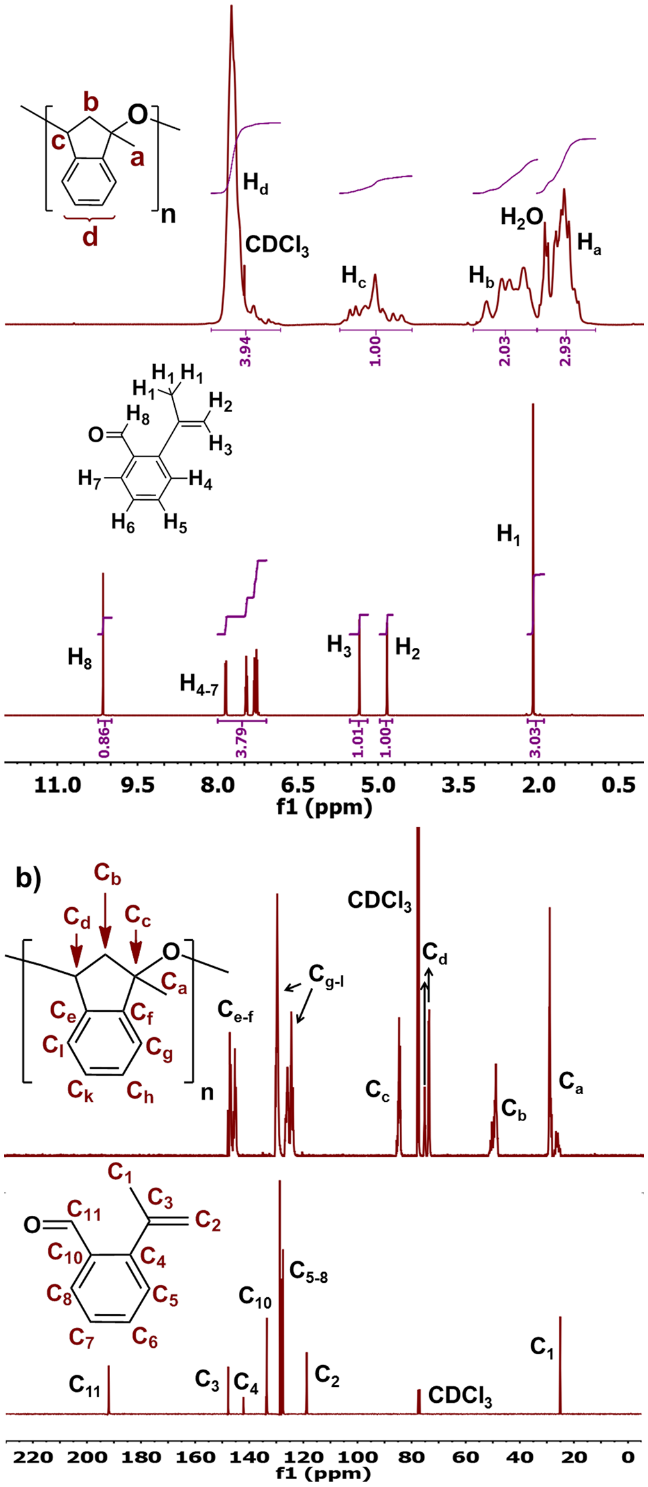


Figure 2. (a) ^{1}H and (b) ^{13}C NMR spectra of poly(*o*-(*α*-methyl)vinylbenzaldehyde) (**10**) and *o*-(*α*-methyl)vinylbenzaldehyde (**2**).

