Anionic Synthesis of Highly Isotactic Polystyrene in Hexane in the Presence of Lithium Hydroxides

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Introduction. Ziegler–Natta catalyzed vinyl polymerizations are known to produce stereoregular polymers such as isotactic polypropylene or isotactic polystyrene.[1,2] An early anionic type polymerization giving fractions of crystallizable polystyrene using Alfin initiators was reported by Williams et al.[3]

Alkyllithium-initiated polymerizations of styrene in hydrocarbon solvents, capable of producing crystallizable polystyrene but of unknown stereochemical composition, were reported by Kern and Braun et al.[4] As shown by Worsfold and Bywater, these polymerizations produce variable amounts of isotactic PS and require the presence of small amounts of water.[5] Likewise, Kawamura et al. using ^{13}C NMR spectrometry of the quaternary aromatic carbon[6] showed that, under similar conditions, PS was obtained with an overall isotactic triad content of about 40% or less.[7]

Here we show the synthesis of highly isotactic PS, uncontaminated with significant quantities of atactic PS, by initiation with *t*-BuLi-, 3,3-dimethyl-1,1-diphenyl-1-lithiobutane (DMPBL), or polyisoprenyllithium (PILi) in hexane, at or below −30 °C, in the presence of LiOH.

Because alkyllithiums typically contain lithium alkoxide or other impurities that may have complicated these polymerizations,[8] we decided to investigate the use of *t*-BuLi that was purified by repeated sublimation under high vacuum. In the presence of this initiator, the polymerization of styrene in hexane at −30 °C was homogeneous and produced atactic/syndiotactic PS with a low isotactic content (mm = 11%). In agreement with a report by Cazzaniga and Cohen,[9] in the presence of *t*-BuOLi (1–2 mol equiv with respect to initiator), we obtained a polystyrene with a modestly increased isotactic triad content (Table 1).[10] The ^{13}C spectrum of the unfractionated polymer essentially is a superposition of a highly isotactic PS with a resonance at 146.70 ppm and an atactic/syndiotactic PS that closely resembles the spectrum of the PS formed in the absence of the alkoxide. The overall isotactic triad content is only about 25% (Table 1). Dissolution in THF followed by precipitation in methyl ethyl ketone (MEK) allowed separation into a MEK-insoluble wide MW distribution isotactic fraction (mm = about 80%) and a larger narrower distribution atactic/syndiotactic fraction. As also pointed out by Worsfold and Bywater, the formation of both isotactic and atactic/syndiotactic fractions indicates the presence of at least two propagating centers that slowly interconvert on the polymerization time scale.[5]

Under the same conditions but in the presence of lithium 2-adamantoxide (AdamOLi), the carbon spectrum was similar except that the amount of highly isotactic polymer was approximately doubled and the isotactic pentad content was much higher (Table 1,
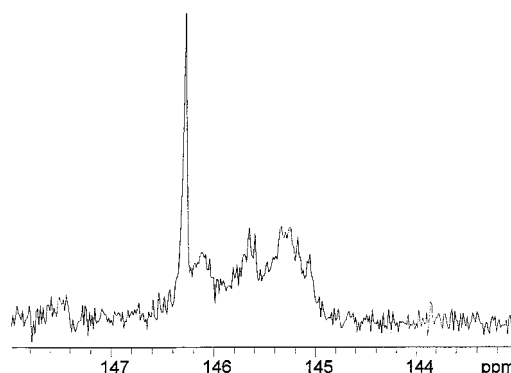

Figure 1. Carbon-13 NMR spectrum of the quaternary carbon of unfractionated polystyrene synthesized in hexane at −30 °C in the presence of lithium 2-adamantoxide.

Figure 1).[10] The lithium alkoxide-mediated polymerizations appeared to be quite slow with yields of 22% less in 48 h and appeared at least partially heterogeneous with some precipitation occurring as the polymerization progressed.

Initiation of styrene by *t*-BuLi in hexane, in or without the presence of lithium alkoxides, generally is incomplete (initiator efficiency is only 10–30%). Because the presence of residual *t*-BuLi may have slowed the polymerizations or affected the polymerization stereochemistry,[8] we carried out a number of polymerizations initiated by 3,3-dimethyl-1,1-diphenyl-1-lithiobutane (DMPBL) formed quantitatively by addition of *t*-BuLi to a slight excess of 1,1-diphenylethylene.[11,12] Styrene initiation by DMPBL is faster than by *t*-BuLi, as judged by the more rapid change in color upon addition of styrene, and the higher polymerization yields. However, the polymerization stereochemistry, in and without the presence of lithium alkoxides, is the same as that of the above *t*-BuLi-initiated polymerizations. In toluene at −30 °C in the presence of *t*-BuOLi or AdamOLi only atactic polymer was produced (Table 1).

