

Synthesis and development of a dilithium initiator and its use for the preparation of ABA-block copolymers in non-polar medium: the use of π -complexing additives

Jurgen Hofmans, Marcel Van Beylen*

Laboratory of Macromolecular and Physical Organic Chemistry, Katholieke Universiteit Leuven, Department of Chemistry, Celestijnenlaan 200 F, B-3001 Leuven, Belgium

Received 4 August 2004; received in revised form 5 November 2004; accepted 8 November 2004
Available online 26 November 2004

Abstract

In a former article the dissociation of organolithium salts due to π -complexing additives is described. Durene and tetraphenylethylene tend to break up at least partly the dimeric structure of polystyryllithium in non-polar solvents, as well as higher aggregates such as those formed by polybutadienyllithium. In this research these π -complexing additives are used to break up a similar association, i.e. the formation of tridimensional insoluble multifunctional initiator mixtures, when a bifunctional initiator is synthesized, using a precursor and a 2-fold excess of butyllithium. As the precursor mainly 1,3-diisopropenylbenzene (*m*-DIB) is used, but also 1,3-di(1-phenylethenyl)benzene (PEB) is examined. Subsequent addition of styrene in the presence of durene and tetraphenylethylene gives satisfying results in the synthesis of SBS-triblock copolymers.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Anionic polymerization; π -Complexing additives; Dilithium initiator

1. Introduction

The synthesis of styrenic thermoplastic elastomers generally consisting of two glassy end blocks connected by an amorphous polydiene block through the use of living anionic polymerization is well documented [1].

The method of the use of a bifunctional initiator with which first butadiene is polymerized anionically and subsequently styrene requires that the polybutadiene block has the highest 1,4-microstructure possible in order to guarantee that this polybutadiene block has the required elastomeric properties. This could only be obtained in non-polar solvents with organolithium compounds as initiators.

However, in order to avoid the aggregation of such initiators in non-polar medium due to the strong interaction of the ionic charges and resulting in the formation of insoluble tridimensionally associated species, small

amounts of σ -complexing polar solvents such as tetrahydrofuran (THF) or triethylamine were often added to break up the association. However, addition of even small amounts of such additives invariably caused an undesirable increase of the content of 1,2-microstructure of the polybutadiene.

Thus Yu et al. showed that the use of precursors such as 1,3-diisopropenylbenzene (*m*-DIB) containing two non-conjugated double bonds and having a low ceiling temperature with twice the amount of butyllithium (BuLi) in non-polar medium such as cyclohexane [2–5] did not result in a soluble well-defined truly bifunctional initiator and that an association process might be at the origin of this effect. Therefore we looked in this work for an additive that is capable of complexing with the Li^+ -cation, thereby breaking up partially or completely the association without, however, interacting as strongly with the Li^+ -cation as σ -complexing agents would do, in order that this Li^+ -cation can still undergo the proper interaction with the diene monomer, which is thought to be necessary for the preferential formation of 1,4-structures.

* Corresponding author. Tel.: +32 1632 74 31; fax: +32 1632 79 90.

E-mail address: marcel.vanbeylen@chem.kuleuven.ac.be (M. Van Beylen).

It was already advocated by O'Driscoll et al. [6] that a π -complexing agent such as 1,2,4,5-tetramethylbenzene (durene) could display a similar but much weaker effect than THF [7] on the anionic propagation of polystyryllithium (PStLi) in benzene increasing initially the rate but slowing it down at higher concentration of additive.

This effect which was attributed to the formation of a π -complex between durene and the Li^+ -cation, has escaped further attention of the researchers in the field, making, however, frequent use of the dissociative capacity of σ -complexing agents such as ethers and amines in anionic polymerization.

Therefore an extensive study of the influence of a series of π -complexing agents was made by us in a previous publication [8] as well as a detailed kinetic study of the anionic propagation of PStLi in cyclohexane in the presence of durene as an additive [9] which was also confirmed by quantum chemical calculations [10]. We could show that the dissociation constant (K_d) of the dimers of PstLi, which is estimated to be around 10^{-7} M in pure cyclohexane, was equal to 6.2×10^{-3} M when 0.56 M durene was added [9]. This means that at a formal concentration of PStLi of 10^{-3} M, about 79% of the dimeric aggregates are disrupted. This percentage can if wished still be increased at higher durene concentrations. This induced us to think that this new kind of additives, although much weaker than the σ -complexing agents, might to a large extent dissociate the organolithium aggregates, when added in sufficiently high concentration, without, however, interacting too strongly, as σ -complexing agents would do, with the Li^+ -cation so as to prevent e.g. the interaction of the Li^+ -cation with the butadiene monomer.

1,3-Diisopropenylbenzene was reacted in cyclohexane with a twofold excess of *t*-BuLi, which was shown by Yu et al. [2] to be more effective than *s*-BuLi for the synthesis of a dilithiuminitiator, in the presence of at least 0.5 M durene.

Previous experiments in our laboratory [8] showed that, when tetraphenylethylene (TPhE) is used as an additive, much smaller amounts than in the case of durene can be used to bring about the dissociation of the dimeric aggregates of PStLi in cyclohexane, the difference being as large as a factor 100. Other π -complexing additives like benzene and tetramethylethylene (TME) proved too weak to produce sufficient dissociation of the aggregated chain-ends. 1,3,5-Trimethylbenzene (mesitylene), hexamethylbenzene (HMB) and 2,2-diphenylpropane are also examined as potential π -additives in the synthesis of the triblock copolymers but proved ineffective due to side reactions.

We also checked the use of the double diphenylethylene type precursor 1,3-di(1-phenylethenyl)benzene (PEB) of Dow Chemical as a precursor instead of *m*-DIB with BuLi. Different research groups have studied precursors based on double 1,1-diphenylethylene, most of the work, however, being done by co-workers of Dow Chemical [11,12]. It is reported that the dilithium initiator based on 1,3-di(1-phenylethenyl)benzene (PEB), although soluble in

hydrocarbon solvents such as cyclohexane and benzene, produces both polystyrenes and polybutadienes with bimodal molecular weight distribution [13]. Since it was possible that the observed bimodality could result from either chain-end association effects or from branching effects due to inexact stoichiometry, the effect of added Lewis base, THF, was examined [13]. In a more recent series of papers Tung and Gatzke [14–17] suggested a whole range of different studies, mostly about 1,3-di(1-diphenylethenyl)benzene (PEB) and 1,3-di[(1-methylphenyl)ethenyl]benzene (MPEB). The addition reactions of the precursors were found to be clean and rapid. The resulting initiators were insoluble, but when freshly prepared, they were fine suspensions and would coagulate into hard particles only upon standing for several hours or more. The fine suspensions were effective in initiating butadiene polymerization and became soluble after contacting them with the monomer.

2. Experimental section

2.1. Chemicals

The reagents are purified in a similar way as described in our previous papers [8,9]. Mesitylene, 1,3-diisopropenylbenzene and 2,2-diphenylpropane are purified as styrene using CaH_2 and PStLi or BuLi.

2.2. Synthesis of precursor 1,3-di(1-phenylethenyl)benzene (PEB)

Quirk and Ma [13] also used PEB as a precursor in the synthesis of a difunctional initiator and they refer to Schulz and Höcker [18]. Following them we used a Wittig reaction to synthesize PEB. At 0 °C benzoylbenzophenone (well dried and degassed) was added to methylphosphorane. The reaction was stirred for some hours and kept overnight. Then, it was decomposed by addition of ca. 300 mL of water. After extracting the water layer with ether, the organic phases were dried over MgSO_4 and the solvent was stripped off. After column chromatography with chloroform, the product was distilled several times using a vacuum line. It was identified by mass-spectrometry and NMR. The purity was proven by high liquid chromatography, where only one single peak was detected.