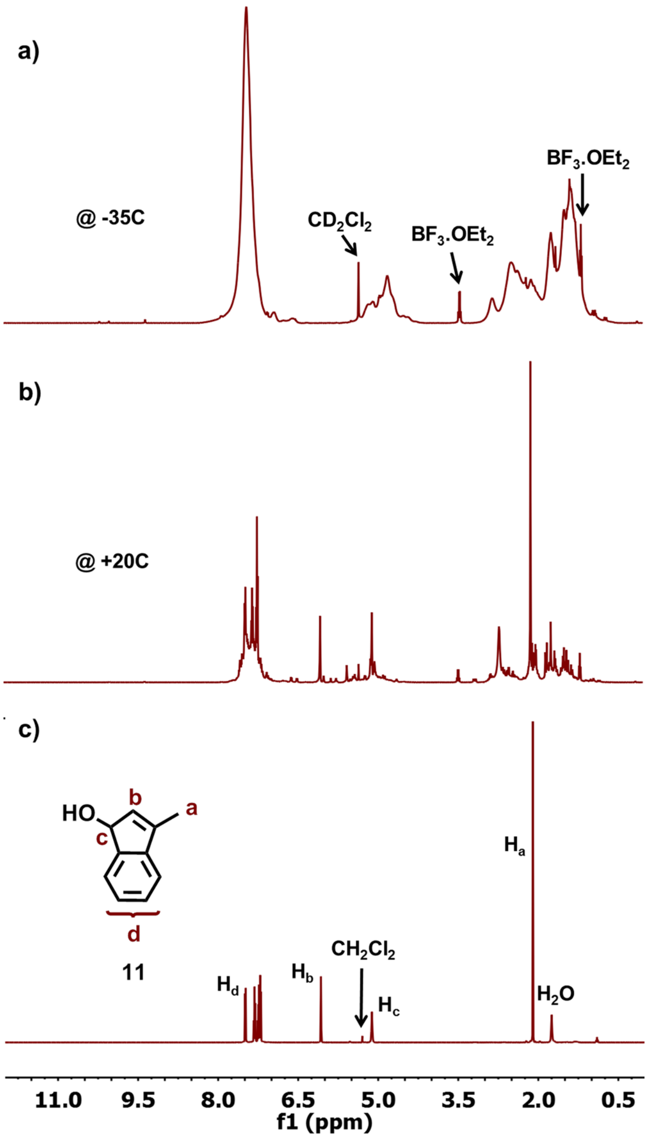
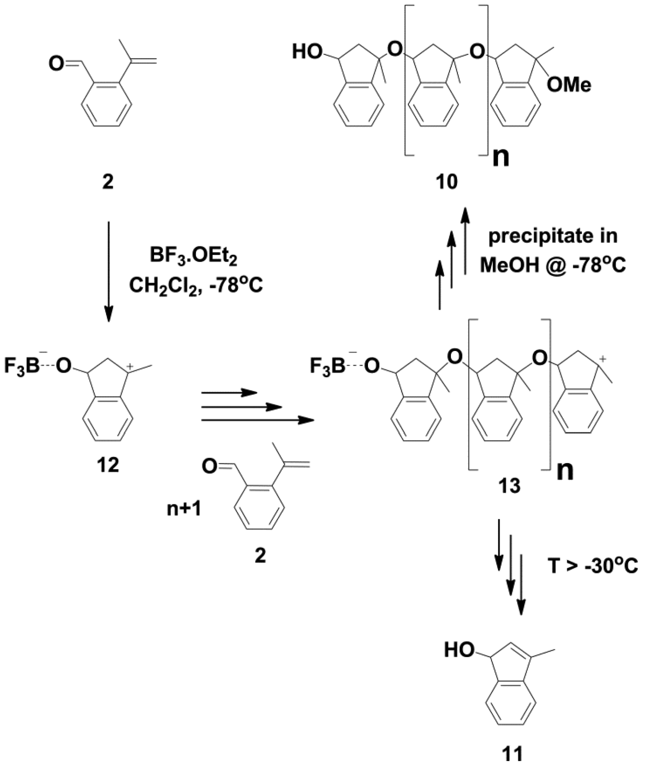


Figure 3. Variable temperature (VT) ^{1}H NMR analysis of *o*-(α-methyl)vinylbenzaldehyde (**2**) polymerization: (a) monomer (**2**) in CD$_2$Cl$_2$ with 10 mol % BF$_3$·OEt$_2$ at −35 °C, (b) crude degradation product at 20 °C, (c) purified degradation product. As the temperature increases, irreversible degradation yields 3-methyl-1*H*-inden-1-ol (**11**).