Lithium Hydroxide-Mediated Polymerizations. The *t*-BuLi-initiated polymerization of styrene in the presence of carefully controlled amounts of water yielded polystyrenes with a much higher overall isotactic content of the *unfractionated* PS (Table 1). The amounts of water were controlled by addition of known volumes of rigorously dried hexane that was subsequently saturated with distilled water. The isotactic triad content increased with increasing amounts of LiOH until a mm content of at least 70% was reached at a LiOH/initiator molar ratio of one, beyond which there was essentially no change (Table 1, entries 13, 14, 16, 17). This is consistent with the involvement of a 1:1 PSLi–LiOH complex. As in the case of the lithium alkoxides as additives, the initiation and polymerization rates were significantly slower than in the absence of any additives, and the polymerizations were heterogeneous. Thus, the yields of isotactic PS were low, but this is improved by longer reaction times. Higher temperatures also improve the yields, but this comes at the expense of a much lower isotactic content.[13]

Precipitation in MEK yielded a very highly isotactic (mm > 90%, mmmm > 80%) PS fraction along with MEK soluble fractions of atactic PS of lower MW and narrower distribution. Wide MW distributions (1.4 <

Table 1. Polymerization of Styrene Initiated by *t*-BuLi, DPBDML, and PILi as Initiators in Hexane at −30 °C in the Presence of Lithium Hydroxide[a]

run	initiator/ROLi[e]	[LiOR]/[InLi]	M_n^b (SEC)	MWD[b]	yield[c] (%)	mm[d] (%)	mmmm[d] (%)
1	*t*-BuLi		3400	1.30	45	11	0
2	*t*-BuLi/*t*-BuOLi	2.0	2400	1.70	10	23	5
3	*t*-BuLi/*t*-BuOLi	2.0	9600	1.80	6	25	7
4	*t*-BuLi/AdmOLi	2.2	10800	2.30	14	43	26
6	DMPBL/*t*-BuOLi	1.5	11000	1.80	22	21	5
9	DMPBL/*t*-BuOLi(g)	1.7	9400	1.15	58	14	0
11	DMPBL/AdmOLi(g)	1.3	2200	1.26	78	10	0
13	DMPBL/LiOH	0.3	21000	2.20	15	24	5
14	DMPBL/LiOH	0.6	33500	2.10	10	55	41
16	DMPBL/LiOH	0.9	25200	5.50	05	65	60
17	DMPBL/LiOH	1.2	18300	7.90	08	72	65
19	*t*-BuLi/LiOH(g)	1.5	12100	1.25	60	14	0
25	PILi[f]		6300	1.20	25	10	0
35	PILi[f]	1.4	12400	6.20	12	90	82
36	PILi[f,h]	1.2	15600	7.4	15	95	90

[a] Initiator concentration 0.01−0.07 M, [styrene] = 1.0 M.; reaction time is 48 h. [b] SEC data, calibration using PS standards. [c] Polymer yield determined gravimetrically; precipitation in methanol. [d] Determined by ^{13}C NMR of quaternary carbon in CDCl^{13} at room temperature. [e] For the case of DPMLi *t*-BuLi was reacted with a slight excess of DPE prior to monomer addition. [f] Polyisoprenyllithium prepared by addition of isoprene to *t*-BuLi in hexane at 30 °C. M_n = 9800. [g] In toluene at −30 °C. [h] At −60 °C.

D < 7.4) were obtained that broadened as the LiOH/initiator ratio increased (Table 1).

Polymerizations under the above conditions but in the presence of LiOH prepared by the reaction of *t*-BuLi with water and subsequently dried and added as a solid had no effect on the stereochemistry. Apparently, the in-situ formation of LiOH and the subsequent formation of PSLi−LiOH complexes are essential in the stereocontrol. Also in the presence of LiOH but with less carefully purified *t*-BuLi, the PS stereoregularity was much lower, and this may be due to the presence of lithium alkoxide or other impurities in the initiators that may form PSLi−ROLi complexes and that, as reported earlier, are less effective in stereoregulation.[8] Interestingly, polymerizations carried out in toluene under otherwise identical conditions in the presence of either lithium alkoxides or hydroxides produced only atactic/syndiotactic PS that was indistinguishable from the PS produced in the absence of additives.

