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Stereoregulation in the anionic polymerization of styrene initiated by superbases

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Abstract

Polystyrenes with different stereoregularities were obtained by initiation of the styrene anionic polymerization via alkyllithium/alkali metal alkoxide systems in hydrocarbon media. Depending on the nature of the metal alkoxide associated to alkyl lithium and more particularly of the alkali metal counter-ion (lithium, sodium, potassium), the synthesis of polystyrene exhibiting predominantly isotactic or syndiotactic triads was achieved. The use of soluble metal alkoxide improves the stereospecificity as well as the initiation efficiency with respect to initial alkyl lithium. The contribution of propagating active species yielding a single type of polymer chains with stereochemical irregularities is supported by the solubility characteristics of the isotactic and syndiotactic rich polystyrenes. A reaction mechanism involving the formation of bimetallic complexes between the alkyllithium and the alkali metal alkoxide and ligand–metal exchanges is discussed.

Keywords: Stereoregulation; Superbases; Polystyrene

1. Introduction

The control of chain stereoregularity during polymerization is of great interest as it may result in polymeric materials with new thermomechanical properties. Since the discovery in 1955 by Natta of the first stereoregular polymer [1] important breakthroughs have been achieved in stereospecific polymerization. Although isospecific Ziegler–Natta catalysts allowing the preparation of isotactic polystyrene [2] have been developed a long time ago, this is much more recently that hemi-metallocene transition metal derivatives have been described for the preparation of highly syndiotactic polystyrene [3].

The use of alkali metal anionic initiator in order to combine the stereospecific and living characters of the polymerization of styrene monomers has been very scarcely investigated and remains only partly successful. The preparation of partially stereoregular polystyrene exhibiting some cristallisable fraction was first achieved using sodium [4–6] and alfin-type [7–9] catalysts. Another important route is based on the addition of lithium hydroxide [9–17] or lithium alkoxides [16–18] to conventional alkyllithium initiators in hydrocarbons: depending on the additive, the preparation of a highly isotactic polystyrene fraction, generally in admixture with an atactic one, was obtained in more or less important proportions. The presence of atactic chains, indicative of the presence of several types of active species, and the very low polymerization rates remain important drawbacks of these anionic systems.

The polymerization of vinyl monomers and dienes by ‘superbases’ constituted by the association of an alkyllithium and an alkali metal alkoxide, also called Lochmann bases [19–24], has been investigated a long time ago [25–27]. As compared to alkyllithium initiators alone, the styrene polymerization rate was observed to decrease when lithium was used as counter-ion for the alkoxide, whereas an activation was observed with Na, K, Cs and Rb alkoxides. Activation is believed to proceed through transmetallation reactions in the mixed alkyllithium–alkali metal alkoxide complexes [28]. Although the tacticities of polystyrene prepared with superbases was not investigated, studies concerning the polymerization of 1,3 dienes have shown that polydiene microstructures are strongly influenced by the nature of the alkoxide cation [29].

In this article we report a study of the stereoregulating aspects of anionic styrene polymerization in hydrocarbon

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media in presence of various alkali metal alkoxides and *sec*-butyllithium as superbases. The influence of their structure and solubility characteristics, the ratio [ROMt]/[*sec*-BuLi] as well as the effect of polymerization temperature on the polystyrene tacticity and characteristics are investigated.