2.3. Synthesis of triblockcopolymers

The synthesis of the triblockcopolymers was carried out using a bifunctional initiator, obtained by the reaction of *t*-BuLi and mostly *m*-DIB, although in a few cases also the precursor PEB was used to further test our method. The synthesis was carried out under high vacuum using highly purified reagents and in the presence of the desired π -complexing agent. After completion of the reaction the

active centers were deactivated. The polymers were then precipitated in an excess of methanol, repeatedly washed and dried to constant weight.

2.4. Characterization techniques: size exclusion chromatography

The molecular weights (M_n) of the polymers (containing only one monomer) were measured using a Waters apparatus, with THF as elution solvent. The columns (10^6 , 10^5 , 10^4 , 10^3 and 500 \AA) were calibrated with polystyrene standards. Therefore it was necessary to recalculate the results if the samples are polybutadiene. In our laboratory a calibration was done using polybutadiene standards. The difference between both standards is linear and by a factor of 0.40. Using polystyrene standards for polybutadiene samples, forced us to reduce the measured molecular weight (M_n) with 40%. In the laboratory of Theyssié a similar study was performed and they arrived at a value of 55% of the measured M_n [2].

For the SBS-triblock copolymers the same problem arises. To solve this problem a mixture of $\text{OsO}_4/\text{H}_2\text{O}_2$ was used to eliminate the polydiene middle block in SBS-triblock copolymers and then the molecular weight of the polystyrene outer blocks was measured. This procedure was reported by Kolthoff et al. [19] and was also applied by Yu et al. [2].

2.5. Nuclear magnetic resonance (NMR)

In this research NMR was mainly used to determine the microstructure of the polybutadiene blocks and to determine the ratio of butadiene versus styrene monomers in the block copolymers. All NMR-spectra were obtained on a Bruker AM 400 MHz. The percentage of 1,4- and 1,2-units of polybutadiene can be calculated using the integration of a ^1H NMR spectrum. The signal at δ 5.4 represents 2 protons of a 1,4-unit and at δ 5.6 we have 1 proton of a 1,2-unit. The *cis*- and *trans*-1,4-units of polybutadiene can be determined using ^{13}C NMR. The signal at δ 2.7 is the one of *cis*-1,4 and *trans*-1,4 is situated at δ 3.3. Determination of 1,4- and 3,4-units of polyisoprene is possible by ^1H NMR. For polyisoprene we do not have 1,2-microstructure in the polymer when Li^+ is the counter-ion but instead there are 3,4-units. There is a signal of 1 proton of a 3,4-unit at δ 4.7. Here δ 5.1 is also a peak of 2 protons of the 1,4-microstructure. To determine the ratio styrene/butadiene in copolymers only ^1H NMR is used. From the ratio of the integration at δ 7–7.3 and the sum of the integration at 5.4 and 5.6, we obtain a ratio styrene/butadiene. Knowing that the peak at δ 7–7.3 represents 5H of the aromatic ring of styrene and that the signal at δ 5.4 represents 2H of a 1,4-addition unit and that the one at δ 5.6 is due to the absorption of 1H of a 1,2-addition unit, the signal at 4.9 is due to 2H also of the vinyl units.

3. Results and discussion

We used 1,3-diisopropenylbenzene (*m*-DIB) as precursor molecule in almost all experiments for different reasons. One of the most important is the low ceiling temperature (T_c). The anionic polymerization of *m*-DIB in THF at low temperature is reversible with a ceiling temperature close to room temperature [20]. This reversibility was advantageously used for the synthesis of a supposedly bifunctional anionic initiator [21,22]. However, it has been observed by Yu et al. [3] that the anionic polymerization of *m*-DIB took place even at $50 \text{ }^\circ\text{C}$ in cyclohexane, which indicated that the ceiling temperature of *m*-DIB must be higher. Size exclusion chromatography and ^1H NMR spectroscopy showed that the molecular weight of the oligomers and the amount of unreacted vinyl groups did not change beyond 1 h of reaction, even for a long period of time.

The precursor should have a low ceiling temperature, the reaction of *m*-DIB and *t*-BuLi is in competition with homopolymerization. It is most favorable to have a low ceiling temperature, which efficiently prevents homopolymerization to occur. Therefore the experiments in which *m*-DIB is involved, are carried out at elevated temperature, i.e. $40\text{--}45 \text{ }^\circ\text{C}$. Lutz et al. [23] also reported that the two double bonds of *m*-DIB are almost isoreactive, for the *para*-isomer, however, the first addition is faster than the second. This equal reactivity of both sides of *m*-DIB is most in favor of its use in the preparation of triblock copolymers. Yu et al. [2] showed that the use of *t*-BuLi is preferable to that of *s*-BuLi. Therefore only *t*-BuLi is used instead of *s*-BuLi, although the latter is commonly known to be more reactive.

In this work we will use Li-DIB as an abbreviation for the bifunctional initiator and the other possible reaction products of the reaction. These compounds could be either monofunctional, bifunctional or multifunctional. The use of the symbol Li-DIB does not imply that the initiator is monofunctional.

3.1. Durene as additive in the synthesis of SBS-triblock copolymers

The reaction that was studied is the addition of two molecules of *t*-BuLi to *m*-DIB. The reaction is of course more complicated than the synthesis of a dicarbanionic species. Due to association of the bifunctional initiator, the latter becomes insoluble. Also oligomerization of the precursor molecule itself can be a problem in this reaction, although working at elevated temperatures can prevent this partly on account of the low ceiling temperature of *m*-DIB.

In the literature it is reported that the addition of polar additives can break down the aggregates so at least the dilithium initiator is present in the unassociated form and remains soluble while no oligomers are formed in the system. Based on the work of O'Driscoll [6] and our own [8] concerning the effect of durene on polystyryllithium we

used durene as a dissociating additive in the synthesis of the dilithium initiator from *m*-DIB and *t*-BuLi.

A first experiment was carried out at room temperature with a concentration of 10^{-3} M *t*-BuLi and 5×10^{-4} M *m*-DIB in cyclohexane in the presence of 0.8 M durene. A maximum in absorbance was obtained around 310 nm, which can be attributed to the dilithium initiator of *m*-DIB. Lutz et al. [23] studied the kinetics of the reaction of butyllithium with *m*-DIB and they reported a maximum in absorbance at 315 nm in benzene and at 310 nm in cyclohexane. Therefore it can safely be assumed that the peak at 310 nm is due to Li-DIB, knowing that the absorbance of possible side-products is situated at lower wavelengths, as will be discussed more in detail later on. We estimated that ϵ should have a value around $11,000 \text{ l mol}^{-1} \text{ cm}^{-1}$ per reactive center. After 100 h a plateau level is reached, which indicated that the reaction is completed.

3.1.1. Effect of temperature

The reaction of *t*-BuLi with *m*-DIB was very slow at room temperature. Therefore we tried similar experiments at more elevated temperature, i.e. 40 °C. In all reactions the concentration of the formed Li-DIB is followed at a wavelength of 310 nm. Fig. 1 shows that there is a marked acceleration in (a, b, c) compared with (d, e, f) which are reactions at 40 and 20 °C, respectively. The leveling off is much faster reached at 40 °C than at 20 °C.

