Communication

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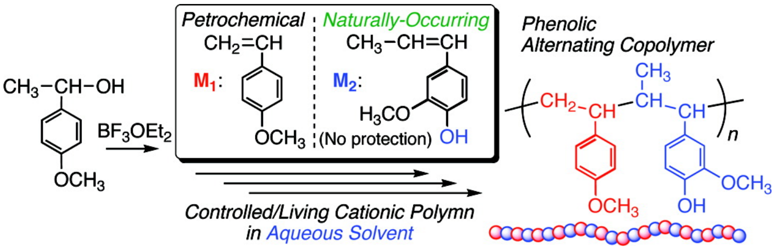

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A Linear Lignin Analogue: Phenolic Alternating Copolymers from Naturally Occurring *β*-Methylstyrene via Aqueous-Controlled Cationic Copolymerization

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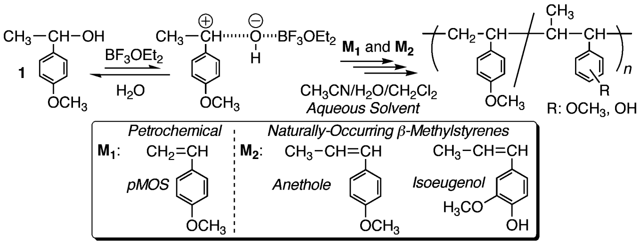
In the vinyl polymerization industry, β-methylstyrenes have rarely been employed because such 1,2-disubstituted olefins exhibit little or no tendency to undergo homopolymerizations due to the steric inhibition.[1] On the other hand, such compounds and their polymers are often found in natural products as *phenylpropanoids*. The most abundant natural polymer is lignin, which is the main component of the plant cell and mainly consists of the coniferyl [(4-hydroxy-3-methoxyphenyl)propenyl] moiety that has many biochemical functions, such as an anti-oxidant and sunburn protection due to the phenolic hydroxyl group.[2] However, its complex cross-linked structure, formed by oxidative coupling biosynthesis, has not been realized in synthetic polymers. In contrast, similar but different phenol-based petrochemical-derived vinyl polymers are applicable to photoresists, epoxy-curing agents, adhesives, and anti-oxidants.[3]

Bio-based polymer materials from renewable resources have recently been attracting much attention from the viewpoint of environmentally benign and sustainable chemistry.[4] In this communication, we focus our attention on the naturally occurring β-methylstyrenes, which are usually abundantly produced in natural plants. For example, *trans*-anethole (Ane: 4-methoxy-β-methylstyrene) is extracted from anise or fennel oil and isoeugenol (IEu: 4-hydroxy-3-methoxy-β-methylstyrene) or its precursor, eugenol, from clove or ylang−ylang oil, thousands of tons of which are annually used in the flavor and fragrance industry.[5] Although there are several reports on the conventional cationic (co)polymerizations of these β-methylstyrenes, they afforded ill-defined polymers or resulted in low molecular weight oligomers in low yields especially for the phenolic monomer, IEu.[6,7] Although the recently developed living radical polymerization might be the most suitable for controlling the (co)polymerization of IEu due to the highly tolerant nature to functional groups,[8] the phenolic moiety is fatal to the radical polymerization due to its antioxidative properties.

Recently, we have found a unique and rather surprising system to control the cationic polymerization of styrene derivatives including a phenolic monomer, *p*-hydroxystyrene (pHS), which can be directly polymerized into living polymers without any protection of its phenolic group in the presence of borontrifluoride etherate (BF_3OEt_2) coupled with an alcohol as an initiator [**1**: the adduct of water and *p*-methoxystyrene (pMOS)].[9] In sharp contrast to the conventional living cationic polymerizations in rigorously dried reaction media,[10] the system is also unique in requiring a fairly large amount of water (approximately equimolar to the monomer and large excess over BF_3OEt_2) for controlling the polymerization. During the polymerization, the aliphatic C−OH bond in the initiator (**1**) or at the growing terminal is selectively dissociated by the highly oxophilic and somewhat water-tolerant BF_3OEt_2 to generate the growing carbocationic species, which can be subsequently and reversibly converted into the covalent C−OH bond by the hydroxide or water.