2. Experimental

2.1. Materials

sec-Butyllithium (1.3 M in cyclohexane from SAFC, France), lithium *tert*-butoxide (1.0 M in hexane from SAFC), sodium *tert*-butoxide (powder 97% from SAFC) and potassium *tert*-butoxide (powder 95% from SAFC) were used as received. 2-Ethyl-hexyl sodium was prepared by reacting 2-ethyl-hexyl chloride with dispersed sodium (10 equiv.) in dry cyclohexane at 20 °C for 1 h and the solution of 2-ethyl-hexylsodium was recovered by filtration on a glass filter and stored under vacuum at low temperature. Diphenylmethylpotassium (ϕ_2CHK) was prepared by reacting first naphthalene and potassium metal in dry THF followed by addition of distilled diphenylmethane. After seven days at 20 °C, the red/orange solution was filtered, and THF was distilled off and the derivative was dried under high vacuum for several hours. It was then washed with cyclohexane and freeze-dried before use. Lithium, sodium and potassium 2-methyl-2-butoxide (*tert*-amyloxide, *tert*-amylOMt) were prepared by reaction of 2-methyl-2-butanol with small pieces of the corresponding alkali metal in dry cyclohexane at 80 °C for 2 days. The alkoxide solutions were kept under argon at room temperature over an excess of the metal. Potassium 3,7-dimethyl 3-octanoxide ($C_{10}H_{21}OK$) was synthesized by the same procedure. Cyclohexane and methylcyclohexane (both 99.5% from SAFC) were degassed over freshly crushed CaH_2, purified and stored over polystyryllithium and distilled before use. THF (99% from JT Baker) was degassed over freshly crushed CaH_2, purified and stored over sodium/benzophenone and distilled before use. Styrene (99% from SAFC) was degassed over freshly crushed CaH_2, stored over *n*,*s*-dibutylmagnesium and distilled before use.

2.2. Polymerization

Polymerizations were carried out under vacuum or argon atmosphere in cyclohexane (at 20 °C) or methylcyclohexane (for temperatures below 5 °C) in glass flasks fitted with PTFE stopcocks. The initiating systems were prepared under argon in thermostated polymerization flasks by addition of *sec*-butyllithium to the alkali metal alkoxide dispersed or solubilized into the hydrocarbon solvent. The polymerization was started by styrene addition to the superbase initiating system at a given temperature. The reaction was finally quenched by addition of degassed methanol in excess. Polymerization kinetics were followed by monitoring the monomer consumption by UV–visible spectrometry ($\lambda = 290$ nm). In this case, glass flasks equipped with a quartz cell were used as polymerization vessels.

2.3. UV–visible spectroscopy

Polymerization kinetics and absorption spectra of the polystyryllithium/alkali metal alkoxide species were recorded on a UV–Vis spectrometer Varian-Cary 3E using a quartz cell (0.01 cm path-length) attached to the glass reactor; $\varepsilon_{\mathrm{PSLi}} = 13,000\ \mathrm{mol\ dm^3\ cm^{-1}}$ at 326 nm, $\varepsilon_{\mathrm{styrene}} = 450\ \mathrm{mol\ dm^3\ cm^{-1}}$ at 290 nm.

2.4. Polymer characterization

The average polystyrene molar masses and their molar mass distributions were determined by size exclusion chromatography on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU, refractive index/UV detectors and TSK Gel columns calibrated with polystyrene standards.

The stereochemistry of the polystyrene was determined in D-chloroform by ^{13}C NMR on Brücker AC 250 or DPX 200 on the aromatic quaternary carbon signal [30]. Calculation of tacticity (triad and pentad levels) was carried out by deconvolution of the signals between 145.5 and 147 ppm using the 'WINNMR1D' software: mm between 146.6 and 147 ppm; mr between 146.2 and 146.6 ppm; rr between 145.7 and 146.2 ppm.

Fractionation attempts of the polystyrene samples into highly tactic (insoluble) and atactic (soluble) fractions were performed by selective solubilization in methylethyl ketone at 80 °C [16]. All our samples were completely soluble in these conditions.

3. Results and discussion

The use in hydrocarbon media of mixtures of *sec*-butyllithium with alkali metal alkoxides as anionic polymerization initiator of vinyl monomers represents an interesting alternative to alkali metal alkyls other than alkyllithium, since the latter are generally insoluble and unstable in non polar solvents. The polymerization of a large number of monomers has been investigated using these initiating systems, and their stereoregulating effect on diene polymerization is reported in some details [26,28,31–34], however no attention has been paid yet to the impact of superbase initiators on the microstructure of polystyrene.

