

# Synthesis and Characterization of Poly(ethylene-co-styrene)

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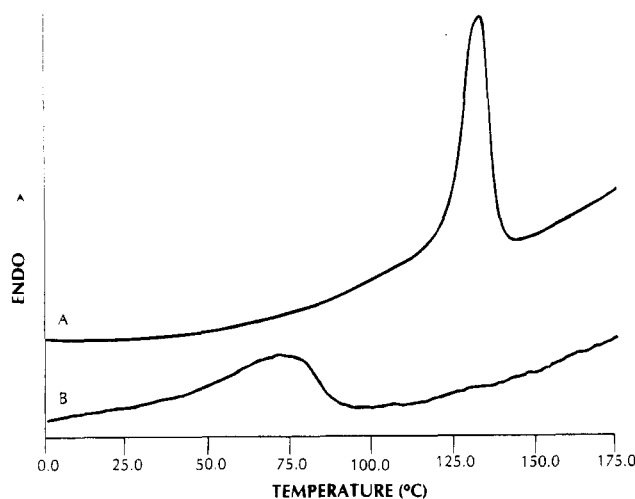
**Introduction.** Copolymerizations of olefins and styrene by a conventional Ziegler–Natta catalyst have been reported by several authors since 1964.<sup>1–4</sup> Ziegler–Natta catalytic methods are commonly used throughout the polymer industry, especially for the production of ethylene copolymers, and have a history tracing back to 1957. However, for a vinyl aromatic comonomer such as styrene, the polymerization activity is low, such that an ethylene/styrene copolymer has a maximum of only about 1 mol % styrene units in the copolymer. In addition, conventional Ziegler–Natta catalysts consist of multiple active species which differ in the oxidation states of their transition metals, stereospecificity, etc. Therefore, the reported copolymer is actually a mixture of polymer chains of varying length, some having more than 1% by mole of styrene per individual chain and many, if not most, having no styrene groups. Recently, the introduction of metallocene and cyclopentadienyl–amide catalyst systems makes possible the synthesis of poly(ethylene-co-styrene) containing up to 50 mol % styrene. This has only been reported in the trade and patent literature.<sup>5–8</sup> Furthermore, the details of structure characterization remain unreported. In this paper, we present the details of both the synthesis and the structural characterization of poly(ethylene-co-styrene) polymers.

**Experimental Section. Chemicals and Solvents.** Ethylene (Matheson; research grade 99.99%), methyl aluminoxane (MAO; Ethyl Corp.; 10 wt %), and isopropylidene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride<sup>9</sup> (Boulder Scientific) were used as purchased. Toluene (Aldrich; anhydrous) and styrene (Aldrich) were stirred over CaH<sub>2</sub> overnight and vacuum distilled before use.

**Polymerizations.** In an argon atmosphere glovebox, a glass polymerization reactor was charged with 200 mL of purified anhydrous toluene, 12 mL of freshly distilled styrene, and 10 mL of MAO (10 wt % in toluene). After stirring for approximately 2 min, 10 mg of metallocene catalyst were added into the reactor. The reactor was then attached to the ethylene polymerization line, and ethylene was fed on demand at 30 psig to start and maintain the polymerization at 40 °C. After the polymerization was carried out for 30 min, a small amount of methanol was added to terminate the polymerization. The polymers were precipitated in 5% acidic methanol and isolated by solvent fractionation using toluene.

**NMR Spectroscopy.** Solution-state <sup>13</sup>C NMR data were obtained at 100.6 MHz on a Bruker DMX400. The acquisition conditions used were analogous to those prescribed<sup>10</sup> by proposed ASTM method X70-8605-2, namely, a 10-s pulse delay and a 90° pulse width. Spectra were acquired with inverse-gated decoupling to avoid nuclear Overhauser enhancement (NOE) effects, which might skew the quantitative analysis.

**Differential Scanning Calorimetry.** DSC thermograms were obtained using scanning rates of 10 °C/

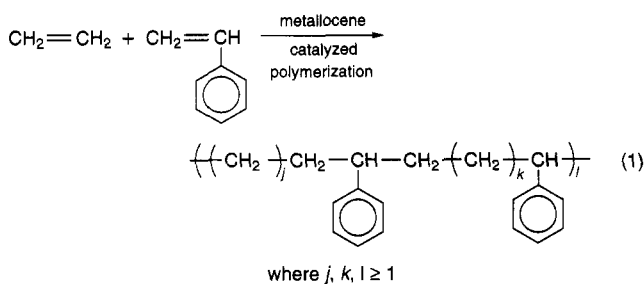


**Figure 1.** DSC trace of (A) polyethylene and (B) poly(ethylene-co-styrene).

min on a Perkin-Elmer DSC 7 instrument with associated robotics.

**Size-Exclusion Chromatography.** SEC analyses were performed on a Waters Model 150C gel permeation chromatograph with five polystyrene gel columns (10<sup>7</sup>-, 10<sup>6</sup>-, 10<sup>5</sup>-, 10<sup>4</sup>-, and 10<sup>3</sup>-Å pore sizes) and 1,2,4-trichlorobenzene as solvent at 135 °C.

