

# NOTE

## Synthesis of Functional Styrene Derivatives–Carbon Monoxide Copolymer

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### INTRODUCTION

In the last 10 years, many articles have reported on copolymers of carbon monoxide and olefins.<sup>1–9</sup> Interest in them is not only due to the low cost of carbon monoxide constitutive units<sup>10</sup> but also due to their potential practical application from their photodegradable properties.<sup>11–13</sup> These copolymers are characterized by high crystallinity, high melting points, and very low solubility in most common solvents.

The photo-Fries rearrangement of aromatic esters and amides, which was first reported by Anderson and Reese,<sup>14</sup> has been tested with a number of polymeric materials, such as aromatic polyesters<sup>15–17</sup> and polyamides.<sup>18</sup> The photo-Fries reaction of polymers containing aromatic ester or amino groups might be applied in polymeric imaging systems for application in microelectronics. For example, it is expected that the light-induced Fries rearrangement of poly(*p*-acetoxystyrene–carbonmonoxide) (AcOSTCO) will yield a rearranged polymer containing pendant phenolic groups. Such a rearrangement would afford a basis for the development of an image from a thin film of the polymer as the unexposed and exposed areas of the polymer would have greatly dissimilar dissolution in appropriate solvent systems.

In order to develop new materials, in the present work, the novel alternating copolymers of acetoxy-styrene with carbon monoxide was prepared. Many alternating copolymers of carbon monoxide and styrene derivatives (SDCO) have been prepared by chemical modification of AcOSTCO and by copolymerization of styrene derivatives with carbon monoxide (Scheme I).

### EXPERIMENTAL

#### Materials

Carbon monoxide (CP grade, >99.9%) was supplied by Dalian Science and Engineering University. All other chemicals were purchased from Huabei Special Chemical Co. Methanol was dried by anhydrous MgSO<sub>4</sub> and then distilled. Styrene derivatives were dried by CaH<sub>2</sub> and then vacuum-distilled.

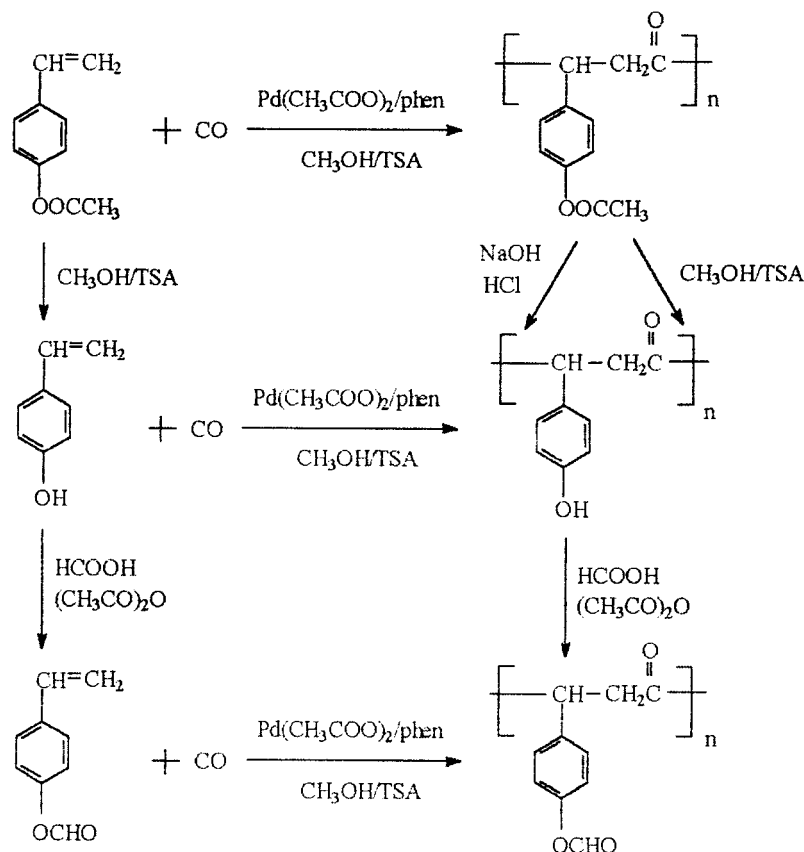
#### <sup>1</sup>H-Nuclear Magnetic Resonance, Fourier Transform Infrared, and EA Analysis

For characterization, the <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker AC-P200 Model spectrometer. The chemical shifts were referenced to internal tetramethylsilane (TMS). The Fourier transform infrared (FTIR) analysis of the Nicolet 5DX Model was adopted for effecting the analysis of carbonyl group and substituted groups using KBr pellets. The C and H analyses were determined on an elemental analyzer, PE-2400 Model.