The stereochemistry of the anionic polymerization of styrene initiated by *sec*-butyllithium/alkali *tert*-butoxide superbases has been investigated first at 20 °C in cyclohexane. The superbase complexes were prepared in situ by addition of *sec*-butyllithium on the alkali metal alkoxide (molar ratio 1:1) solubilized or dispersed in cyclohexane. In

Table 1
Polymerization of styrene initiated by *s*-BuLi in the presence of alkali metal alkoxides: influence of the alkali metal cation on the microstructure (cyclohexane, 20 °C, 4 h, [Mt]/[Li] = 1,0 $M\bar{n}_{th} = 10,000$ g mol^{-1})

Initiating species	Yield[a] (%)	$M\bar{n}_{exp}$ (g/mol)	MMD	f[b] (%)	Tacticity[c]		
					Iso	Atactic	Syndio
sec-BuLi	100	10,000	1.1	100	0.12	0.23	0.65
sec-BuLi/*tert*-BuOLi	74	15,500	1.1	47	0.14	0.23	0.64
sec-BuLi/*tert*-BuONa	73	11,500	1.1	63	0.34	0.31	0.36
sec-BuLi/*tert*-BuOK	73	185,000	1.7	4	0.58	0.31	0.11
sec-BuLi/*tert*-amylOLi	74	16,000	1.3	47	0.14	0.23	0.64
sec-BuLi/*tert*-amylONa	84	8,000	1.3	98	0.34	0.35	0.31
sec-BuLi/*tert*-amylOK	92	73,000	2.0	13	0.52	0.32	0.16
sec-BuLi/$C_{10}H_{21}OK$	93	13,000	1.5	72	0.52	0.32	0.16

[Initiator] = 5.10^{-3} M, [styrene] = 0.48 M.

[a] Polymer yield determined gravimetrically after 4 h reaction.

[b] Initiator efficiency $f = (\text{yield}_{wt} \cdot M\bar{n}_{th})/M\bar{n}_{exp}$.

[c] Determined by ^{13}C NMR of quaternary carbon in $CDCl_3$ at room temperature.

a first set of polymerization experiments, the influence of the nature of the alkali metal cation associated to *tert*-butoxide was examined. As indicated in Table 1, the change of the alkoxide counter-ion leads to a drastic modification of the polystyrene tacticity (Fig. 1): from predominantly syndiotactic with the lithium alkoxide cation (syndiotactic triads 64%)—a value close to that observed with *sec*-butyllithium alone (syndiotactic triads 65%)—the polystyrene

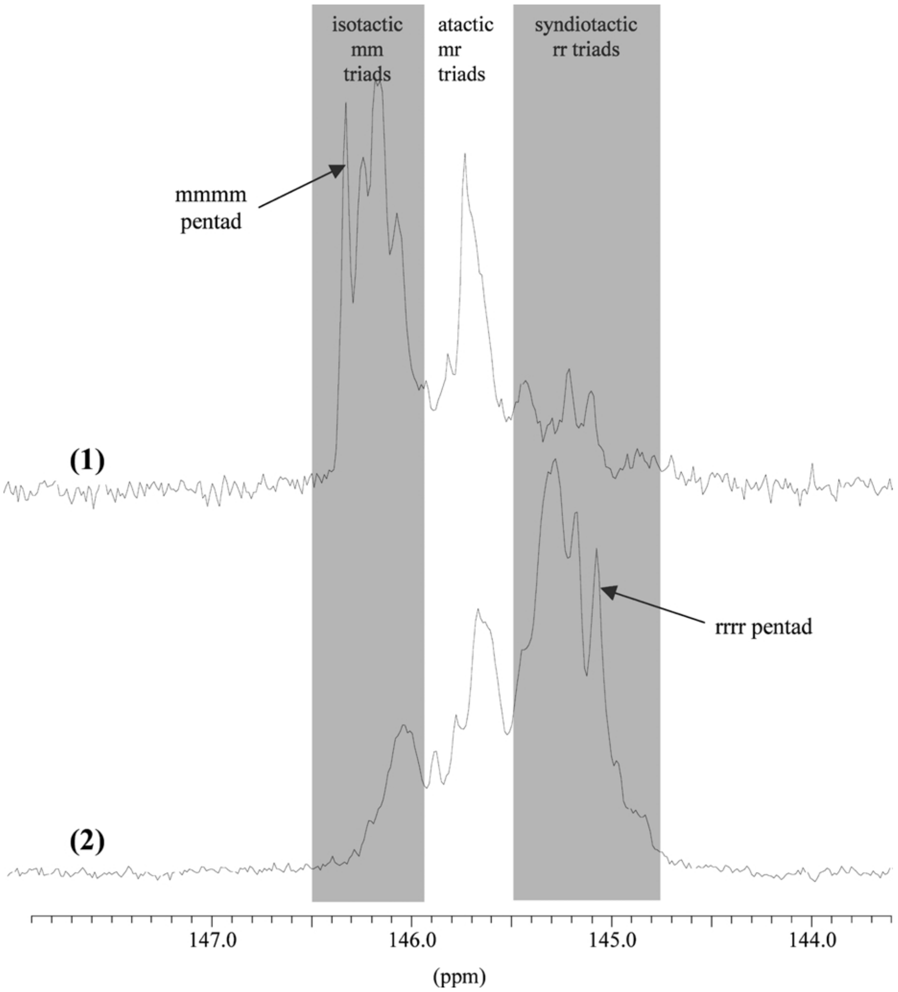
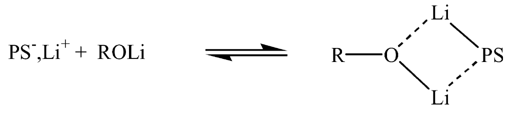