**Results and Discussion.** In this paper we report on the synthesis of poly(ethylene-co-styrene), as described in eq 1. In order to provide an internal check



on the ability of ethylene and styrene to copolymerize rather than homopolymerize, we also attempted to prepare homopolymers of polyethylene and polystyrene using the conditions outlined above. Styrene did not homopolymerize to any detectable extent at this temperature (40 °C) as long as freshly distilled styrene was employed. It is interesting to note, however, that styrene can homopolymerize under these conditions if the temperature exceeds 60 °C. As a result, care was taken to ensure that this competing reaction did not occur. Unlike styrene, ethylene can homopolymerize under these conditions.

The DSC trace of our reaction product is given in Figure 1. For reference purposes, the DSC trace for an ethylene homopolymer prepared under these conditions is also shown in Figure 1. The fact that the reaction product has a lower melting point (71 °C) than the ethylene homopolymer (138 °C) is suggestive of the formation of a copolymer.

Given in Figure 2 is the <sup>13</sup>C NMR spectrum of the reaction product. The figure is dominated by a large peak at 30 ppm which can be readily assigned to isolated ethylene units.<sup>10,11</sup> In addition to this peak, there are four smaller ones that can be shown to be due to the presence of styrene incorporation along the polymer

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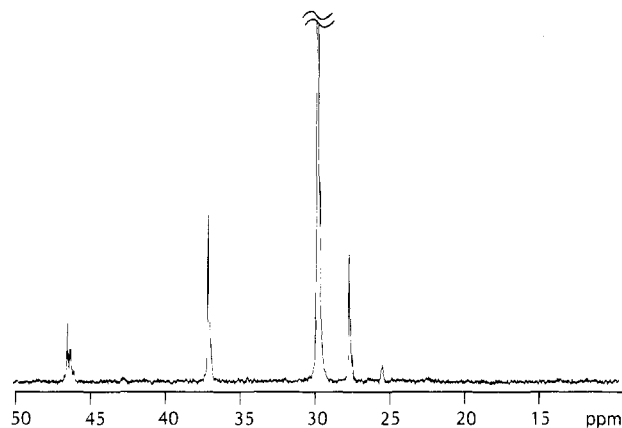
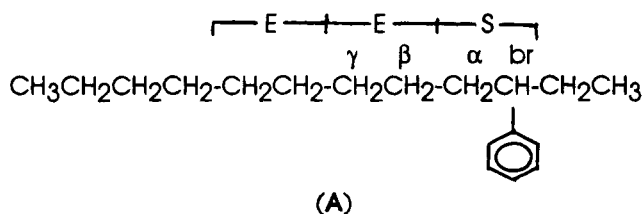
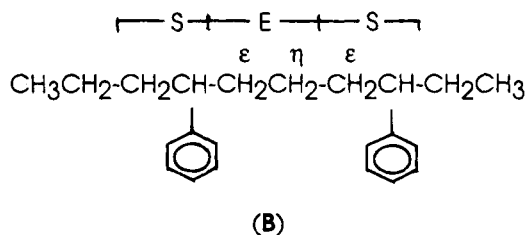


Figure 2.  $^{13}\text{C}$  NMR spectrum of poly(ethylene-co-styrene).

chain. To understand these shifts, consider 3-phenyl-dodecane (**A**) as a model compound. As shown, this



compound is a reasonable model for a styrene unit adjacent to two ethylene ones. Literature  $^{13}\text{C}$  NMR shifts<sup>11</sup> for **A** are as follows: br = 48 ppm,  $\alpha$  = 37 ppm,  $\beta$  = 28 ppm, and  $\gamma$  = 30 ppm. Note that, within an error of  $\pm 1$  ppm, these are the same shifts observed in Figure 2. In addition to these, a small peak at 26 ppm is also observed. Based on simple chemical shift additivity arguments, we believe that this peak is the result of a styrene-ethylene-styrene arrangement in which the styrene units are arranged, relative to one another, in a "head-to-tail" configuration. In such a structure (**B**), it



is reasonable to expect the  $\eta$  carbon to appear at 26 ppm

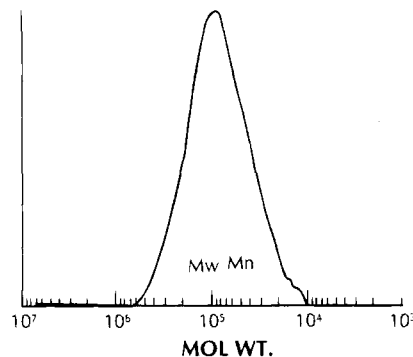


Figure 3. SEC trace of poly(ethylene-co-styrene).

and the  $\epsilon$  carbons to appear at 37 ppm, overlapping with the  $\alpha$  carbons assigned earlier. Integration of the spectrum given in Figure 2 indicates that the copolymer contains 10 mol % styrene incorporation.

The SEC chromatogram of the poly(ethylene-co-styrene) reaction product is shown in Figure 3. The narrow molecular weight distribution is indicative of polymers synthesized by single-site catalysts.

Work is currently underway to synthesize and characterize a series of ethylene-styrene copolymers over a range of monomer compositions. Such samples are permitting us to fully understand the microstructure, insertion behavior, and melting behavior of these copolymers. This work will be reported in the near future.

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