

Cationic Oligomerization of *p*-Hydroxystyrenes: Selective Preparation of Linear Styrene Dimers with Functional Groups

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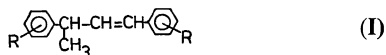
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ABSTRACT: This paper describes the selective synthesis of multifunctional, linear unsaturated oligomers of *p*-hydroxy-, *p*-acetoxy-, and *p*-hydroxy-*m*-methoxy-styrenes (*p*-HOST, *p*-AcOST, and *p*-HO-*m*-MeOST, respectively). A linear unsaturated dimer of *p*-AcOST was selectively formed by oxo acids or their derivatives (CF₃SO₃H or AcClO₄) in benzene at 70°C. *p*-AcOST trimer and tetramer were also produced in high yields by the proper choice of catalysts and reaction conditions. Base-catalyzed hydrolysis of the *p*-AcOST dimer and trimer quantitatively gave the corresponding *p*-HOST oligomers not obtainable by direct reactions by *p*-HOST itself. This finding provides a new method for preparing multifunctional phenols with linear unsaturated backbone, which are attractive as "reactive oligomers." *p*-HO-*m*-MeOST, whose oligomers are structurally related to lignin, was also converted to a linear unsaturated dimer in good yield by iodine or CH₃SO₃H catalyst.

KEY WORDS Oligomerization / Selective Dimerization / Cationic Polymerization / *p*-Acetoxystyrene / *p*-Hydroxystyrene / *p*-Hydroxy-*m*-methoxystyrene / Oxo Acids /

We recently found that linear unsaturated dimers (I) of a series of styrenes can be obtained in high yields by cationic oligomerization with oxo acids or their derivatives under the proper conditions.



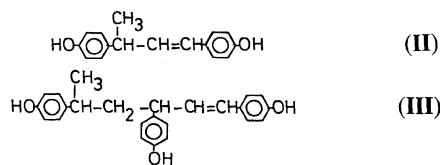
R = H^{1,2}; *o*-, *m*-, *p*-CH₃^{3,4}; *o*-, *m*-,
p-Cl⁵; *p*-OCH₃⁵

One interesting and important use of these dimers is as "reactive oligomers," *i.e.*, oligomeric synthetic intermediates that give valuable materials or chemical modification of their functional group(s). From this viewpoint, however, the dimers I hitherto prepared are unsatisfactory because of the small reactivities of their ring-substituents and internal olefinic double bonds. We thus decided to synthesize linear dimers of type I with more reactive substituents in the rings.

There are no papers which describe the controlled oligomerization of styrene derivatives having re-

active substituents except for that of *p*-isopropenyl phenol (*p*-hydroxy- α -methylstyrene).⁶ Cationic oligomerization of hydroxy-,⁷ *p*-acetoxy-,⁸ and *p*-hydroxy-*m*-methoxy-styrenes⁹ have been studied. Hydroxy- and *p*-hydroxy-*m*-methoxystyrenes formed high-molecular-weight compounds with uncontrolled chain-lengths, but *p*-acetoxystyrene has not been polymerized by a cationic mechanism.

The first object of the present work is to prepare the linear unsaturated dimer (II) and trimer (III) of *p*-hydroxystyrene.



II and III are new di- and tri-functional phenols, respectively, and are quite attractive as reactive oligomers. We further examined the linear dimerization of *p*-hydroxy-*m*-methoxystyrene, an interest-

ing derivative of *p*-hydroxystyrene, whose oligomers are structurally related to lignin. A linear dimer was very recently reported as obtainable in a 33% yield from oligomers resulting from *p*-hydroxy-*m*-methoxystyrene on standing at room temperature.¹⁰ However, this method for producing the linear dimer may be impractical in consideration of the long reaction time.