Fig. 1. ^{13}C NMR spectra of polystyrenes prepared by *sec*-butyllithium/potassium *tert*-butoxide (1) and *sec*-butyllithium/lithium *tert*-butoxide (2) in cyclohexane at 20 °C—extension of the aromatic quaternary carbon domain. Solvent $CDCl_3$, room temperature, see Tables 1 and 2.



Scheme 1.

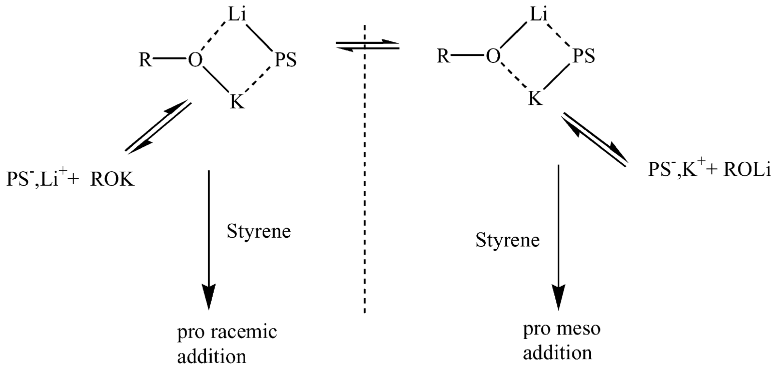
microstructure becomes predominantly isotactic (isotactic triads 58%) with the potassium *tert*-butoxide. Interestingly with the sodium derivative a completely atactic polystyrene is formed (1/3 isotactic, 1/3 atactic, 1/3 syndiotactic in triads). Conversely, the nature of the alkoxide group was not observed to strongly affect the polymer stereostructure at 20 °C.

Assuming a limited contribution of termination and transfer reactions, the polymerization initiation efficiency was determined from the theoretical over experimental polystyrene molar masses ratio, $f = \bar{M}_n\text{th}/\bar{M}_n\text{exp}$. $\bar{M}_n$th was calculated assuming quantitative initiation by initial *sec*-butyllithium, i.e. one PS chain formed by *sec*-butyllithium molecule. As shown in Table 1 the nature of the alkoxide group and of the counter-ion have a strong influence on the initiator efficiency and on the polymerization rate. This may be explained partly by solubility characteristics of the initial alkali metal alkoxides and of the corresponding complexes formed with *sec*-butyllithium: superbases containing Li and Na alkoxides are soluble in cyclohexane whereas in the K alkoxide series only the system obtained from potassium 3,7-dimethyl octanoxide is fully soluble in cyclohexane at 20 °C, allowing a much higher initiating efficiency than other potassium alkoxides.