Another experimental observation was that the reaction mixtures of (a, b, c) were generally more transparent than those of (d, e, f). This could be due to the fact that the reactions of the latter were much slower, so that a higher possibility exists of a competitive reaction taking place such as an attack of a methyl group leading to formation of a

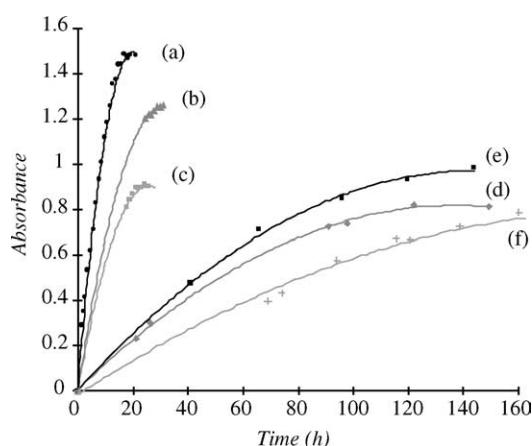


Fig. 1. Increasing absorbance due to formation of Li-DIB after different times in the reaction of *t*-BuLi with *m*-DIB in the presence of durene. (a) reaction temperature = 40 °C, [durene] = 0.5 M, [Li-DIB] = $1.3 \cdot 10^{-3}$ M; (b) 40 °C, [durene] = 0.8 M, [Li-DIB] = $1.1 \cdot 10^{-3}$ M; (c) 40 °C, [durene] = 0.8 M, [Li-DIB] = $0.8 \cdot 10^{-3}$ M; (d) 20 °C, [durene] = 0.5 M, [Li-DIB] = $1.3 \cdot 10^{-3}$ M; (e) 20 °C, [durene] = 0.5 M, [Li-DIB] = $1.0 \cdot 10^{-3}$ M; (f) 20 °C, [durene] = 0.5 M, [Li-DIB] = $1.0 \cdot 10^{-3}$ M.

benzyl-type anion. The differences of the finally reached plateau were the result of a slight difference of initial *t*-BuLi that should be the same as the final Li-DIB initiator concentration. The absorbance plateaus reached in (d, e, f) were lower because in the latter some precipitation occurred giving some scatter, which led to a wrong result when we compared this with the absorbance of the samples which were transparent at the end. The reaction solution also contained then less Li-DIB species because there was some *t*-BuLi lost in side reactions.

The formation of a benzylic anion could give a slight precipitate. If this happens, it would be a supplementary advantage to work at elevated temperature. Indeed, the main reaction was much faster and the competitive reaction was occurring to a comparatively lesser extent. It can be seen that the plateau level reached at 20 °C was not only reached after a longer time but also the plateau itself is not as high as the one with a similar concentration at 40 °C. The temperature 40 °C is much closer to the ceiling temperature. The reaction can go more easily to completion with simultaneously a smaller loss of *t*-BuLi in possible competitive reactions.

3.1.2. Initiation of styrene with Li-DIB

In a preliminary test we added styrene to the synthesized Li-DIB in order to check the functionality of the Li-DIB initiator. In this test-experiment we were able to determine the concentration of Li-DIB and the concentration of PStLi and to compare these with the concentration of initially added *t*-BuLi. PStLi could easily be measured because its maximum in absorbance is situated in cyclohexane at 326 nm. At this wavelength there was no interference of the absorbance of durene, which has a maximum in absorbance at 278 nm. This determination of living-ends would not be possible if butadiene would be added because the maximum in absorbance of PBLi is also situated at 278 nm, i.e. exactly the same as that of durene.

We used two different samples of Li-DIB as initiator for the polymerization of styrene in the presence of 0.5 M durene. A first sample was prepared by the reaction of *t*-BuLi with *m*-DIB under the same conditions as the other reaction, i.e. 45 °C for about 30 h in cyclohexane, but without durene added to the solution. This is called the blank. A first visual observation was that there were solubility problems and precipitation, with the Li-DIB initiator in the blank. These problems were inexistent in the second sample containing durene. In both experiments the formation of the Li-DIB initiator was followed by UV/Vis-spectrophotometry at 310 nm. In the study with the additive a nice evolution of the reaction occurred as shown in Fig. 2. In the blank, this was not the case at all as shown in the same plot. In the latter no continuous line could be drawn through the different points.

Both Li-DIB initiators were used for the polymerization of styrene at 40 °C. A well-known amount of styrene was added, so the molecular weight ($M_n(\text{calc})$) of the polymer

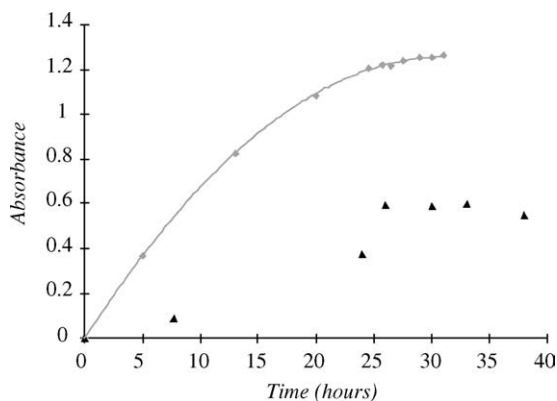


Fig. 2. Progress of the reaction of *t*-BuLi with *m*-DIB at 310 nm: (◆) in cyclohexane with 0.65 M durene at 45 °C and (▲) in cyclohexane without any additive at 45 °C.

could be predicted and compared with the M_n measured by size exclusion chromatography ($M_n(\text{SEC})$). These values are given in Table 1. We could also determine the concentration of PStLi from the UV-spectra, this is represented by [PStLi]. [*t*-BuLi] is the initial concentration of *t*-BuLi that we used in the reaction with *m*-DIB with a molar ratio of 2/1 of both reagents.

It can be seen that the concentration of PStLi as well as the $M_n(\text{SEC})$ matched much better with, respectively, [*t*-BuLi] and $M_n(\text{SEC})$ in (a) than in (b). This led to the conclusion that durene had a well-defined positive influence on the reaction of *t*-BuLi with *m*-DIB and on the subsequent initiation of styrene by Li-DIB and that the initiator in the presence of durene acted as a truly bifunctional initiator. Taking notice of the polydispersity (*D*) in (a) and (b), it can be seen that in (a) a monodisperse polymer is obtained while in (b) some undesirable side reactions must have taken place, with higher polydispersity as a consequence.

3.1.3. Effect of reagent concentration

It is obvious that the molar ratio of the concentration of *t*-BuLi and *m*-DIB cannot be changed, it always has to be exactly 2. Higher ratios would result in an excess of *t*-BuLi and therefore would lead to contamination with diblock copolymers in the synthesis of triblock copolymers. Lower ratios lead to an excess of *m*-DIB and would result in multifunctional initiator molecules due to oligomerization.

The reaction of *t*-BuLi with *m*-DIB was also carried out with different initial concentrations in the presence of 0.5 M durene. A known amount of butadiene was added to the initiator, so we were able to predict the molecular weight of the polymer. This is given in Table 2 as $M_n(\text{calc})$. $M_n(\text{calc})$

Table 2
 $M_n(\text{calc})$ versus $M_n(\text{exp})$ using different concentrations of the initiator based on a 2 *t*-BuLi/*m*-DIB system at 40 °C with 0.5 M durene

[<i>t</i> -BuLi] (M)	$M_n(\text{calc})$	$M_n(\text{exp})$
1.0×10^{-3}	16,600	17,500
3.9×10^{-3}	6700	13,300
9.6×10^{-3}	15,000	38,400

is the value calculated assuming that there were two growing centers per molecule. $M_n(\text{calc})$ is then compared with the value of M_n obtained from SEC ($M_n(\text{exp})$).

In Table 2 it can be seen that only in the first case the $M_n(\text{exp})$ correspond to the $M_n(\text{calc})$. In the second and third experiment we detected some precipitation and after addition of the monomer the yellow color of the initiator did not disappear completely. We assumed that in these two experiments the initiator was still too much associated in aggregated species so all initiator molecules are not available anymore to initiate the polymerization. Both findings point in the same direction: in the first experiment the initiator initiated difunctionally and in the other cases the initiator was not able to initiate the polymerization in the correct way. Because we could not record the absorbance of the polybutadienyllithium, which has a maximum absorbance at 278 nm, we determined a concentration at a wavelength of 295 nm although this is on the slope of the absorption band. This calculation resulted in equal concentrations for the PBuLi and *t*-BuLi concentrations of 1.0×10^{-3} M in the first experiment.