Given the insolubility of isotactic PS in hexane at −30 °C, the occurrence of heterogeneous polymerizations is not surprising. Thus, the isotactic PS may have been formed under homogeneous conditions. We reasoned that initiation of styrene by a carbonlithium species attached to a long hexane-soluble polymer could allow some or all of the styrene propagation process to occur under homogeneous conditions. Such a species could be readily generated by the *t*-BuLi-initiated polymerization of isoprene that is known to produce a narrow distribution hexane-soluble *cis*-1,4-polyisoprenyllithium (PILi) that, in turn, can initiate styrene.[14] As initiation is quantitative in this case, the subsequent polymerization of styrene is not complicated by the presence of residual *t*-BuLi.

The *t*-BuLi-initiated polymerization of isoprene in hexane, after cooling to −30 °C and addition of styrene, produced a narrow distribution PI−PS block copolymer containing an atactic/syndiotatctic PS block (Table 1). In the presence of equimolar LiOH, generated through the addition of approximately $^1/_2$ equiv of water to the living PILi, the polymerization of styrene in hexane at −30 °C was homogeneous initially but later developed an opalescence that appeared to be due to the formation of an emulsion rather than a precipitate. NMR analysis of the *unfractionated* wide MW distribution polymer showed the presence of highly isotactic PS block with
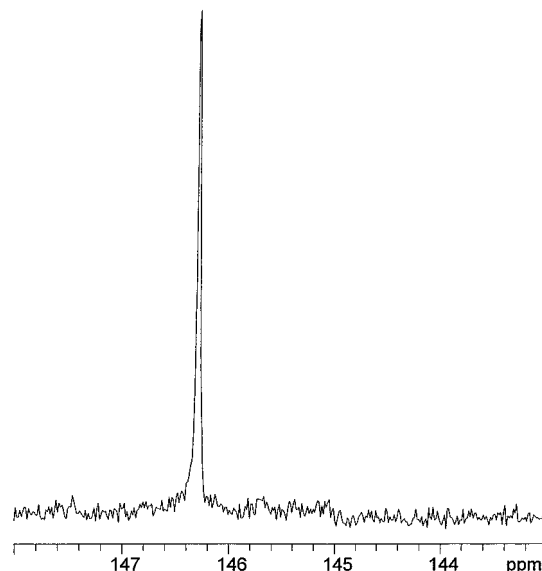

Figure 2. Carbon-13 NMR spectrum of the quaternary carbon of a polystyrene−polyisoprene block copolymer synthesized in hexane at −60 °C in the presence of lithium hydroxide.

triad and pentad contents of 90% and 82%, respectively (Table 1).[15] This result would appear to be consistent with stereocontrol occurring under homogeneous conditions as a precipitated phase-dependent mechanism would lead to a lower rather than a higher isotactic content in this case. Increasing the LiOH/initiator molar ratio beyond one did not affect the stereochemistry. At −60 °C under the above conditions the triad and pentad contents of the unfractionated polymer were even higher, increasing to values in excess of 95% and 90%, respectively, and the ^{13}C NMR C1 spectrum was virtually identical to that of a highly isotactic PS sample prepared by a Ziegler type catalyst and fractionated subsequently (Figure 2).[16]

The PSLi chains under our conditions remain capable of further reaction as shown by the polymerization of residual styrene upon addition of THF to the polymerization solution and by the rapid disappearance of the yellow color of the PSLi upon addition of water, alcohols, or carbon dioxide. Thus, the synthesis of end-functionalized isotactic PS would appear to be possible.

Discussion. Bywater and co-workers have shown that the polymerization of styrene in benzene is one-

half order in polystyryllithium, and they concluded that propagation occurs through undissociated PSLi that is in equilibrium with a less reactive PSLi dimer.[17] In the presence of 1:1 PSLi/ROLi complexes the polymerization still is found to be one-half order in chain ends. Given the very small size of the LiOH stereocontrol is surprising, and it is possible that dimeric or larger clusters consisting of several PSLi−LiOH complexes are involved in stereoregulation. The formation of isotactic PS in the presence of highly hindered lithium alkoxides such as AdamOLi hints at steric factors in the stereocontrol mechanism. For instance, isotactic poly(2-vinylpyridine) (P2VP) was shown to form in toluene at −78 °C in the presence of hindered alkoxides such as *t*-BuOLi or AdamOLi but not in the presence of primary or secondary alkoxides. The absence of stereoregulation under our conditions in the presence of toluene hints at coordination of one of the chain-end Li ions with penultimate or prior phenyl groups of the chain and/or with the styrene. Coordination of alkali ions by aromatic molecules has been described.[18] At this time detailed interpretations would seem to be premature. Further experiments on similar polymerization systems that are soluble are being planned.

The synthesis of isotactic polystyrene without the presence of significant quantities of atactic PS or of isotactic polystyrene−polyisoprene block copolymers may be of interest in the synthesis of end-functionalized isotactic PS or isotactic PS−PI and similar block copolymers. We are continuing to investigate the mechanism of these interesting polymerizations.

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