EXPERIMENTAL

Materials

p-Acetoxystyrene (Maruzen Oil Co. Ltd.) was distilled over CaH_2 just before use: purity 97% by gas chromatography. *p*-Hydroxystyrene was obtained by hydrolysis of *p*-acetoxystyrene in an aqueous KOH solution.¹¹ *p*-Hydroxy-*m*-methoxystyrene was synthesized by decarboxylation of ferulic acid in quinoline at 210°C.¹² mp 9–11°C; purity >99% by gas chromatography. Other materials were purified and used as previously described.²

Oligomerization

Oligomerization was carried out under a dry nitrogen atmosphere at 30 to 70°C as reported.² The oligomeric products were analyzed and fractionated by high performance liquid chromatography (HLC) on a JASCO FLC A-700 chromatograph equipped with a differential refractometer. For the *p*-acetoxystyrene oligomers, HLC was run in chloroform with a 50 cm column packed with JSP-101 polystyrene gel; for oligomers of *p*-hydroxystyrene and *p*-hydroxy-*m*-methoxystyrene, HLC was run in tetrahydrofuran (THF) using two 50 cm columns packed with Shodex 802 polystyrene gel. The structure of the products was determined by 90 MHz ^1H nuclear magnetic resonance (NMR) spectroscopy (JEOL NMR FX-90Q) in CDCl_3 at room temperature.

Hydrolysis of *p*-Acetoxystyrene Oligomers

For *p*-acetoxystyrene dimers and trimers, the hydrolysis was conducted by the following two methods.

Method A.¹³ A sample of the *p*-acetoxystyrene oligomers (0.5 g) was dissolved in 1,4-dioxane (9 ml) and hydrazine hydrate (1 ml, 0.02 mol) was added. The mixture was stirred for 4 h at room temperature, neutralized with concentrated hydrochloric acid, and then extracted with ethyl acetate (100 ml).

The ethyl acetate phase was washed with distilled water and evaporated, and the residue was vacuum-dried to give a viscous liquid in quantitative yield.

Method B. A sample of the *p*-acetoxystyrene oligomers (0.5 g) was dissolved in methanol (50 ml) and 40% aqueous sodium hydroxide (1 ml) was added. The solution was stirred for 1 h at room temperature and worked up in the same manner as in Method A; yield 100%.

RESULTS AND DISCUSSION

Oligomerization of *p*-Hydroxystyrene

The oligomerization of *p*-hydroxystyrene (*p*-HOST) with acetyl perchlorate (AcClO_4) was attempted at 70°C in a nonpolar solvent (hexane) ($[\text{M}]_0 = 0.10 \text{ M}$). The monomer is hardly soluble in hexane, and the heterogeneous reaction gave a product with a broad molecular weight distribution (MWD) and a fairly high molecular weight, which was insoluble in hexane, benzene, and chloroform, and was soluble in acetone, THF, and alcohol. *p*-HOST readily dissolves in polar solvents and gives polymers in the presence of an acid catalyst.⁷

The difficulty in producing lower oligomers by the reaction of *p*-HOST can be explained in terms of the high reactivity of the monomer induced by its strongly electron-donating hydroxy group. We therefore examined an indirect synthesis of *p*-HOST oligomers *via* the selective oligomerization of a less reactive monomer that might give a product convertible subsequently into the desired *p*-HOST oligomer.

Oligomerization of *p*-Acetoxystyrene

Selective Dimerization. *p*-Acetoxystyrene (*p*-AcOST) having a less electron-donating acetoxy group was employed as a monomer. Figure 1 shows the effects of the catalysts and solvents on the MWD of *p*-AcOST oligomers produced at a high temperature (70°C) at a low monomer concentration ($[\text{M}]_0 = 0.10 \text{ M}$). These conditions are preferable to the formation of lower oligomers according to our previous study.²

Dimers were obtained in high yield by an oxo acid ($\text{CF}_3\text{SO}_3\text{H}$) or an oxo-acid derivative (AcClO_4) in a nonpolar solvent (dimer yield: 79 wt% with $\text{CF}_3\text{SO}_3\text{H}$; 91 wt% with AcClO_4). In a polar solvent, higher oligomers as well as the dimer were yielded by AcClO_4 . In contrast, a metal-halide