3.1.4. Propagation of monomers in the presence of durene

It has been pointed out several times in this work that polar additives are unfavorable for the microstructure of polydienes when polar additives are present in the mixture during propagation. It should be clear now that durene and also the other π -complexing additives are much weaker complexing agents than the σ -complexing additives. Even so the question arises if they are not complexing too strongly to permit the right interaction between the monomer that is being built in into the growing chain and the Li^+ -cation, since they are apparently strong enough to break down the aggregates or at least an important part of the aggregates. The microstructure remained the same when π -complexing compounds were added for different monomers, i.e. isoprene and butadiene as well as in different solvents, i.e. cyclohexane and benzene. As pointed out many times in several studies the greatest problem with σ -complexing additives like THF or Et_3N , is that they resulted in

Table 1
Styrene initiated by Li-DIB: (a) in cyclohexane with 0.65 M durene and (b) in cyclohexane without any additive

	[<i>t</i> -BuLi] (M)	[PStLi] (M)	[Sty] (M)	$M_n(\text{calc})$	$M_n(\text{SEC})$	D^a
(a)	1.4×10^{-3}	1.3×10^{-3}	0.18	41,600	39,800	1.06
(b)	1.4×10^{-3}	1.0×10^{-3}	0.20	33,500	54,600	1.66

^a Molecular weight distribution.

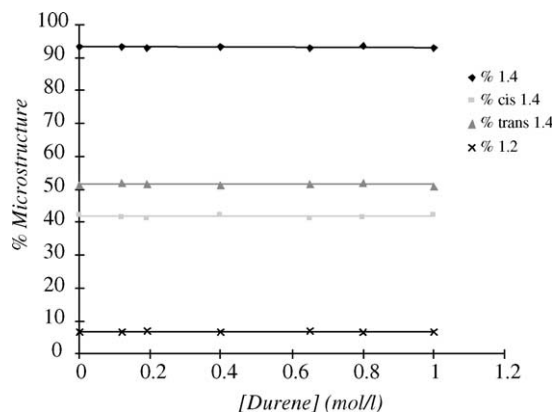


Fig. 3. Microstructure of polybutadiene with varying concentrations of durene in cyclohexane, $[P\text{BuLi}] \approx 10^{-3}$ M.

considerable amounts of 1,2-units in the studies with polybutadiene and of 3,4-units with polyisoprene. As seen in Fig. 3 durene did not contaminate the microstructure of polybutadiene even in a concentration ratio of 1000 compared to the $P\text{BuLi}$ species. There are small differences, but these are negligible. Comparing this figure with a similar one of THF, the difference is tremendous. In the latter only small amounts such as 0.1 wt% already resulted in more than 40% vinyl content.

3.1.5. Metalation of durene in the reaction system

In a former discussion we already mentioned the possibility of competitive reactions in the reaction system. We carried out detailed studies about this side reaction, which is a metalation of durene by carbanionic species, especially with $t\text{-BuLi}$, because this is one of the most reactive organolithium species in the different stages of the synthesis of SBS-triblock copolymers.

At the start of our research a mixture of 0.5 M durene and 10^{-2} M $t\text{-BuLi}$ in cyclohexane was prepared and put at 20 °C. After stirring for 24 h we could, however, not detect any change in the reaction mixture. Then it was heated to 45 °C and the mixture was followed using UV/Vis spectrometric analysis. At this relatively elevated temperature one could see a light yellow color developing and after longer times even precipitation of yellow particles, which became orange or even red at higher conversions. There was definitely a reaction of $t\text{-BuLi}$ with durene. In the past some studies have been made about the attack of $P\text{StLi}$ on toluene [24,25]. The only difference between toluene and durene is that the latter contains three extra methyl substituents on the aromatic ring. It seemed reasonable to assume that the reaction in both cases was of the same type.

The reaction that occurs is the abstraction of a proton from a methyl group to yield a benzyl type-anion, the negative charge of which is delocalized in the aromatic ring. Benzyl lithium is known to be insoluble in hydrocarbon solvents and it is therefore accepted that this benzylic type Li^+ -salt is formed and that it is the cause of the broad band

in the spectrum. We studied the reaction of $t\text{-BuLi}$ with durene from different viewpoints. First some experiments were carried out at different temperatures, viz. 6, 25 and 45 °C followed by a series of experiments with concentrations of $t\text{-BuLi}$ varying from 10^{-3} M to 10^{-1} M $t\text{-BuLi}$.

In both series of experiments an increase in absorbance in the region of 300–340 nm was observed with time and after at least 35 h a decrease in absorbance was seen at 310 nm together with the formation of a second smaller band at higher wavelength (~ 375 nm). This was probably caused by precipitation. The maximum of the absorbance is always situated around 310 nm, attributable to benzyl lithium-type products.

An interesting point to know is whether the reaction mixture containing the benzyl lithium-type molecules is still able to react with $m\text{-DIB}$. Therefore a mixture of 2×10^{-3} M $t\text{-BuLi}$ and 0.5 M durene in cyclohexane was heated to 45 °C. We added $m\text{-DIB}$ after the $t\text{-BuLi}$ had reacted with durene for 4 h. The progress with time was followed at 310 nm and compared to the reaction of $t\text{-BuLi}$ with $m\text{-DIB}$ together from the beginning in the presence of durene as represented in Fig. 2. This comparison is shown in Fig. 4.

The reaction rates looked comparable during the first 5 h of the reaction, the difference being due to a small difference in concentration of $t\text{-BuLi}$ in both cases (i.e. 2×10^{-3} M for the reaction of $t\text{-BuLi}$ /durene (4 h) + $m\text{-DIB}$ and 1.4×10^{-3} M for $t\text{-BuLi}$ + $m\text{-DIB}$ in the presence of durene), but then in the experiment of the reaction of the product of $t\text{-BuLi}$ /durene with $m\text{-DIB}$ the absorbance reached a maximum and diminished later on. To explain this difference in behavior, we were inclined to think that, when a certain amount of benzyl lithium-type product had been formed before the addition of $m\text{-DIB}$, the production of this benzyl lithium-like product went on, even after addition of $m\text{-DIB}$, and in contrast with $t\text{-BuLi}$, this product did not react with $m\text{-DIB}$, but the addition product of $t\text{-BuLi}$ to $m\text{-DIB}$ and the benzyl lithium-like product absorb at approximately the same wavelength. The spectroscopic

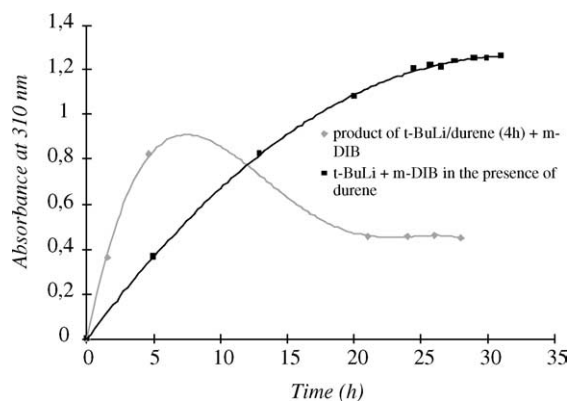


Fig. 4. Comparison of the reaction of $t\text{-BuLi}$ with $m\text{-DIB}$ in the presence of durene (■) and the reaction of the reaction product of $t\text{-BuLi}/\text{durene}$ with $m\text{-DIB}$ (♦), both at 45 °C.

evolution of curve b therefore probably represents the sum of two competitive reactions: one is the reaction of *t*-BuLi with *m*-DIB and the other is the reaction of *t*-BuLi with durene, leading to benzyllithium-like products that became increasingly insoluble. This could explain the decrease of the absorbance at later stages.