Table 2
Distribution of triads and pentads in isotactic-rich and syndiotactic-rich polystyrenes prepared by *sec*-butyllithium/potassium *tert*-butoxide (1) and *sec*-butyllithium/lithium *tert*-butoxide (2), at 20 °C, see Table 1

Polystyrene sample	Main triad	%	Main pentad	%
(1)	mm	58	mmmm	8
(2)	rr	64	rrrr	11

The nature and structure of the propagating polymer ends and in particular their stereoregulating character towards styrene polymerization is strongly dependent of the alkali metal of the alkoxide. In the case of RLi/ROLi systems, lithium is necessarily the counter-ion associated to styryl ends, even if it is in a complex form, see Scheme 1. This likely explains that the polymer stereostructure is close to the one observed with alkyl lithium initiator alone in similar conditions. When Na and K alkoxides are associated to *sec*-butyllithium, metal–metal exchanges in mixed complexes may result in the formation of *sec*-butylsodium or *sec*-butylpotassium moieties complexed to lithium alkoxide, see Scheme 2. A similar situation may also prevail during propagation yielding the corresponding polystyryllithium complexed to the alkali metal alkoxide and/or polystyrylsodium or polystyrylpotassium species associated to lithium alkoxide. The rate and extent of the ligand to metal exchange depends very likely on both the alkoxide structure and the alkali metal. In these bimetallic systems, in particular at 1:1 *sec*-butyllithium/alkali metal alkoxide molar ratio, it is also possible that polymerization proceeds simultaneously into distinct PSLi and PSMt (Mt = Na, K) moieties or into growing species bearing successively the lithium and the other alkali metal counter-ions. This situation would result in distinct stereoregulation effects along the polymerization. According to the data, it should correspond to a preferential pro-racemic monomer addition with lithium counter-ion and a pro-*meso* styrene addition with potassium and—to a lesser extent—with sodium. Whether these two processes occur successively at the same polymer growing end—considering long lived species—through reversible sodium (or potassium)-lithium counter-ion exchanges or at two different chain ends would result in one type of polystyrene chains with stereo-defects or in distinct polymer fractions of high and low tacticities. Fractionation of various polystyrene samples of either higher isotactic or syndiotactic character were attempted in methyl ethyl ketone (MEK) at 80 °C [16]. Complete solubility of the samples in these conditions as well as in several common organic solvents (toluene, THF) at room temperature is in agreement with the formation of stereo-regular PS chains with a significant amount of in-chain stereoirregularities. This conclusion is further supported by the very low amount of the predominant tactic pentads with respect to the corresponding triad both in isotactic and syndiotactic rich PS samples, see Table 2 and Fig. 1,



Scheme 2.

Table 3
Polymerization of styrene initiated by *s*-BuLi in the presence of *t*-amylONa and *t*-amylOK: influence of the ratio [Mt]/[Li] on the polystyrene microstructure; comparison with 2-ethylhexylsodium and diphenylmethylpotassium (cyclohexane, 20 °C, 4 h, $M\bar{n}_{th} = 10,000$ g mol^{-1})

Initiating system	[Mt]/[Li]	Yield[a] (%)	$M\bar{n}_3$ (g/mol)	MMD	f[b] (%)	Tacticity[c]		
						Iso	Atactic	Syndio
sec-BuLi/*tert*-amylONa	1	84	8,000	1.3	98	0.34	0.35	0.31
	5	71	9,000	1.4	79	0.23	0.37	0.40
	10	89	11,000	1.5	83	0.27	0.24	0.49
2-EthylhexylNa	–	90	22,500	1.2	44	0.33	0.38	0.29
sec-BuLi/*tert*-amylOK	1	92	73,000	2.0	13	0.52	0.32	0.16
	5	88	15,000	1.5	61	0.51	0.33	0.16
	10	93	11,000	1.5	85	0.51	0.34	0.15
DiphenylmethylK[d]	–	97	200,000	2.2	5	0.50	0.37	0.13

[Initiator] = 5.10^{-3} M, [styrene] = 0.48 M.