Scheme 2. Mechanistic Proposal for the Polymerization of *o*-(α-Methyl)vinylbenzaldehyde (2)

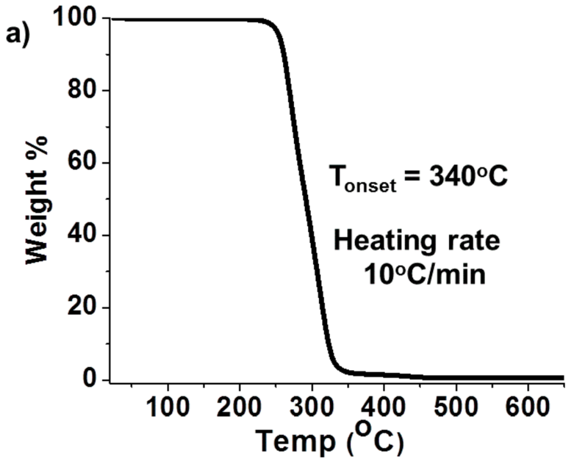


unit for polymer **10**. To complete the primary structure characterization, end groups were evaluated with matrix-assisted laser desorption/ionization (MALDI) analysis (SI, Figures 36−40). Two separate populations of polymer chains were observed where formation of methoxy end-capped and indenyl terminated polymer chains were confirmed. Interestingly, when prechilled (−78 °C) EtOH was used for precipitation, indenyl-terminated and ethoxy end-capped polymer chains were detected (SI, Figure 38). Indenyl-terminated polymer was exclusively recovered when anhydrous pyridine was used to quench the polymerization (SI, Figure 39). Quenching cyclopolymerization of monomer (**2**) with judicious choices of nucleophiles may provide opportunities for further end functionalization of polymer (**10**).

Temperature-dependent polymerization behavior of monomer (**2**) was further investigated with in situ variable temperature (VT) ^{1}H NMR experiments (Figure 3). Polymer formation was observed with 10 mol % catalyst loading in CD$_2$Cl$_2$ at low temperatures ($T < -30$ °C). As the temperature reached to −30 °C, irreversible degradation of poly(*o*-(α-methyl)vinylbenzaldehyde) (**10**) started (SI, Figure 14) and complete breakdown of the polymer was observed at 20 °C. Isolation of the small molecule from the crude degradation product indicated the formation of 3-methyl-1*H*-inden-1-ol (**11**).

To determine the underlying mechanism of a temperature-dependent degradation profile described in Figure 3, poly(*o*-(α-methyl)vinylbenzaldehyde) (**10**) was subjected to polymerization conditions (SI, Figure 2). After vigorous stirring, polymer (**10**) solution in CH$_2$Cl$_2$ with BF$_3$·OEt$_2$ (5 mol %) at −78 °C for 1 h, the polymerization vessel was warmed to RT and degradation of polymer **10** was observed (SI, Figures 2 and 19). On the other hand, when aforementioned polymer solution was subsequently precipitated with excess MeOH at −78 °C, polymer was recovered (SI, Figures 2 and 20). We propose that the monomer (**2**) to polymer (**10**) transformation begins with cyclization to form the intermediate (**12**; formation of indanyl intermediate is supported by trapping experiments described above) promoted with BF$_3$·OEt$_2$ (Scheme 2). After propagation, intermediate (**12**) generates growing polymer chain (**13**), followed by precipitation onto MeOH at −78 °C to irreversibly form polymer (**10**). As evidenced with VT ^{1}H NMR studies, increasing the polymerization temperature above −30 °C forms 3-methyl-1*H*-inden-1-ol (**11**). To test the reversibility of transformation from intermediate (**13**) to alcohol (**11**), pure 3-methyl-1*H*-inden-1-ol (**11**) was subjected to polymerization conditions (SI, S7) and alcohol (**11**) was exclusively recovered after 1 h (SI, Figures 17 and 18).