It can be concluded that *t*-BuLi attacks durene in a concentration range from 10^{-3} M to 10^{-1} M and in a temperature range of 6–45 °C but that the formation of benzyllithium-like product was insignificant, when durene was not in the presence of *t*-BuLi before *m*-DIB was added to it. It is not advisable therefore to store durene together with *t*-BuLi in cyclohexane. The reaction product of this mixture is a benzyllithium-like compound, which was not able anymore to react with *m*-DIB. It was also rather insoluble in cyclohexane but in THF it was very soluble. That made it possible to measure an absorbance spectrum of the compound, but in this solvent it showed rapid termination. For the purpose of partially or completely disrupting the aggregation of the living ends, as in this work, we feel that durene can safely be used provided that it is not stored with or added to the solution of the organolithium reagent before *m*-DIB is added to the organolithium species.

3.1.6. Cross-over reaction in the presence of durene

In the next step of the synthesis of a SBS-triblock copolymers the second monomer is to be added to the dilithium polybutadiene compound to result in the two outer blocks. In several of our experiments we added styrene to polybutadienyllithium (PBLi), which we obtained after reaction of Li-DIB with butadiene in the presence of durene. In none of the experiments, was there a sign of a reaction of the PBLi with styrene monomer when durene is present. Even after more than 6 weeks at 40 °C there was not any change of the color. The color is a very good parameter in this case, because if there would be a reaction we would obtain formation of a styryl-anion, which has a broad absorption over the UV/Vis-spectrum with a maximum in absorbance at 328 nm in cyclohexane and a high extinction coefficient of $13,300 \text{ M}^{-1} \text{ cm}^{-1}$. This broad absorption results in a yellow color in the visible part of the spectrum. The color change would be already detectable with the naked eye but even with the UV/Vis-spectrophotometer we could not detect any change.

However, it is well known that styrene does add to PBLi living chains [26,27] in the absence of any polar additive, be it at a low rate. In the course of this work we first added styrene to PBLi which had been prepared in the presence of durene and this durene was still there when we added styrene to PBLi. So the durene must be the cause that no reaction with styrene occurred. If it is accepted that in non-polar medium reaction with a monomer occurs by association of this monomer to the Li^+ -cation and that is then inserted into the C^--Li^+ bond, this complexation (which is probably responsible for the predominantly 1,4-microstructure of polybutadiene in butadiene

polymerization) can apparently not take place for styrene when the Li^+ -cation is complexed with durene. Although durene seems to be a rather weak complexing agent compared e.g. with THF, it reduces the reactivity tremendously (see Ref. 9) apparently so much that the reaction of PBLi with styrene, which is already very slow in pure cyclohexane without durene, does not take place any more when durene is present. The reaction of PBLi with butadiene in cyclohexane and in the presence of durene does, however, still occur because butadiene monomer forms a stronger complex with PBLi than durene, so that the reaction of butadiene with PBLi can still occur (with conservation of 1,4-content). With the more weakly complexing styrene this is not the case. Styrene still reacts with the more reactive PstLi in the presence of durene but as mentioned (see Ref. 9) at a much reduced rate.

However, from the literature we know that in most cases of the preparation of SBS-triblock copolymers the authors added some Et_3N or THF to the mixture of BuLi with *m*-DIB or another precursor already in the beginning of the reaction and then there was no problem of course at the time of the addition of styrene. This effect of addition of THF or Et_3N is ascribed to the fact that they destroy the complex with durene but then lead to another reaction mechanism since it is known that polymerization of butadiene in the presence of such polar agents gives less 1,4- and much more 1,2-microstructure. Therefore 3 V% THF was added to the reaction mixture when the propagation of butadiene was completed. After the right amount of styrene was first added to the solution, the reaction started immediately. Using this procedure there is no danger of losing some of the 1,4-microstructure of the diene block because this block is already synthesized before THF was present.

As an experiment to test whether one could use TMEDA instead of THF at this stage, butadiene was polymerized in cyclohexane initiated by *t*-BuLi and in the presence of durene and styrene was added. After addition of a small amount, i.e. 0.3 V% TMEDA, the reaction started immediately. This again illustrates that the σ -complexing agent TMEDA (or THF) is a much stronger complexing agent for organolithium compounds than the π -complexing agent durene, but as pointed out earlier, the latter left the microstructure of polydienes unaltered when these are polymerized in non-polar medium.

3.1.7. SEC Study of the bifunctional initiator

Syntheses were performed in the presence and in the absence of durene in order to be able to make a good comparison of the quality of the bifunctional initiator. The SEC-spectra are given in Figs. 5 and 6, respectively. In the SEC-spectrum of the Li-DIB, which was synthesized in the presence of durene we could detect 2 different peaks. This was not a bimodal sample but there are two different components. The one with the highest M_n is the signal of the bifunctional initiator. In our SEC-apparatus this corresponds

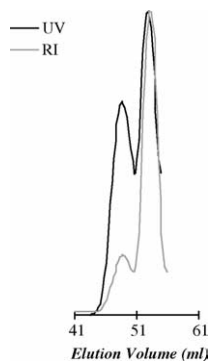


Fig. 5. SEC-trace of the terminated dilithium initiator synthesized in the presence of durene.

with 52.85 mL. The other signal in the spectrum is due to durene.

In the other spectrum we see a signal of a low molecular weight species and some other signals of higher molecular weight material. Maybe this is due to the fact that *t*-BuLi was not able to react with all the *m*-DIB present and that some of the *m*-DIB was able to polymerize. Another striking difference is the fact that there was a lot of precipitation at the end of the reaction in the case of the synthesis without durene and this was not the case in the mixture where durene was present. The question arises whether the peak of the Li-DIB in Fig. 5 is actual a monomodal peak or a combination of several individual peaks due to monofunctional, bifunctional and maybe even multifunctional initiator. However, another application of SEC can be the measurements of the central diene block and the final triblock for a qualitative study. It is a fact that there definitely was an increase of the molecular weight after addition of styrene to the reaction mixture of PBuLi and that both blocks were monomodal. This is clearly illustrated in Fig. 7.

3.2. Study and characterization of the synthesized triblock copolymers

3.2.1. Study of the molecular weight

After the bifunctional initiator was synthesized the first

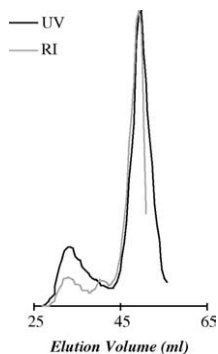


Fig. 6. SEC-trace of the terminated dilithium initiator synthesized without durene.

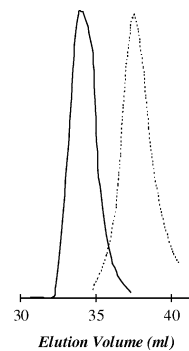


Fig. 7. SEC-traces of polybutadiene at the higher elution volume (V_e) shifted to lower V_e after addition of styrene.

monomer, i.e. butadiene was added. After complete polymerization a small sample was taken of the reaction mixture. After termination and precipitation in methanol, a 2 wt% solution of the recovered polybutadiene is measured by SEC. A recalculation of the figures is necessary because the columns of the instrument were calibrated with polystyrene. To the remaining of the reaction mixture some THF as well as the second monomer, i.e. styrene, is added. The resulting SBS-triblock copolymers of this step can also be terminated and precipitated to prepare a sample for SEC measurements. For this kind of polymers the same problem arises, i.e. the columns of the instrument are calibrated with polystyrene. Indeed, the principle of SEC is based on the size of the polymer cluster and this is different depending on the nature of the polymer. On the other hand it is possible to calculate the molecular weight of polystyrene using the measured M_n of the polybutadiene block and the ratio of butadiene–styrene, which can be determined by NMR. It is not possible to determine whether the styrene is attached to either one side of the polybutadiene block or whether it is attached on both sides. A concentration measurement of the PStLi can, however, solve this problem; an example of this method will be given in the next section.

To solve this problem it is possible via the $\text{OsO}_4/\text{H}_2\text{O}_2$ -elimination technique to measure the molecular weight of the polystyrene outer blocks. Using a mixture of $\text{OsO}_4/\text{H}_2\text{O}_2$ it is possible to eliminate the polydiene middle block in SBS-triblock copolymers and then measure the molecular weight of the polystyrene blocks.