#### Synthesis of *p*-(Formyloxy) Styrene

A formylating mixture consisting of 9.0 g of formic acid and 19.9 g of acetic anhydride was prepared by mixing the two reagents slowly while keeping the temperature below 45°C according to the procedure of Stevens and Van Es.<sup>19</sup> After cooling to room temperature, the formylation reagent was treated with a mixture of 0.35 g of pyridine and 10.9 g of *p*-hydroxystyrene, and the solution was stirred for 72 h. The solution was concen-

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Scheme 1

trated in vacuum, leaving a yellowish residue, which was purified by fractional distillation (bp 83°C/3 mm Hg) to yield 10.0 g (74.5%) of *p*-(formyloxy) styrene.

### Copolymerization

AcOSTCO was obtained in the homogeneous catalytic system<sup>15</sup> composed of Pd(CH<sub>3</sub>COO)<sub>2</sub>, 0.011 g; 1.10-phenanthroline, 0.085 g; *p*-toluenesulfonic acid, 0.117 g; and *p*-benzoquinone, 0.20936 g. The copolymerization were carried out under 4.0 MPa and 60°C conditions for 4 h. A 100-mL autoclave was dried, and then the catalyst, 5 mL of methanol and 5 mL of acetoxystyrene, were charged. Then, CO was introduced first through a high-pressure hose. The mixture was heated to the polymerization temperature. At the end of the copolymerization, AcOSTCO was purified by precipitation with methanol and dried in vacuum at ambient temperature for 24 h.

IR: 1761.1 (vs), 1709.0 (vs), 1697.5 (vs), 1610.7 (w), 1506.5 (s), 1371.5 (vs), 1207.5 (vs), 1168.9 (vs), 912.4 (m), 844.88 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR: 7.1–6.4 (4H, br), 4.1 (1H, s), 3.0 (1H, s), 2.6 (1H, s), 2.2 (3H, s). ANAL.

Calcd. for AcOSTCO: C, 69.46; H, 5.30. Found: C, 69.92; H, 5.52.

The filtrate was then concentrated in vacuum, leaving a red residue, which was purified by washing with CHCl<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>. The residue was poly(*p*-hydroxystyrene–carbon monoxide) (HOSTCO).

IR: 1707.1 (vs), 1697.5 (vs), 1612.6 (w), 1514.3 (vs), 1361.8 (w), 1248.0 (vs), 1174.7 (s), 851.59 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR: 7.1–6.4 (5H, br, Ar–H, and OH), 3.9 (1H, s), 3.0 (1H, s), 2.6 (1H, s). ANAL. Calcd. for HOSTCO: C, 72.97; H, 5.41. Found: C, 73.32; H, 5.70.

The copolymerization of *p*-hydroxystyrene [or *p*-(formyloxy)styrene] with carbon monoxide was carried in the same way as the copolymerization of acetoxystyrene with carbon monoxide.

### Hydrolysis of AcOSTCO

A suspension containing 1 g of the AcOSTCO copolymer in 50 mL water and 1 g NaOH was refluxed under

N<sub>2</sub> for 1 h. Following centrifugation to remove trace amounts of solid residue, a light brown polymer was obtained by addition of aqueous HCl to the resultant solution. The polymer was washed with hot water several times and dried under vacuum. Yield was 0.72 g (92%).

#### Hydrogenation of AcOSTCO

A suspension containing 1 g of the AcOSTCO copolymer in 50 mL THF and 1 g LiAlH<sub>4</sub> was refluxed under N<sub>2</sub> for 4 h. Following the decomposition of residual LiAlH<sub>4</sub> by a small amount of water, a light brown polymer solution was obtained by filtration. The polymer was dried under vacuum. Yield was 0.70 g (89%).

#### Formylation of HOSTCO

The formylating agent was prepared by reaction of 3.87 g of formic acid with 8.54 g of acetic anhydride while keeping the temperature of the mixture below 40°C. A solution of HOSTCO in 30 mL of THF containing 0.1 g of pyridine was then added to the stirred formylating agent, and the mixture was stirred for 72 h at room temperature. After precipitation in water, the polymer was washed and dried to afford 4.6 g of poly[*p*-(formyloxy) styrene-carbon monoxide] (FOSTCO). Spectroscopic analysis of the polymer confirmed that a very small amount of unreacted *p*-hydroxystyrene units remain unchanged in the polymer.

IR: 1761.0 (vs), 1738.2 (vs), 1205.3 (vs), 1169.5 (s), 1107.1 (s), 849.5 (m) cm<sup>-1</sup>. <sup>1</sup>H-NMR: 8.2 (1H, s), 7.6–6.2 (4H, br), 4.0 (1H, s), 3.0 (1H, s), 2.7 (1H, s). ANAL. Calcd. for FOSTCO: C, 68.16; H, 4.58. Found: C, 68.52; H, 4.77.

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