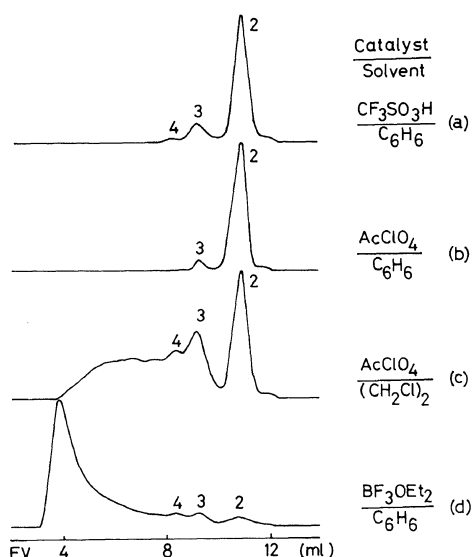


Figure 1. MWD of *p*-AcOSt oligomers formed at 70°C: $[\text{M}]_0 = 0.10 \text{ M}$; catalysts and solvents as indicated. $[\text{C}]_0$ (mM): a, 0.50; b, 1.0; c, 0.50; d, 20. Conversion: 55~85%. The numbers indicate the degree of polymerization.

catalyst (BF_3OEt_2) gave higher oligomers and only a small amount of the dimer. Such considerable effects of catalysts on the MWD of product have already been reported for the oligomerization of styrene and its derivatives.^{2,4,5}

It should be mentioned here that, contrary to the previous report,⁸ *p*-AcOSt readily yielded its dimer or higher oligomers on treatment with an oxo acid.

Figure 2 shows the effects of temperature on the MWD of *p*-AcOSt oligomers formed by AcClO_4 in C_6H_6 . The dimer yield clearly increased at a higher temperature and reached about 90 wt% at 70°C.

Synthesis of Trimer and Tetramer. Figure 3 shows the effects of monomer concentration on the MWD of oligomers obtained with $\text{CF}_3\text{SO}_3\text{H}$ at 30°C. These experiments at higher $[\text{M}]_0$ and the lower temperature were conducted in an attempt to obtain *p*-AcOSt trimers and tetramers in high yields; $\text{CF}_3\text{SO}_3\text{H}$ was selected as catalyst because at 70°C it gave a higher trimer yield than AcClO_4 did (Figure 1). The formation of oligomers in higher yield than the trimer was promoted by an increase in monomer concentration; for instance the product at $[\text{M}]_0 = 2.0 \text{ M}$ consisted of 18 wt% trimers and 16 wt% tetramers.

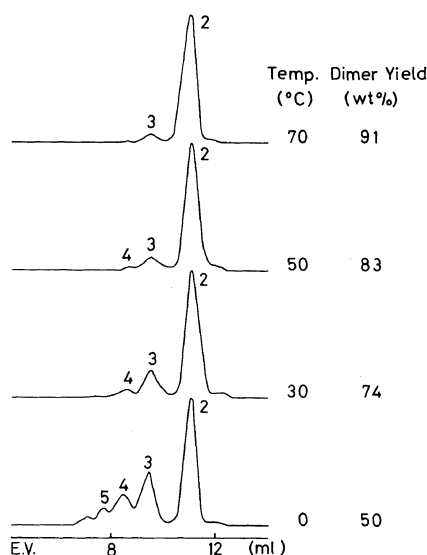


Figure 2. Effect of temperature on MWD of *p*-AcOSt oligomers formed by AcClO_4 in C_6H_6 ($[\text{M}]_0 = 0.10 \text{ M}$, $[\text{C}]_0 = 1.0 \sim 2.0 \text{ mM}$). Conversion: 60~80%. The numbers indicate the degree of polymerization.