We carried out a detailed study of the attack of $\text{OsO}_4/\text{H}_2\text{O}_2$ on several kinds of polymers, such as homopolymers like polystyrene (PS) and polybutadiene (PB), but also diblock copolymers (SB) with a polystyrene block and a block of polybutadiene. Finally we did two experiments with triblock copolymers (SBS) with polybutadiene as an inner block and polystyrene as the outer blocks. In the samples containing polystyrene homopolymers the same molecular weight was obtained before and after using $\text{OsO}_4/\text{H}_2\text{O}_2$. The polystyrene remained exactly the same, and was not affected by the reaction with $\text{OsO}_4/\text{H}_2\text{O}_2$. In the homopolymer of polybutadiene we did not find any trace of

polymer anymore in SEC after reaction. The polymer had completely disappeared, as it should. In the following samples of the diblock copolymers, which were prepared by reaction of polystyryllithium of known molecular weight with butadiene there was no polybutadiene attached anymore after reaction with $\text{OsO}_4/\text{H}_2\text{O}_2$, since the values of the molecular weight of the polystyrene were very similar. In NMR there was no trace of polybutadiene either.

Also in the cases of the triblocks all polybutadiene was gone after reaction with $\text{OsO}_4/\text{H}_2\text{O}_2$. This was proven by the molecular weight of the polystyrene and by NMR-measurements. It is also proven that the polystyrene was not attacked by $\text{OsO}_4/\text{H}_2\text{O}_2$ because in none of the pure polystyrene samples was there a notable change of the molecular weight or the molecular weight distribution after treatment with $\text{OsO}_4/\text{H}_2\text{O}_2$.

We can conclude that we got now a very positive result for the preparation of SBS-triblock copolymers using Li-DIB as an initiator in the presence of 0.8 M durene as can be seen in the last sample of Table 3. The M_n of the polystyrene calculated with NMR and on the basis of the molecular weight of the first synthesized block, matched very well with the M_n of the polystyrene after reaction with $\text{OsO}_4/\text{H}_2\text{O}_2$. The given molar masses of the polystyrene blocks are the molar masses of one outer block. Thus the total molar mass of polystyrene is double of the mentioned value.

3.2.2. Spectroscopic study

We also performed a spectroscopic study of the different steps of the synthesis. We found the concentration of PBuLi in cyclohexane to be nearly the same as the concentration of Li-DIB, for example 1.08×10^{-3} M and 1.06×10^{-3} M in the experiment of Fig. 8.

The ϵ 's we used together with the corresponding wavelengths are:

$$\begin{aligned}\epsilon(\text{Li-DIB})_{310 \text{ nm}} &= 11,500 \text{ M}^{-1} \text{ cm}^{-1} \\ \epsilon(\text{PBuLi in CH})_{295 \text{ nm}} &= 5700 \text{ M}^{-1} \text{ cm}^{-1} \\ \epsilon(\text{PBuLi in THF})_{320 \text{ nm}} &= 4570 \text{ M}^{-1} \text{ cm}^{-1} \\ \epsilon(\text{PStLi in THF})_{330 \text{ nm}} &= 12,000 \text{ M}^{-1} \text{ cm}^{-1}\end{aligned}$$

Table 3

Detailed study of the reaction of $\text{OsO}_4/\text{H}_2\text{O}_2$ on different kinds of polymers (between brackets the molecular weight distribution of the polymers is given)

Kind of polymer	$M_n(\text{PS})$	$M_n(\text{PB})$	$M_n(\text{SB(S)})$	$M_n(\text{P})$ (after OsO_4)
Polystyrene	3800 (1.46)	–	–	3900 (1.53)
Polystyrene	20,000 (1.22)	–	–	19,000 (1.27)
Polybutadiene	–	346,000 (1.29)	–	No trace
Diblock SB	55,900 (1.21)	111,800 ^a	162,700 (1.35)	55,000 (1.38)
Diblock SB	55,800 (1.17)	125,900 ^a	164,700 (1.21)	57,600 (1.34)
Diblock SB	10,800 (1.21)	49,400 ^a	61,200 (1.15)	10,000 (1.31)
Triblock SBS ^b	10,000 ^a	50,900 (1.17)	89,000 (1.32)	7500 (1.31)
Triblock SBS ^b	25,700 ^a	48,600 (1.15)	103,700 (1.24)	26,000 (1.42)

^a Molecular weights calculated, using the molecular weight of the first synthesized block and the ratio of the different monomers, this ratio is calculated using ¹H NMR.

^b Syntheses in the presence of durene and using Li-DIB as an initiator.

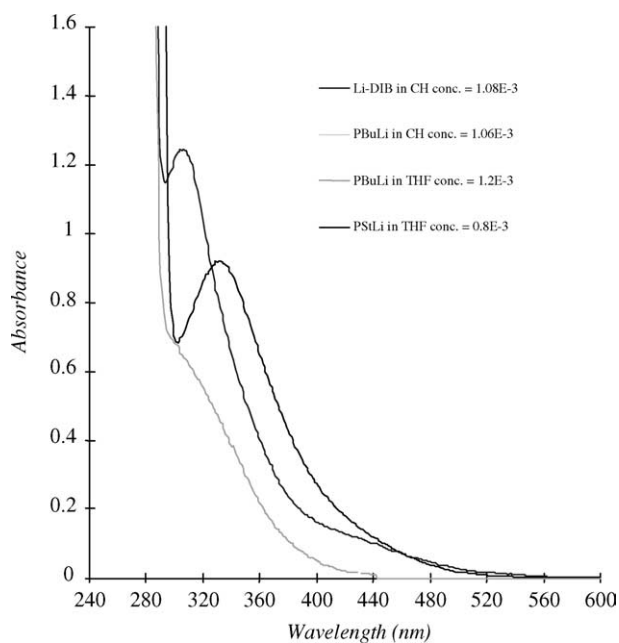


Fig. 8. Spectroscopic study of the different steps in the synthesis of SBS.

All these extinction coefficients are values concerning only one functional group of the bifunctional molecule.

In the case of polybutadienyllithium in cyclohexane and tetrahydrofuran we can only calculate of the absorbance on the slope of the curve, because the maximum is covered by the absorbance of durene. The absorbance below 290 nm in all spectra is due to durene. This spectroscopic study was made on the last but one mentioned in Table 3, with $M_n(\text{PS})$ of 10,000 and $M_n(\text{PB})$ 50,900. Fig. 8 and Table 3 combined indicate convincingly that we obtained a completely regular triblock copolymer.

3.2.3. General study of triblock copolymers

In the final consideration of the structure of the triblock copolymers we can use all the previously mentioned parameters, i.e. concentration of the initially added *t*-BuLi and *m*-DIB ([*t*-BuLi]), concentration of Li-DIB, PBuLi and PStLi; molecular weight of the polybutadiene ($M_n(\text{PB})(\text{calc})$) and polystyrene block ($M_n(\text{PS})(\text{calc})$)

calculated using the added amounts of each monomer, molecular weight of polybutadiene ($M_n(\text{PB})(\text{SEC})$) and polystyrene ($M_n(\text{PS})(\text{SEC})$) measured by SEC, after treatment with $\text{OsO}_4/\text{H}_2\text{O}_2$, and the molecular weight of polystyrene calculated using the molecular weight of the polybutadiene block and the ratio butadiene/styrene as determined by NMR ($M_n(\text{PS})(\text{NMR})$). The polystyrene molar masses represent only the molar mass of one single polystyrene outer block.

The results of five syntheses are given in Table 4. The data in this table are all obtained using a reaction sequence and reaction conditions as they are given in Fig. 9. All the steps of the synthesis were carried out under high vacuum and with highly purified reagents as discussed in the Section 2.