Scheme 1. Aqueous-Controlled Cationic Copolymerization of Naturally Occurring β-Methylstyrenes



This communication reports the controlled cationic copolymerizations of the naturally occurring β-methylstyrenes (Ane and IEu) with *p*-methoxystyrene (pMOS) by the **1**/BF_3OEt_2 system (Scheme 1). The copolymerization of IEu and pMOS produced an alternating phenolic copolymer, which can be regarded as a well-defined linear lignin analogue with 4-hydroxy-3-methoxyphenyl groups, for the first time.

The homopolymerizations of Ane and IEu were investigated using the **1**/BF_3OEt_2 system in the presence of a large amount of water ($[M]_0 = [H_2O]_0$) at 0 °C, that is, under similar conditions for the controlled polymerizations of pMOS or pHS.[9,11] The homopolymerization of both monomers did not proceed in CH_3CN/CH_2Cl_2 (8/2) in the presence of water, whereas their polymers were obtained in low yields in the absence of water as already reported (Supporting Information).

The two monomers were then copolymerized with pMOS by **1**/BF_3OEt_2 in the presence of water. They were simultaneously consumed with pMOS, in which the consumption rate of IEu was almost the same as that of pMOS, while Ane was consumed slower than pMOS. Furthermore, these β-methylstyrenes were not polymerized at all after the depletion of the counterpart comonomer, pMOS. Figure 1 shows the number-average molecular weights (M_n), molecular weight distributions (MWDs), and size-exclusion chromatograms (SEC) of the obtained copolymers. In both cases, the M_n's increased in direct proportion to the monomer conversions and were close to the calculated values assuming that one molecule of **1** generates one living polymer chain, in which the deviation from the calculated values most probably resulted from the polystyrene calibration. The SEC curves shifted to high molecular weights as the reactions proceeded, while retaining relatively narrow MWDs ($M_w/M_n = 1.2{-}1.4$). The M_n's increased up to 23 400 with varying $[\mathbf{1}]_0$. The comonomer compositions in the copolymers and the copolymer structures were confirmed by ^{1}H NMR (Supporting Information).

To investigate the copolymerizability and the controlled nature of the copolymerization, a fresh feed of pMOS was added to the reaction mixture just before the initial charge of pMOS had completely been consumed while almost half of the Ane remained (Figure 2). The addition of pMOS resumed the consumption of the remaining Ane to induce the second-stage copolymerization,

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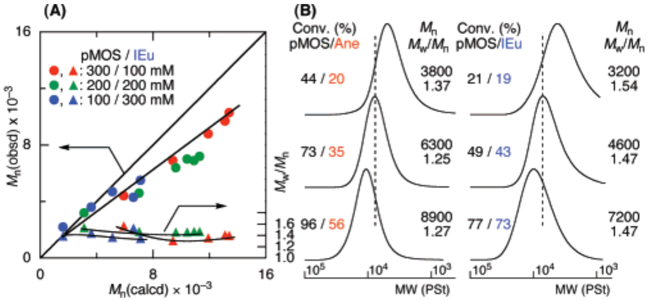

Figure 1. M_n and M_w/M_n curves of pMOS/IEu copolymers (A) and size-exclusion chromatograms of pMOS/Ane and pMOS/IEu copolymers (B) obtained with **1**/BF_3OEt_2/H_2O (4.0/10/100 mM) in CH_3CN/CH_2Cl_2 (8/2) at −15 °C: $[pMOS]_0 + [IEu]_0 = 400$ mM (for A), $[pMOS]_0 = [\beta\text{-methylstyrene}]_0 = 200$ mM (for B).