[a] Polymer yield determined gravimetrically after 4 h.

[b] Initiator efficiency $f = (\text{yield}_{wt} \cdot M\bar{n}_{th})/M\bar{n}_{exp}$.

[c] Determined by ^{13}C NMR of quaternary carbon in $CDCl_3$ at room temperature.

[d] Polymerization for 24 h.

approximately 15% of the mm or rr triads only give rise, respectively, to the corresponding mmmm or rrrr pentads. This situation is indicative of the formation of a high proportion of very short stereoregular sequences separated by isolated styrene units or in very short sequences with a different configuration.

To determine the contribution of Li counter-ion which could be detrimental for the stereoregulating process since it may allow the polymerization to proceed through PSLi species, the use of higher [ROMt]/[alkylLi] ratio (Mt = Na or K) was investigated. Polymerization data using *sec*-BuLi/*tert*-amylOMt (Mt = Na or K) as initiating system and [Mt]/[Li] ratios ranging from 1 to 10 are given in Table 3. The use of higher proportion of sodium 2-methyl-2-butoxide (*tert*-amylONa) affects the proportion of syndiotactic triads which increases from 0.3 to almost 0.5 whereas the efficiency of initiation remains close to one, i.e. quantitative reaction of *sec*-butyllithium with one PS chain formed per mole of *sec*-butyllithium. This could indicate a modification of the proportion of *sec*-butyl sodium and remaining *sec*-butyl lithium and of their relative contribution to the polymerization. In systems with potassium 2-methyl-2-butoxide, see also Table 3, the predominant isotactic character of the polymer chains remains unchanged at different [ROK]/[*sec*-BuLi] ratios, whereas the initiation efficiency significantly increases in agreement with a better solubilization of the active species in presence of potassium 2-methyl-2-butoxide in excess.

The influence of the polymerization temperature on the stereoregulation character of styrene polymerization was further investigated for a series of superbases prepared from *sec*-butyllithium and various potassium alkoxides. The superbases were first prepared in cyclohexane or methylcyclohexane at 20 °C. After 1 h reaction the glass reactor

Table 4
Polymerization of styrene initiated by *s*-BuLi in the presence of various potassium alkoxides: influence of the polymerization temperature on polystyrene microstructure ($M\bar{n}_{th} = 10,000$ g mol^{-1})

Initiating species	[K]/[Li]	T (°C)	Yield (%)	$M\bar{n}_{exp}$ (g/mol)	MMD	Tacticity		
						Iso	Atactic	Syndio
sec-BuLi	–	20[a]	90	9,500	1.1	0.12	0.23	0.65
	–	0[b]	50	7,000	1.1	0.16	0.23	0.62
	–	−40[c]	50	1,800	1.1	0.20	0.27	0.53
sec-BuLi/*tert*-BuOK	2	20[a]	84	13,000	1.1	0.50	0.30	0.20
	2	0[b]	88	4,300	1.5	0.32	0.32	0.37
	2	−40[c]	11	4,100	1.7	0.22	0.30	0.49
sec-BuLi/*tert*-amylOK	2	20[a]	86	17,000	1.1	0.58	0.28	0.14
	2	0[b]	88	13,500	1.5	0.68	0.22	0.10
	2	−40[c]	38	16,000	7	0.51	0.22	0.28
	10	−40[c]	33	8,800	15	0.57	0.23	0.20
s-BuLi/$C_{10}H_{21}OK$	1	20[a]	93	13,000	1.5	0.52	0.32	0.16
	10	−40[c]	22	6,200	2.0	0.61	0.31	0.08

[a] Cyclohexane, polymerization time 4 h (20 °C).

[b] Methylcyclohexane, polymerization time 6 h (0 °C).

[c] Methylcyclohexane, polymerization time 48 h (−40 °C).