To a solution of durene in cyclohexane *m*-DIB and *t*-BuLi were added, which were also dissolved in some cyclohexane. We thus obtained a reaction mixture of, respectively, $5.0 \times 10^{-4} \text{ M}^{-1}$ DIB and $1 \times 10^{-3} \text{ M}^{-1}$ *t*-BuLi. This was kept overnight at 40 °C.

To the obtained Li-DIB, butadiene was added after the absorbance reached its maximum value. The polymerization was carried out at 40 °C because at room temperature the reaction was too slow. The reaction is complete after stirring overnight. Because there was no reaction of PBuLi with styrene under these reaction conditions, 3 V% THF was added at this stage. Then the concentration of PBuLi and PStLi in this polar medium could be easily calculated. The pertinent results are summarized in Table 4.

Before adding styrene a sample of the mixture is taken so M_n of PB could be measured. This is given as $M_n(\text{PB})(\text{SEC})$ and can be compared with M_n which can be calculated from the added amount of butadiene. This value is given as $M_n(\text{PB})(\text{calc})$. After propagation of styrene the diene block of the triblock was eliminated using $\text{OsO}_4/\text{H}_2\text{O}_2$ and the molecular weight of the resulting polystyrene was measured. This is given as $M_n(\text{PS})(\text{SEC})$ and this can

be compared with the calculated molecular weight $M_n(\text{PS})(\text{calc})$, assuming a bifunctional initiator was obtained and therefore the M_n of a single polystyrene outerblock.

When [*t*-BuLi] and [PBuLi] are compared in Table 4, it can be seen in all the experiments, there was a very good agreement between the different concentrations. Another positive result was that $M_n(\text{PB})(\text{calc})$ matched quite well with $M_n(\text{PB})(\text{SEC})$. Moreover the molecular weight distribution was narrow for the polybutadiene polymer. If the amount of butadienyl reactive centers is right and if we get the right M_n , then we can conclude that the polymer grows on both sides. This is seen to be correct in Table 4.

In the next step to synthesize the triblock copolymer, we had to polymerize styrene as the blocks attached to the central diene block on both sides. When doing this we got styryl-anions instead of butadienyl-anions.

One can see that in most cases the concentration of PStLi is comparable to the initial concentration of *t*-BuLi. The concentration of PStLi is almost the same as [*t*-BuLi] and [PBuLi]. The comparison of $M_n(\text{PS})(\text{calc})$ and of $M_n(\text{PS})(\text{SEC})$ proved satisfactory in A, B, C and D. As described before it was possible to measure the ratio of the amounts of the different monomers by NMR. Using this ratio we were able to calculate $M_n(\text{PS})$ using $M_n(\text{PB})(\text{SEC})$. We divided this by two because we did not want to know the global M_n of styrene, but the M_n of one of the styrene blocks. This is given in Table 4 as $M_n(\text{PS})(\text{NMR})$. When we compared this with $M_n(\text{PS})(\text{calc})$, we see a good agreement in case A, B and C. We can also compare it with $M_n(\text{PS})(\text{SEC})$, which is the M_n of PS after the reaction of SBS with $\text{OsO}_4/\text{H}_2\text{O}_2$. These three different values should be the same in the ideal situation. In case of again A, B and C, they were comparable. Only in the case of D there was some discrepancy for the value of $M_n(\text{PS})(\text{NMR})$ although there was satisfactory agreement between $M_n(\text{PS})(\text{calc})$ and $M_n(\text{PS})(\text{SEC})$. The reason for this is not clear.

The agreement is satisfactory even though some of the values are not exactly the same, because in the use of SEC measurements an experimental error of 5% is not exceptional. It can be concluded that particularly in the case of B all different calculations and comparisons point into the same direction, namely a central diene block with a very narrow molecular weight distribution and on both sides a styrene block of about 25,000. The final SBS-block copolymer had a polydispersity of 1.2.

As a concluding remark it can be noted that the molecular weight measurements combined with the concentration measurements are sufficient proof for the success of the synthesis in the presence of durene.

3.3. Hexamethylbenzene as additive

Hexamethylbenzene (HMB) can be thought to be a more strongly complexing alternative than durene due to the two additional methyl substituents on the phenyl ring. On

Table 4
Results of different syntheses of SBS-block copolymers in the presence of durene

	[<i>t</i> -BuLi] (M)		[PBuLi] (M)		[PStLi] (M)	
A	1.1×10^{-3}		1.2×10^{-3}		0.86×10^{-3}	
B	1.1×10^{-3}		0.95×10^{-3}		1.3×10^{-3}	
C	1.0×10^{-3}		1.2×10^{-3}		1.11×10^{-3}	
D	1.0×10^{-3}		1.0×10^{-3}		0.97×10^{-3}	
	$M_n(\text{PB})$ (calc)	$M_n(\text{PB})$ (SEC) and D	$M_n(\text{PS})$ (calc)	$M_n(\text{PS})$ (SEC)	%B/%S (NMR)	$M_n(\text{PS})$ (NMR)
A	34,900	34,200 (1.12)	24,000	30,000	67/33	22,000
B	41,100	48,600 (1.15)	21,000	26,000	55/45	25,700
C	18,300	25,200 (1.15)	23,400	19,600	60/40	27,100
D	31,000	35,000 (1.19)	21,600	22,500	39/61	13,100

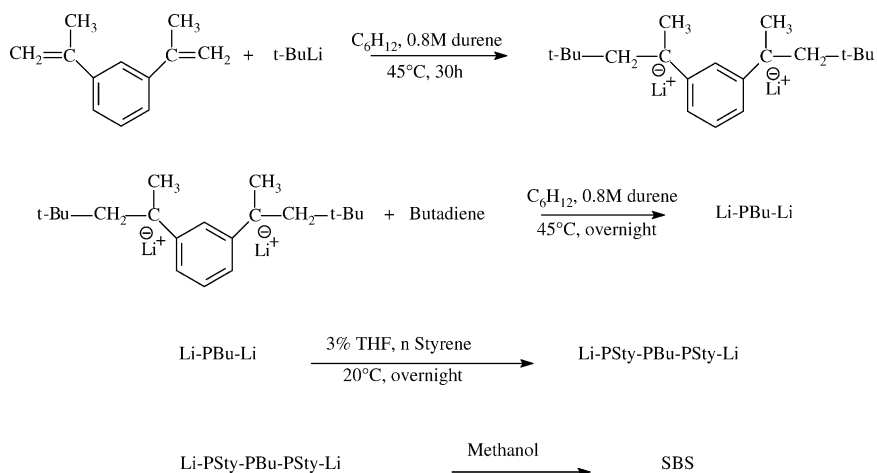


Fig. 9. Reaction sequence and reaction conditions used in the study of SBS-triblock copolymers.

account of the electron donating properties of a methyl group it is to be expected that the π -cloud of the phenyl will be richer in electrons in the case of HMB, and thus it will be a better π -complexing agent for the Li^+ cation resulting in a better dissociation of aggregated organolithium compounds in non-polar solvents. To verify this, some kinetic measurements were performed on the propagation of polystyryllithium in cyclohexane in the presence of varying concentrations of HMB under high vacuum [8]. At comparable concentrations the increase in rate of propagation with increasing HMB concentrations is larger than with durene.

There was, however, a serious problem in using HMB. Even at a concentration of HMB as low as 0.09 M it reacted with PStLi at room temperature, the concentration of polystyryllithium being 10^{-3} M. This was clearly seen in the UV/Vis spectra. As explained in the previous discussion about durene, the methyl groups of toluene, durene and HMB can be metalated, which will result in a benzyl-lithium-type compound. It could be clearly seen that the absorbance maximum of PStLi shifted from 328 nm to a lower wavelength of 310 nm where benzyl-lithium-type products are known to absorb and this even before all styrene had been consumed.

