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Syndiotactic Polymerization of Styrene: Mode of Addition to the Double Bond

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ABSTRACT: By ^{1}H NMR analysis of a syndiotactic copolymer of perdeuteriostyrene with *cis*-styrene-*β*-*d*, it is observed that the mode of addition of the growing chain end to the double bond of the monomer is cis.

Introduction

Syndiotactic polymerization of styrene in the presence of catalytic systems consisting of hydrocarbon-soluble compounds of titanium or zirconium, such as tetrabenzyltitanium and tetrabenzylzirconium, and methylaluminoxane has been reported in previous papers.[1-3] In these papers it has been also reported that the statistical model of the stereospecific propagation is Bernoullian[1] and that the insertion of the monomer into the reactive metal–carbon (or even metal–hydrogen, in the initiation step) bonds is secondary,[2,3] e.g.,

$$\text{Mt–P} + \text{C}_8\text{H}_8 \rightarrow \text{MtCH(C}_6\text{H}_5\text{)CH}_2\text{–P}$$

where Mt = metal of the catalytic complexes and P = growing polymer chain.

In order to complement the basic information concerning the stereochemical reaction mechanism we report in this paper the mode of addition of the growing chain end to the double bond of the monomer.

Results and Discussion

A syndiotactic polymer can be described as a sequence of mirror-related syndiotactic dyads. According to the literature,[7] the allowed conformations of a syndiotactic dyad, in solution, are those shown in Figure 1. The population of the TT conformer P_{TT}[8] is larger than that of the GG conformer P_{GG} ($P_{\text{TT}} + P_{\text{GG}} = 1$). By considering the Karplus function describing the magnitude of the vicinal proton–proton coupling constant J as a function of the dihedral angle in the H–C–C–H bond system[9] and the averaging of the J's arising from fast equilibration with each other of the conformers of Figure 1,[10] one could anticipate that the coupling constants between the methylene and the methine protons of syndiotactic polystyrene would be

$$\bar{J}_{12} = \bar{J}_{34} = P_{\text{TT}}J_{\text{t}} + P_{\text{GG}}J_{\text{g}}$$

$$\bar{J}_{13} = \bar{J}_{24} = P_{\text{TT}}J_{\text{g}} + P_{\text{GG}}J_{\text{t}}$$

where $\bar{J}_{ij}$ is the coupling constant between vicinal protons i, j averaged for the interconversion of the two conformers, P_{TT} and P_{GG} are the populations of the two conformers, and J_{g} and J_{t} are the coupling constants of the H–C–C–H bond system for H–C–C–H dihedral angles of 60° and 180°, respectively.

As discussed in a previous paper concerning syndiotactic polypropylene[11] $P_{\text{TT}}J_{\text{t}} + P_{\text{GG}}J_{\text{g}}$ and $P_{\text{TT}}J_{\text{g}} + P_{\text{GG}}J_{\text{t}}$ cannot be determined simply from the ^{1}H NMR spectrum of syndiotactic polymers because the resonance of the chemically equivalent methylene protons (Figure 2A), coupled to each other, is a deceptive triplet. These coupling constants[11] can be determined from the ^{1}H NMR spectrum of syndiotactic polystyrene-*β*-*d* reported in Figure 2B. In this case the resonance of the methylene protons is a doublet of doublets and the larger spacing (9.$_0$ Hz) corresponds to $P_{\text{TT}}J_{\text{t}} + P_{\text{GG}}J_{\text{g}}$ while the smaller spacing (5.$_4$ Hz) corresponds to $P_{\text{TT}}J_{\text{g}} + P_{\text{GG}}J_{\text{t}}$. The resonance of the methine protons is less resolved because of the coupling with two vicinal deuteriums, which broadens the components of the resonance. The assignments

$$P_{\text{TT}}J_{\text{t}} + P_{\text{GG}}J_{\text{g}} = \bar{J}_{12} = \bar{J}_{34} = 9._0 \text{ Hz}$$

$$P_{\text{TT}}J_{\text{g}} + P_{\text{GG}}J_{\text{t}} = \bar{J}_{13} = \bar{J}_{24} = 5._4 \text{ Hz}$$

are a consequence of the fact, previously mentioned, that $P_{\text{TT}} > P_{\text{gg}}$ and that, according to the Karplus equation, $J_{\text{t}} > J_{\text{g}}$. When a small amount of, e.g., styrene-*β*-*d* is copolymerized with a large amount of perdeuteriostyrene, most of the *β*-*d* units will be flanked by perdeuterio units. As a consequence, most of the methylene protons will be coupled with only one methine proton (e.g., H^1) and the spectrum of the aliphatic protons will consist of two doublets. The spacing between the components of the doublet will be either $P_{\text{TT}}J_{\text{t}} + P_{\text{GG}}J_{\text{g}} = \bar{J}_{12} = 9._0$ Hz or $P_{\text{TT}}J_{\text{g}} + P_{\text{GG}}J_{\text{t}} = \bar{J}_{13} = 5._4$ Hz, depending on the structure (cis or trans) of the styrene-*β*-*d* and the mode of addition (cis or trans) of the growing chain end to the double bond of the monomer.

One can easily visualize by ball-and-stick models that cis addition to the double bond of the trans monomer and trans addition to the double bond of the cis monomer will lead to the syndiotactic dyad shown in a TT conformation in Figure 3a, while trans addition to the trans monomer and cis addition to the cis monomer will lead to the syndiotactic dyad shown in Figure 3b.

