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# Synthesis of isotactic polystyrene in hydrocarbons by initiation with *t*-BuLi in the presence of sodium dodecylbenzenesulfonate

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## ABSTRACT

Isotactic rich polystyrene was synthesized at 30 °C by the *t*-BuLi initiated polymerization in the presence of sodium dodecylbenzenesulfonate (SDBS) in hexane or cyclohexane. The polymerization rates at 30 °C were very fast and typically gave quantitative conversions. At SDBS/*t*-BuLi molar ratios between 0.5 and 1.0, the unfractionated polystyrene had almost the same stereoregularity, with triad and pentad contents of about 45% and 19%, respectively. The polymers could be fractionated into a more isotactic PS ($mm = 0.77$) and other fractions with lower isotactic content. The influence on the stereochemistry of lithium and potassium dodecylbenzenesulfonates or other sulfonate derivatives, reaction temperature and solvent have also been investigated. Density functional theory (DFT) was used to simulate the reactive sites using 1-lithio-1,3-diphenylbutane and 4-methylbenzenesulfonate (SBS) were used as simplified models of polystyryllithium and SDBS respectively. DFT calculation results indicated that unlike the simpler LDPB model and LDPB-styrene complexes, the *pro-m*-SBS-LDPB-styrene complexes were the preferred stereochemical configuration consistent with the formation of long isotactic pentad sequences.

## 1. Introduction

The stereochemistry of polystyrene (PS) continues to be a topic of interest because of the high crystallinity, high melting points and superior mechanical properties of both isotactic and syndiotactic PS. Compared with Ziegler–Natta [1] and metallocene [2] catalyzed polymerizations the degree of stereocontrol in the anionic polymerization of styrene has been relatively modest [3]. However, there are potential advantages including relatively narrow MW distributions and the potential for the synthesis of block copolymers.

Several groups have reported on the formation of isotactic PS through anionic polymerization [4–10]. For instance, Kern found that PS having some isotactic content is obtained through the *n*-butyllithium-initiated (BuLi) anionic polymerization in hydrocarbons at −30 °C [4]. Braun et al. suggested that association of organolithium complexes was responsible for the observed tacticity in heptane and other hydrocarbons [5]. On the other hand, Worsfold and Bywater [6] reported that these experiments could not be reproduced but found that the presence of water significantly increased the PS isotactic content indicating that the results by Kern were most plausibly due to the presence of LiOH formed by adventitious water (see below). Cazzaniga and Cohen [7] reproducibly prepared fractions of highly isotactic polystyrene (iPS) along with stereoirregular PS at −30 °C using *n*-BuLi/lithium *tert*-butoxide (*t*-BuOLi) complexes. They also synthesized semi-crystalline ABA type isotactic PS-polybutadiene triblock copolymers [8]. The ratio of isotactic polystyrene to polybutadiene (wt% iPS $\geq$ 66%) in these copolymers resulted in various microphase-separated morphologies at a scale typical of diblock copolymers. Makino et al. [9] have demonstrated the synthesis of highly iPS (triad and pentad contents of 95% and 90% respectively at −60 °C) and uncontaminated with significant quantities of stereoirregular PS, by initiation with 3,3-dimethyl-1,1-diphenyl-1-lithiobutane (DMPBL) in the presence of equimolar LiOH in hexane, at temperatures between −30 and −60 °C. Initiation of styrene with polyisoprenyllithium (PILi) gave the PI-b-iPS AB block copolymers. Hence as pointed out above, the earlier results by Kern and Braun are probably due to partial conversion of BuLi into *n*-LiOH that was shown to mediate isotactic styrene polymerization as also shown in Ref. [6].

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Also, Deffieux and coworkers [10,11] have reported the synthesis of isotactic PS in the presence of superbase $R_2Mg/ROM$ (M = Li, Na, K) initiators. The highest isotactic (as triad content (85%)) was obtained in methylcyclohexane at −40 °C at low (5%) monomer conversions. Higher conversions (91%) but lower isotactic contents ($mm = 0.65$) were obtained at 20 °C but relatively low fractions of *mmmm* pentads were reported.

In the following we report that the *t*-BuLi initiated polymerization of styrene in hexane or cyclohexane at ambient temperatures or above in the presence of one equivalent or less of sodium dodecylbenzenesulfonate gives isotactic rich polystyrene. The polymerizations differ in that they tend to give blends of highly isotactic PS along with less stereoregular but still predominantly isotactic PS. We show that this polymerization occurs with reaction rates that are much faster than that of the *t*-BuLi initiated polymerization in the absence of SDBS indicating that the polymerizations occur through PSLi-SDBS complexes. They are also much faster compared with the LiOH mediated polymerizations [9]. We also present a rationale of the observed stereochemistry based on DFT calculations.