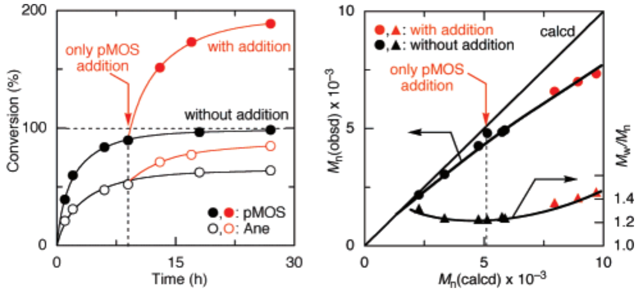

Figure 2. The pMOS addition experiment for pMOS/Ane copolymerization with **1**/BF_3OEt_2 (4.0/10 mM) in CH_3CN/CH_2Cl_2 (8/2) at 0 °C: $[pMOS]_0 = [Ane]_0 = [pMOS]_{add} = 100$ mM, $[H_2O]_0 = 200$ mM.

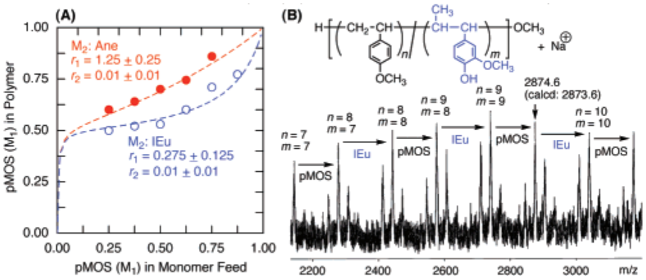

Figure 3. Copolymer composition curves of pMOS with β-methylstyrene (A) and MALDI-TOF-MS spectrum of pMOS/IEu (40/360 mM in feed) copolymer (B). The dashed lines indicate $r_1 = 1.25$, $r_2 = 0.01$ for pMOS/Ane and $r_1 = 0.275$, $r_2 = 0.01$ for pMOS/IEu, respectively.

whereas the remaining Ane was not consumed without the pMOS addition. The M_n of the copolymers further increased as the copolymerization proceeded though the MWDs became slightly broader due to some termination or chain transfer. These results indicate that the growing copolymer chains have a long-lived nature, despite the unusual reactivity of the two monomers.

The copolymerizations of pMOS (M_1) and the β-methylstyrenes (M_2) were further discussed in terms of the monomer reactivity ratio, which was determined by varying the comonomer feed compositions. The copolymer composition curves are shown in Figure 3A. The curve for pMOS/IEu exhibited a typical alternating line, where the M_1 contents in the resulting copolymers were kept close to one-half and independent of the feed ratio. According to the intersection method, the monomer reactivity ratios were calculated as shown in the figure. The reactivity ratio of pMOS/Ane with **1**/BF_3OEt_2 was similar to that with the conventional systems reported in the literature,[6] while that of pMOS/IEu with **1**/BF_3OEt_2 showed a nearly alternating way of monomer addition in which both the monomer reactivity ratios are much lower than unity and close to zero. Furthermore, the matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analysis of the pMOS/IEu copolymers clearly showed an alternating fashion, in which the highest series of peaks are alternately separated by the molecular weight of the pMOS and IEu monomers. The unprecedented cationic alternating copolymerization is most probably due to the highly bulky and electron-donating monomer (IEu); that is, the sterically hindered β-methylstyryl growing cation would not react with the bulky monomer, whereas the less hindered pMOS-derived cation favors the more electron-rich monomer (IEu) (Supporting Information).

Thus, the controlled cationic copolymerizations of plant-derived β-methylstyrenes proceeded with the alcohol/BF_3OEt_2 system to produce a well-defined phenolic copolymer. To the best of our knowledge, this is also the first example of the alternating copolymerization by a cationic process. The properties of the bio-based copolymers as well as the scope and mechanism of this alternating cationic copolymerization are now under investigation.

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Supporting Information Available: Experimental details and polymerization results. This material is available free of charge via the Internet at http://pubs.acs.org.

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