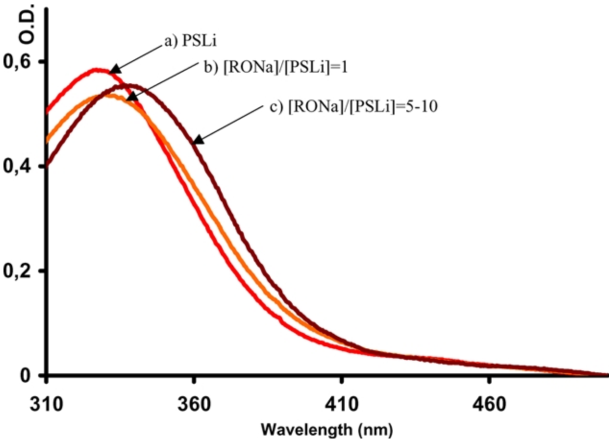


Fig. 2. Influence of increasing amounts of sodium *tert*-amyloxide on the PSLi UV–Visible spectrum (cyclohexane, $T = 20$ °C).

was thermostated at the polymerization temperature and styrene added to start the polymerization. Results collected in Table 4 show that at low temperature the nature of the potassium alkoxide has a significant influence on the stereoregulation process. With the system *tert*-BuOK/*sec*-BuLi ([K]/[Li] = 2) which is insoluble in cyclohexane a temperature decrease yields a drastic decrease of the isotactic triad fraction in the polymer, from 0.50 (20 °C) to 0.22 (−40 °C), suggesting the predominant contribution of atactic series, possibly involving Li, at low temperature. In order to tentatively favor the contribution of isoregulating species at low temperature, soluble potassium alkoxides were used and added in excess to *sec*-butyllithium (ratios 2 and 10). For *tert*-amylOK/*sec*-BuLi the isoregulation first goes up from 20 to 0 °C (0.68 isotactic triads) and then decreases when temperature reaches −40 °C, likely in conjunction with the partial insolubilization of the system at temperatures below 0 °C. The use of a large excess of *tert*-amylOK or of the more branched potassium 3,7-dimethyl 3-octanoxide at −40 °C has some positive but limited effect that does not allow to reach the maximal isoregulation rate obtained at 0 °C: a possible explanation is that the equilibrium is shifted at low temperature towards the formation of an increasing proportion of PSLi species due to the low solubility of potassium species (ROK or PSK).

$$\underset{327\,\text{nm}}{\text{PSLi}} + \text{ROMt} \longrightarrow \underset{336\,\text{nm}}{\text{PSLi}:\text{ROMt}} \rightleftharpoons \underset{336\,\text{nm}}{\text{PSMt}:\text{ROLi}}$$

Scheme 3.

To further study the reaction processes between the two organometallic derivatives, the addition of increasing amounts of alkali metal 2-methyl-2-butoxide (Li, Na and K) onto PSLi seeds has been investigated by means of UV–Vis spectroscopy in cyclohexane at 20 °C. Addition of lithium 2-methyl-2-butoxide to polystyryllithium leads to a small and continuous bathochromic shift of the main initial PSLi band from 327 to about 335 nm which is complete at a ratio lithium 2-methyl-2-butoxide/PSLi, $r = 5$. This is indicative of the interaction of lithium alkoxide with PSLi. This could yield a 1:1 PSLi:ROLi monomeric complex, as shown in Scheme 1, or in a dimeric form $(\text{PSLi:ROLi})_2$ as suggested by Bywater [25]. In a quite similar way, addition of potassium 2-methyl-2-butoxide or sodium 2-methyl-2-butoxide to PSLi seeds yield a PSLi band shift to about 336 nm again in agreement with a strong interaction between ROMt and PSLi (Fig. 2). These results can be interpreted by the formation of $(\text{PSLi:ROMt})_n$ complexes accompanied or not by alkali metal cations exchange as indicated in Scheme 3. Since no direct evidence for such exchange process could be drawn from the UV–visible study of PSLi:ROMt (Li, Na, K) systems, polystyrylsodium and polystyryl potassium were directly prepared in cyclohexane at 20 °C from 2-ethylhexylsodium and benzyl potassium to determine the position of the main polystyryl absorption band as a function of the associated cation and further investigate the direct role of the cation on the stereochemistry of the styrene polymerization. As shown in Fig. 3, PSNa exhibits a UV–visible spectrum characterized by a broad signal with a maximum centered at about 330–335 nm. Addition of lithium 2-methyl-2-butoxide to PSNa does not yield any significant shift of the UV absorption band suggesting that PSLi:RONa and PSNa:ROLi have spectra with a very close or identical wavelength absorption band. Similar UV–visible study could not be conducted with polystyryl potassium due to its very low solubility in cyclohexane. The stereochemical aspects of styrene polymerization initiated with 2-ethylhexylsodium and diphenylmethylpotassium (ϕ_2CHK) were investigated in cyclohexane at 20 °C. Contrarily to superbase systems reactions proceed heterogeneously (in particular with potassium) but yield polystyrenes with tacticities very similar to those observed with PSLi:RONa (Scheme 4) and PSLi:ROK systems, see Table 3. This confirms the determining role of the alkali metal cation associated to polystyryl chains.