The ^{1}H NMR spectrum of the syndiotactic copolymer of cis styrene-*β*-*d* (15% mole fraction) with perdeuteriostyrene (85% mole fraction) is reported in Figure 2C. The resonance of the aliphatic protons consists of two doublets at 1.23 (methylene) and 1.75 ppm (methine). The spacing between the components of the doublets is 9.$_0$ Hz. The spacing corresponds to $\bar{J}_{12}$ thus showing that the methylene and the methine protons are arranged as in Figure 3b. As just discussed, this shows that the actual mode of addition

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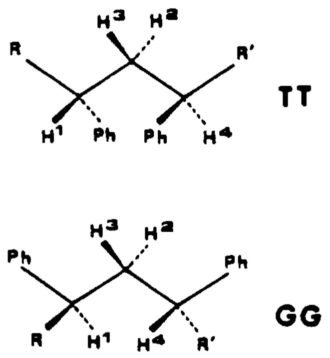

Figure 1. Allowed conformations of a syndiotactic dyad. The labeling TT and GG of the two conformers comes from the internal rotation angles of the bond systems R–C(H^1Ph)–C(H^2H^3)–C(H^4Ph) and C(H^1Ph)–C(H^2H^3)–C(H^4Ph)–R′ which are 180° in the TT and 60° in the GG conformer. (The allowed conformers of the mirror related syndiotactic dyad are TT (180°) and GG (–60°).) The hydrogens are labeled consistently with this figure throughout the paper.

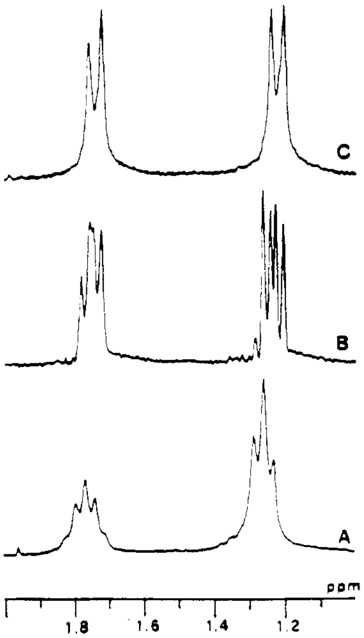

Figure 2. ^{1}H NMR spectra in tetrachloroethane-*1,2*-d_2 solution at 120 °C of (A) highly syndiotactic polystyrene ($\nu_1 = \nu_4 = 1.77$ ppm; $\nu_2 = \nu_3 = 1.26$ ppm); (B) the syndiotactic polymer of *cis*-styrene-*β*-*d*. This spectrum was processed with a line broadening of –1 Hz and GB = 0.35 for resolution enhancement ($\nu_1 = \nu_4 =$ 1.75 ppm; $\nu_2 = \nu_3 = 1.23$ ppm; $J_{12} = J_{34} = 9._0$ Hz; $J_{24} = J_{13} = 5._4$ Hz); and (C) the syndiotactic copolymer of perdeuteriostyrene (85% mole fraction) with *cis*-styrene-*β*-*d* (15% mole fraction) ($\nu_1 = \nu_4 = 1.75$ ppm; $\nu_2 = \nu_3 = 1.23$ ppm; $J_{12} = J_{34} = 9._0$ Hz). HMDS scale.

of the growing chain end to the double bond of the monomer is cis.

Experimental Section

Perdeuteriostyrene was purchased from Aldrich Chemie (isotopic purity 98%). Tetrabenzyltitanium and *cis*-styrene-*β*-*d* were prepared as reported in the literature.[4,5] Methylaluminoxane was prepared according ref 6 and by removing the unreacted $Al(CH_3)_3$ in vacuo. Polymerization of styrene, *cis*-styrene-*β*-*d*, and copolymerization of perdeuteriostyrene (85% mole fraction) with *cis*-styrene-*β*-*d* (15% mol fraction) were performed at 50 °C under a nitrogen atmosphere by using 5 mL of toluene, 0.200 g of methylaluminoxane, 2.5×10^{-5} mol of tetrabenzyltitanium, 4.5 g of monomer for 20 h. The yield was 0.9 g.

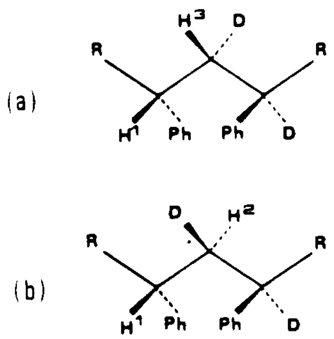

Figure 3. TT conformations of syndiotactic dyads expected from (a) cis addition to the double bond of the trans monomer or trans addition to the double bond of the cis monomer and (b) trans addition to the double bond of the trans monomer or cis addition to the double bond of the cis monomer.

Polymerizations were stopped by pouring the reaction mixture into acidified methanol and the polymers were washed with fresh methanol and dried in vacuo at 80 °C.

^{1}H NMR spectra of the samples dissolved at 120 °C in tetrachloroethane-*1,2*-d_2 in the presence of hexamethyldisiloxane (HMDS) as internal standard were recorded by using an AM 250 Bruker Spectrometer.

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Registry No. *cis*-*β*-Deuteriostyrene, 21370-59-2; perdeuteriostyrene, 19361-62-7; (perdeuteriostyrene)(syndiotactic *cis*-*β*-deuteriostyrene) (copolymer), 110851-45-1.

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