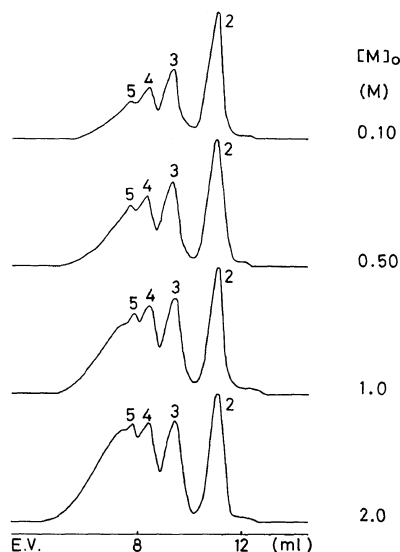


Figure 3. Effect of monomer concentration ($[\text{M}]_0$) on MWD of *p*-AcOSt oligomers formed by $\text{CF}_3\text{SO}_3\text{H}$ in C_6H_6 at 30°C ($[\text{C}]_0 = 1.0 \text{ mM}$). Conversion: 60~80%. The numbers indicate the degree of polymerization.

Thus, *p*-AcOSt trimers and tetramers can be obtained at a low temperature and high monomer concentration.

Structure of the *p*-AcOSt Oligomers. For ^1H

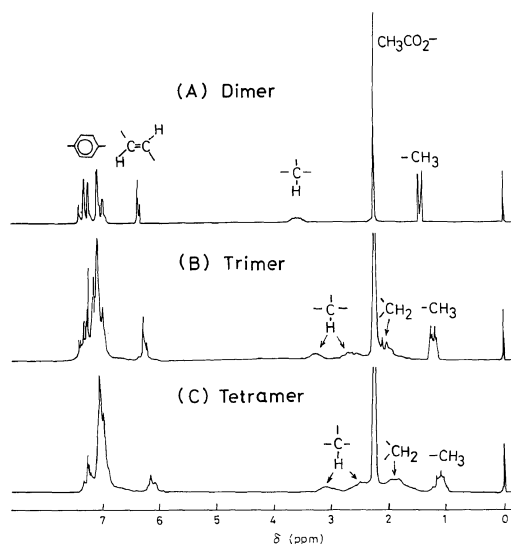


Figure 4. ^1H NMR (90 MHz) spectra of *p*-AcOSt oligomers separated by HLC from the products shown in Figures 1a, 1b, and 3d. Catalyst, solvent, and temp: (A) $\text{CF}_3\text{SO}_3\text{H}$ (or AcClO_4), C_6H_6 , 70°C ; or $\text{CF}_3\text{SO}_3\text{H}$, C_6H_6 , 30°C ; (B) and (C) $\text{CF}_3\text{SO}_3\text{H}$, C_6H_6 , 30°C .

NMR structural analysis, the dimer to tetramer fractions of the *p*-AcOSt oligomers were separated by preparative HLC. The dimer (A) was obtained by the selective dimerization with $\text{CF}_3\text{SO}_3\text{H}$ in C_6H_6 at 70°C (cf. Figure 1). The trimer (B) and the tetramer (C) were both fractionated from the oligomeric product formed by $\text{CF}_3\text{SO}_3\text{H}$ in C_6H_6 at 30°C ($[\text{M}]_0 = 2.0 \text{ M}$; cf. Figure 3). Figure 4 shows their ^1H NMR spectra. The peak assignments shown in Figure 4 are based on our previous work on linear dimers of styrene oligomers.^{1,3-5} These spectra are very similar to those of styrene oligomers except for an acetoxy group. Therefore, all the three *p*-AcOSt oligomers were identified as linear unsaturated oligomers. It should be noted that no signals assignable to other units could be detected. This indicates that in C_6H_6 the oxo-acid catalysts exclusively yield linear *p*-AcOSt oligomers with an unsaturated terminal.