In conclusion it has been shown that the use of superbases PSLi/ROMt as initiator for styrene living anionic polymerization in hydrocarbon media yields polymerization systems exhibiting different stereoregulating characters. It allows to prepare polystyrene with stereostructures ranging from syndiotactic rich (64% syndio-triad with a neat RLi or complex RLi/ROLi) to predominantly isotactic (68% iso-triad with RLi/ROK at 0 °C). The determining parameter in the steroregulating mechanism appears to be the associated metal cation. The latter can be introduced with metal alkoxides associated to *sec*-butyllithium in superbases. The stereoregulating mechanisms could involve either directly

$$\text{PSLi} + \text{RONa} \longrightarrow \text{PSLi}:\text{RONa} \rightleftharpoons \text{PSNa}:\text{ROLi} \longleftarrow \text{PSNa} + \text{ROLi}$$

Scheme 4.

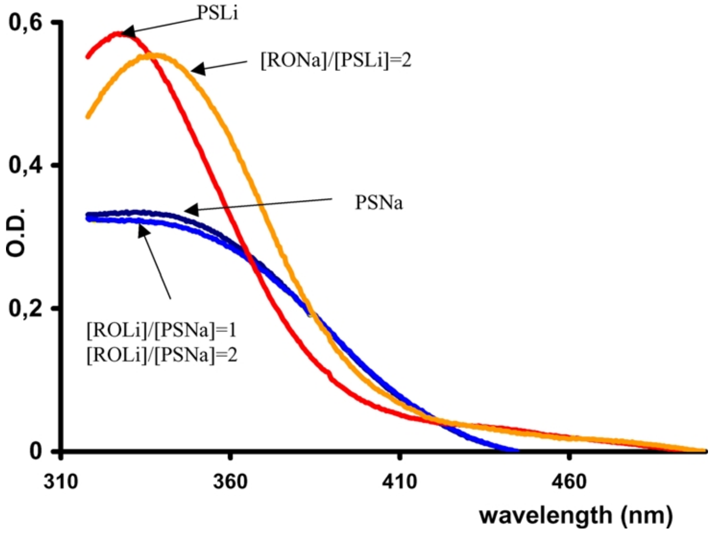


Fig. 3. Influence of increasing amounts of lithium *tert*-amyloxide on the PSNa UV–Visible spectra (cyclohexane, $T = 20\,^{\circ}\mathrm{C}$).

the initial bimetallic complexes formed between *sec*-BuLi and the metal alkoxides or the formation of new PSMt species resulting from transmetallation reactions. The polystyrene solubility characteristics and the statistics of styrene stereoinsertion strongly support the formation of a single type of polystyrene chain with stereochemical irregularities rather than the presence of a mixture of atactic and highly tactic polystyrene fractions as observed in other anionic processes [14–16].

It is believed that some of the limitations observed in the stereoregulation process result from the presence in the polymerization systems of two different counter-ions coming from the two components of the superbases, each one yielding a distinct stereoregulating mechanism. The possibility to improve stereoregulation by using initiators based on the combination of a metal alkoxide and an inert alkyl metal compound, i.e. dialkylmagnesium, will be reported in a forthcoming paper.

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