## 2. Experimental

### 2.1. Materials

*t*-Butyllithium ((1.5 M) in pentane, ACROS), was purified by sublimation *in vacuo* and then diluted with dry hexane. Potassium hydroxide was used as received. Styrene (≥99% from ALDRICH) was dried overnight on the vacuum line over $CaH_2$. The freeze-thaw procedure was repeated three times. Then it was distilled into ampoules equipped with break-seals. Just prior to polymerization it was distilled once again into the reaction flask. Hexane, cyclohexane and toluene were purified by distillation from Na–K alloy and then vacuum distilled before use. Sodium octylbenzenesulfonate (SOBS, 97% Aldrich), sodium dodecyl sulfate (SDS, >97%, GC, Fluka) sodium eicosyl sulfonate (SES, from ALDRICH) and sodium dodecylbenzenesulfonate (SDBS, technical grade Aldrich) were dried overnight on the vacuum line at room temperature and were stored in ampoules equipped with break-seals. Lithium dodecylbenzenesulfonate (LDBS) was prepared by the reaction of dodecylbenzenesulfonic acid with *t*-BuLi in hexane and used directly. Potassium dodecylbenzenesulfonate (KDBS) was formed by reacting dodecylbenzenesulfonic acid with excess potassium hydroxide in THF at room temperature followed by solvent evaporation under vacuum. Then the product was recrystallized three times from a methanol/THF mixture (90/10,V/V) at −20 °C. Dodecylbenzenesulfonic acid (70 wt% in 2-propanol, Aldrich) was evacuated overnight on the vacuum line. Methanol was used as received.

### 2.2. Polymerization

All polymerization reactions were carried out under high vacuum conditions ($10^{-6}$ Torr) using breakseal techniques. Hexane (20 mL) was first vacuum distilled bulb to bulb into the polymerization round bottom flask. SDBS (0.07 g) was then introduced into the polymerization flask by breaking the break-seal of its ampoule. The remaining SDBS was washed off the ampoule wall by condensing hexane into the ampoule. Then 2 mL of *t*-BuLi (0.1 M in hexane) solution was added at once. Traces of initiator left at the wall of the ampoule were also washed into the flask using condensation of hexane vapor. The solution was stirred for 24 h at 30 °C in order to optimize mixing. Styrene was then added one time to the flask by breaking the break-seal. As the reaction progressed (about 0.5–30 min), PS precipitated as a *white solid*. After 24 h the reaction was terminated and precipitated in excess methanol. A methyl ethyl ketone (MEK) soluble PS fraction was obtained through a Soxhlet extraction with boiling MEK for 24 h. The MEK soluble PS fractions were subjected to further fractionation by cooling the MEK solution to 25 °C and isolation of the MEK soluble and insoluble PS. The MEK insoluble fractions were obtained separately. All samples were dried at 70 °C in vacuum oven for 6 h before analysis.

### 2.3. Characterization

Size exclusion chromatography (SEC) measurements were carried out using a Shimadzu Prominence LC-20AT solvent delivery unit equipped with guard and Polymer Laboratories PLgel 5 μm MIXED-C column × 2, Shimadzu refractive index detector RID-10A, Wyatt light scattering detector Dawn DSP and Waters 484 UV detector. Calibration was based on PS standards. The concentrations of the injected PS samples ranged from 0.05 to 0.5% (w/v). The $^{13}C$ NMR spectra of the PS samples dissolved in $CDCl_3$ (3–5% w/v) were obtained using a Varian Mercury 400 FT-NMR at 25 °C, using a 1 s pulse delay with at least 10,000 to 42,000 scans. Calculation of tacticity [12] (triads and pentads levels) was carried out by integrating of the aromatic quaternary carbon *mm*, *mr* and *rr* triads between 146.40 and 145.90 ppm, 145.90–145.40 ppm; and 145.20–144.90 ppm respectively. The *mmmm* pentad occurred between 146.40 and 146.20 ppm.

### 2.4. DFT calculations

Density functional theory (DFT) calculations were performed using a B3LYP hybrid functional. All geometries were optimized using the basis set of 6-31G(d) and confirmed as minima without imaginary frequencies by vibrational frequency computations. The energies were evaluated with the basis set of 6-311+G(d,p). This inexpensive calculation has been successfully applied in evaluating previous mechanism studies [13,14]. Calculations were performed using the Gaussian 03 program [15]. In order to calculate the geometries and energies in cyclohexane solution, the polarized continuum model (PCM) was applied.

## 3. Results

As indicated above, lithium hydroxide or alkoxides have been reported as additives that mediate the formation of isotactic polystyrene (iPS) by the *t*-butyllithium (*t*-BuLi) initiated anionic polymerization along with equimolar concentrations of LiOH ([LiOH]/[*t*-BuLi] = 1.0) [7–11]. Anionic surfactants having $-SO_3M$ or $-OSO_3M$ group (M = alkali metal) have been used as additives in anionic polymerization to prepare styrene-butadiene (isoprene) random copolymers at higher temperatures [16,17]. These compounds proved capable of controlling the microstructure of polybutadiene (e.g. vinyl content) and improving the randomness of copolymers. However, thus far their effect on the stereochemistry of anionic styrene polymerization was not investigated.

Here we report an investigation on the effect(s) of sodium dodecylbenzenesulfonate (SDBS) on the microstructure of polystyrene initiated by *t*-BuLi in hexane and cyclohexane. Polymerizations were carried out by addition of styrene to various SDBS/*t*-BuLi compositions in hexane at 30 °C. The phenylcarbon-13 NMR spectra of a typical sample obtained in the presence of one equivalent of SDBS (Table-1 , #3) and its fractions as described above are shown in Fig. 1. As seen from Table 1, the existence of SDBS exerted a great influence on the PS microstructure. In the absence of SDBS (Table 1, #1) the PS microstructure was predominantly