Preparation of *p*-HOSt Oligomers from *p*-AcOSt Oligomers

The hydrolysis of the *p*-AcOSt oligomers thus obtained was carried out to prepare *p*-HOSt oligomers with controlled chain-lengths and structures,

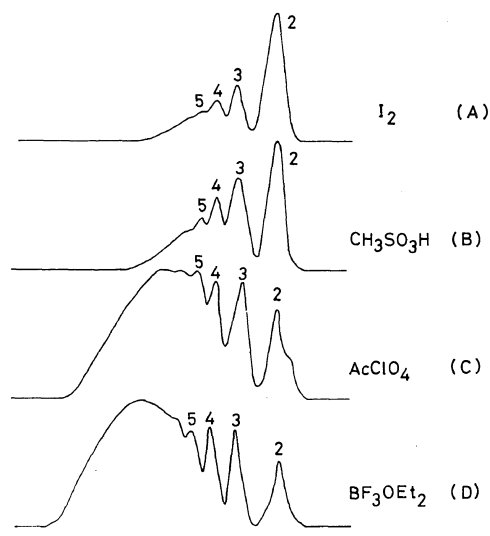


Figure 5. MWD of *p*-HO-*m*-MeOSt oligomers formed in C_6H_6 at 70°C : $[\text{M}]_0 = 0.10 \text{ M}$ $[\text{C}]_0$ (mM): A, 5.0; B, 1.0; C, 0.030; D, 1.0. Conversion $> 65\%$. The numbers indicate the degree of polymerization.

these oligomers were found difficult to synthesize directly from *p*-HOSt (*vide supra*).

The base-catalyzed hydrolysis of the linear *p*-AcOSt dimer and trimer (both separated by HLC) readily proceeded quantitatively at room temperature; see EXPERIMENTAL section. The quantitative deacetylation was confirmed by the absence of acetyl absorptions [IR, 1760 cm^{-1} ($\nu_{\text{C=O}}$); ^1H NMR, $\delta 2.2 \text{ ppm}$ (CH_3CO)] in the products. ^1H NMR and infrared (IR) spectra of the products were consistent with those of the linear unsaturated *p*-HOSt dimer (II) or trimer (III), and a signal assignable to other unit could not be detected. HLC analysis indicated no change in the degree of polymerization during the hydrolysis.

The above mentioned results show that the *p*-HOSt dimer (II) and trimer (III) could be prepared by the hydrolysis of the corresponding *p*-AcOSt linear oligomers.

Oligomerization of *p*-Hydroxy-*m*-methoxystyrene

p-Hydroxy-*m*-methoxystyrene (*p*-HO-*m*-MeOSt), in contrast to *p*-HOSt, was completely soluble even in nonpolar solvents (*e.g.*, C_6H_6) and underwent homogeneous oligomerization in con-

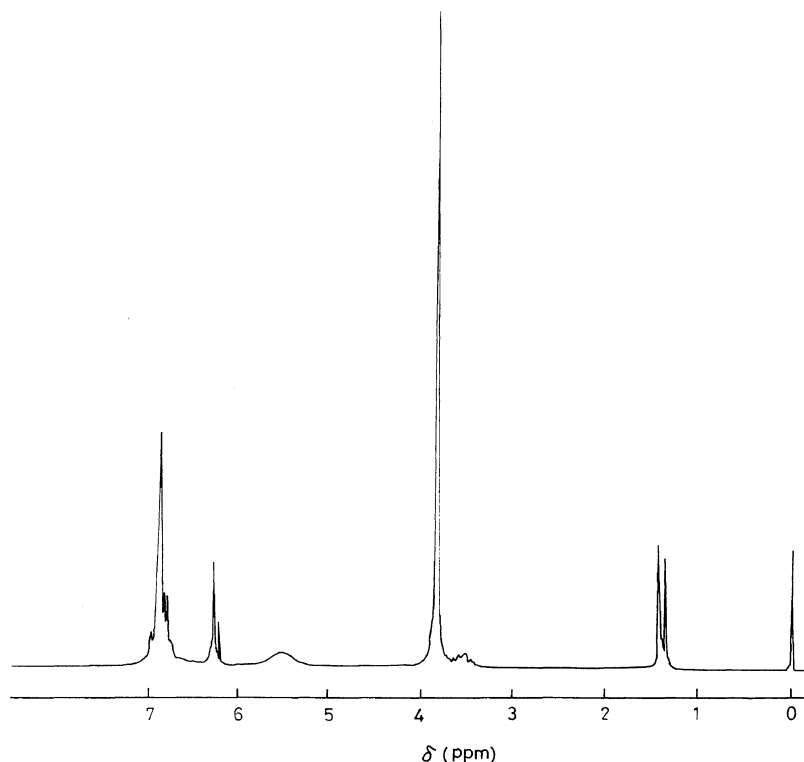
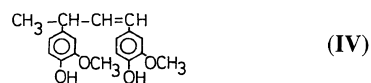