Unlike *o*-(α-methyl)vinylbenzaldehyde (**2**) polymerization, *o*-(α-methyl-β-dimethyl)vinylbenzaldehyde (**3**) generated indanyl alcohol, 2,2-dimethyl-3-methylene-2,3-dihydro-1*H*-inden-



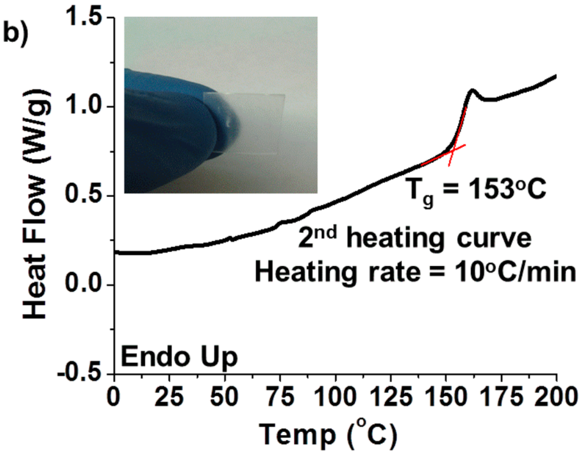


Figure 4. (a) TGA analysis of poly(*o*-(α-methyl)vinylbenzaldehyde (**10**; M_n = 10 kDa, PDI = 1.99). Heating rate = 10 °C/min in N_2 atmosphere; (b) DSC analysis of polymer **10** (M_n = 10 kDa, PDI = 1.99). Second heating curve. Heating rate = 10 °C/min in a N_2 atmosphere. Image showing free-standing polymer film casted from 10 wt % 1,4-dioxane solution.

1-ol (**6**), after 1 h of reaction and subsequent precipitation with excess MeOH at −78 °C (SI, Figure 29). Unavailability of hydrogens at β position for monomer **3** dictated hydride elimination at α position after cyclization. However, longer polymerization times (i.e., 4 h) generated a polymer (confirmed by ^{1}H NMR and MALDI (SI, Figures 29 and 40). Introduction of relatively bulky dimethyl substituents presumably affected intermolecular propagation kinetics to retard the polymerization. Incorporation of aromatic substituents, in this case phenyl, at the α position (monomer **4**) favored elimination to form **7**, probably due to additional resonance stabilization of the cationic intermediate. Similar to *o*-vinylbenzaldehyde (**1**), reaction of *o*-(β-dimethyl)vinylbenzaldehyde (**5**) with $BF_3{\cdot}OEt_2$ at −78 °C generated unreacted starting material. This result indicates the importance of methyl substituent at α position for intramolecular cyclization and intermolecular propagation for *o*-vinylbenzaldehyde based monomers at −78 °C.

Figure 4 presents thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) thermogram of polymer **10**. Thermal decomposition started at 220 °C with onset temperature of 340 °C with heating rate of 10 °C/min. Second heating cycle of amorphous polymer (heating rate = 10 °C/min) displays glass transition temperature (T_g) at 153 °C. Amorphous nature of polymer **10** was also indicated by broad scattering and the absence of crystalline peaks in the powder X-ray diffraction spectra (SI, Figure 41). Polymer **10** is a brittle, glassy plastic with a storage modulus (E') of 3×10^8 Pa and elongation at break of ∼3% (SI, Figures 42 and 43).

In summary, we described the subtle but significant role of the monomer structure for yielding cyclopolymerization of functionally unsymmetrical *o*-vinylbenzaldehyde-based monomers. We demonstrated that by incorporating substituents at α and β positions of monomer **1**, the efficiency of cationic cyclopolymerization and its kinetics can be tuned. Furthermore, polymerization temperature was found to be very critical to this cyclopolymerization. A novel amorphous and brittle polymer, poly(*o*-(α-methyl)vinylbenzaldehyde (**10**), was prepared with T_g of 153 °C, a storage modulus (E') of 3×10^8 Pa and elongation at break of ∼3%. Permeability tests are underway to better understand the properties of polymer **10**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, synthetic procedures, IR and NMR spectra, MALDI mass spectra, DMA, stress−strain curve, and XRD data. 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 work was supported by the Dow Chemical Company through Grant RPS 226772 AA.

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