Figure 6. ^1H NMR (90 MHz) spectrum of a *p*-HO-*m*-MeOSt dimer separated from the oligomeric product (Figure 5B) formed by $\text{CH}_3\text{SO}_3\text{H}$. See Figure 5 for reaction conditions.

junction with acid catalysts. Figure 5 shows the MWD of *p*-HO-*m*-MeOSt oligomers obtained with four catalysts in C_6H_6 at 70°C . In spite of the presence of two electron donating ring-substituents, *p*-OH-*m*-MeOSt yielded its dimers in relatively high yields (up to 50 wt%). The dimer content clearly depended on the catalysts in following order: $\text{BF}_3\text{OEt}_2 < \text{AcClO}_4 < \text{CH}_3\text{SO}_3\text{H} < \text{I}_2$; *i.e.*, the more nucleophilic the counteranion is, the more selectively the dimer is formed, as in the oligomerizations of other styrenes.¹⁻⁵

With the AcClO_4 catalyst, the dimer content was lower than those for other (less reactive) styrene derivatives under similar conditions.¹⁻⁵ Higher oligomers were preferably formed by a metal halide (BF_3OEt_2 , Figure 5D).

The dimer fractions obtained with iodine and $\text{CH}_3\text{SO}_3\text{H}$ were separated by HLC for ^1H NMR spectrum analysis. Both dimer samples gave identical ^1H NMR spectra (*e.g.*, Figure 6) which were assigned to a linear unsaturated dimer of *p*-HO-*m*-



MeOSt (IV). Peak assignments¹⁻⁵ are as follows: δ 1.42 (CH_3 , d, 3H, $J=7.1$ Hz), 3.70 (CH, m, 1H), 3.83 (OCH_3 , s, 6H), 5.54 (OH, s, 2H), 6.29 ($\text{HC}=\text{CH}$, m, 2H), and 6.87 ppm (aromatic, m, 6H). The spectrum, to which a similar spectrum has been reported quite recently,¹⁰ shows definitely that the linear isomer IV is the only dimer formed in accordance with the results for other styrene derivatives presented so far.¹⁻⁵ Neither the *p*-OH nor *m*-OMe group in the monomer reacted under our reaction conditions, although polymers with a phenol-acetaldehyde structure have been obtained from *p*-OH-*m*-MeOSt with BF_3OEt_2 catalyst.⁹

In conclusion, the present work demonstrates that styrene derivatives (*e.g.*, *p*-HO-*m*-MeOSt) with strongly electron-donating groups can be dimerized by using oxo-acid catalysts and iodine. The high

selectivity for the linear dimerization can be explained in terms of the strong interaction between the growing carbocation and the counterion, which promotes β -proton elimination from the former. The linear oligomers **II**—**IV**, endowed with functional groups in their aromatic rings, serves as versatile intermediates in organic synthesis, *i.e.*, as reactive oligomers.

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