This made it impossible to use HMB in the synthesis of triblock copolymers. We would get transfer, probably at all stages, i.e. during the synthesis of the bifunctional initiator Li-DIB, the reaction of Li-DIB with butadiene to polybutadienyllithium and finally at the stage of the addition of styrene with formation of polystyryllithium. Indeed one could expect that if polystyryllithium gives transfer with HMB, t -BuLi will certainly attack HMB, and the possibility to get the proper Li-DIB will be very small or non-existent.

3.4. 1,3,5-Trimethylbenzene as additive

Trimethylbenzene, also called mesitylene, is very similar to durene, which we already described in detail. A great

advantage compared to durene is the fact that mesitylene is a liquid at room temperature. This is not only favorable for practical use in the laboratory but certainly also on an industrial scale. However, it was not very easy to accomplish the purification on a small scale, although solubility is no problem anymore. As for the strength of mesitylene, it could be expected to be less strongly π -complexing than durene. On the other hand much higher concentrations can be used than the 1 M of durene. One can go up to 7.19 M, which is the concentration of pure mesitylene.

In the experiments on the synthesis of triblock copolymers in the presence of varying amounts of mesitylene from 0.29 up to 1.77 M, it is shown that the concentration of the different carbanions in the three steps was not the same as the initial t -BuLi concentration and the molecular weights, calculated using the initially added amount of monomer and of t -BuLi did not correspond with the measured molecular weights.

For an attempt to elucidate the anomalies PStLi is a favorable agent because its maximum of absorbance does not overlap with any other possible agent in the mixture used. Therefore a solution of 10^{-3} M PStLi in cyclohexane was first prepared and after 0.47 M mesitylene was added, the mixture was heated to 45 °C. In a second experiment the concentration of mesitylene was 0.56 M. The other reaction conditions (temperature, [PStLi], reaction time) were exactly the same. A spectrum of PStLi was recorded before the addition of mesitylene and immediately after to determine if there was termination after addition of mesitylene. In that case one would expect a decrease of the absorbance due to termination by some impurities of the mesitylene itself, and due to some dilution after addition, although this effect was minor. Surprisingly there was even a small increase of the absorbance immediately after addition of mesitylene.

This absorbance was a broad band with a maximum around 320–360 nm. In the second experiment, there was an increase in absorbance of about 8%. In the first experiment

the increase was even bigger, about 25%. This seemed to indicate the formation of another carbanion with a wavelength of maximum absorbance of 330 nm, which is unfortunately almost the same wavelength as the maximum of PStLi. After this initial increase there was a severe decrease, which started already after 15 min. Especially in the first 20 h the decrease was most apparent but it also kept decreasing during the next hundred hours.

Considering this as proof of the disappointing results and in spite of the unexpected larger initial increase no further attempt was made to explain this increase and the study of mesitylene was not pursued any further. It looks like a transfer reaction occurred between PStLi and mesitylene, which led to a product that interfered with the synthesis of the triblock copolymers. Therefore it seemed that mesitylene was not a good candidate as an alternative for durene in the synthesis of a bifunctional initiator. We were not able to obtain a final SBS-triblock copolymer of which we could proof it was actually a triblock.

On the other hand, just as in the samples with durene, the microstructure of polybutadiene was not affected by mesitylene and was of the following composition: 7% 1,2 polybutadiene, 51% *trans*-1,4 and 42% *cis*-1,4 polybutadiene.

3.5. Tetraphenylethylene as additive

The concentrations of TPhE needed for dissociation of PstLi dimers, were much smaller than the concentrations of durene to give a similar dissociation effect [8,28]. Comparing them, it can be seen that the maximum rate of propagation in the case of TPhE was situated at 6×10^{-3} M whereas this was 0.5–0.6 M in the case of durene. This is a difference of a factor 100. We could not compare the two additives at the same concentration because at such small concentrations as in the regions of 10^{-3} M, durene was giving no significant dissociation and higher concentrations of TPhE were not possible either because $8\text{--}9 \times 10^{-3}$ M TPhE was the maximum solubility in cyclohexane. At first sight one could say that the dissociating capacity of TPhE is much bigger comparing the ratios of the concentrations of the additive to living ends. These are in the case of TPhE 1–8 and in the case of durene 500–800.

Because the absorbance of TPhE was very high at a wavelength of 280–400 nm, the increase in absorbance at 310 nm due to the formation of Li-DIB is too small to be seen. A synthesis was therefore performed in the presence of 2.1×10^{-3} M diphenylpropane, in which the reaction could be followed, with 5×10^{-4} M *m*-DIB and 1×10^{-3} M *t*-BuLi in cyclohexane and the mixture was heated up to 45 °C for several hours. In the experiment the time of completion was comparable with the synthesis of Li-DIB with 0.5 M durene, namely 30 h. The formation of Li-DIB was estimated to take only 10 h when 6×10^{-3} M TPhE was used. After completion of the reaction of *t*-BuLi with *m*-DIB butadiene was added to the red-orange solution of initiator

and we observed the disappearance of the color after only a few hours, which was much faster than in the experiments with 0.5 M durene.

3.5.1. Effect of TPhE on the synthesis of SBS

As discussed before it was not possible to measure the concentrations of Li-DIB, PBuLi and PStLi in the mixture because the absorbance of TPhE was too high. That is the reason why only the different molecular weights are given in Table 5.

It can be seen that the molecular weights of the polybutadiene block, calculated from the added amount of the monomer matched in most cases with the molecular weights of the polybutadiene block measured using SEC, which are given as $M_n(\text{PB})(\text{calc})$ and $M_n(\text{PB})(\text{SEC})$, respectively, without any noticeable relation to the concentration of the added TPhE to the sample. The molecular weight distributions are given as D between brackets. After the synthesis of polybutadiene some THF was added as well as the second monomer, styrene. The same procedure was used as described before. At first sight all the molecular weights look very satisfying but if we look more closely and calculate the percentage of the difference in molecular weight of the calculated polystyrene block and the one measured with NMR, it can be seen that the samples with 3.9×10^{-3} M and 5.9×10^{-3} M gave better results than the ones with smaller amounts of TPhE. To accomplish the measurement of $M_n(\text{PS})(\text{NMR})$, we used the amount of monomer added and the percentage styrene calculated using the NMR spectra taken of the final block copolymers.

In these last two samples, there was only a difference of 3 and 5% between $M_n(\text{PS})(\text{calc})$ and $M_n(\text{PS})(\text{NMR})$, which was much smaller than the error on the other molecular weights, which were all around 20%. So it can be concluded that one needs at least 4×10^{-3} M TPhE with 10^{-3} M *t*-BuLi to get good results.

To be sure that we actually obtained triblock copolymers instead of diblock copolymers the method of $\text{OsO}_4/\text{H}_2\text{O}_2$ was used again. One can see that there are no big differences between $M_n(\text{PS})(\text{NMR})$ and $M_n(\text{PS})(\text{OsO}_4)$, especially in the samples with higher concentrations of TPhE.

3.5.2. Reaction between *t*-BuLi and TPhE

A negative effect could be the transfer reaction as it occurred with durene or hexamethylbenzene. It was caused by the metalation of the methyl groups. TPhE does not have such groups; nevertheless we did an experiment to study specifically the case of TPhE. Because TPhE had such a big absorbance over the whole wavelength range, from 400 nm down to 200 nm, it was impossible to follow the reaction spectroscopically.

After 2–3 days we did not see any visible change in the sample containing 10^{-3} M *t*-BuLi and 2×10^{-3} M TPhE in cyclohexane at 45 °C, whereas this was certainly the case

Table 5
Molecular weights of the different blocks of triblock copolymers synthesized in the presence of TPhE

[TPhE] (M)	[<i>t</i> -BuLi] (M)	[B] (M)	[Sty] (M)	$M_n(\text{PB})(\text{calc})$	$M_n(\text{PB})(\text{SEC})$ and D
0.87×10^{-3}	0.95×10^{-3}	0.510	0.106	45,000	67,100 (1.15)
1.8×10^{-3}	1.10×10^{-3}	0.561	0.097	55,000	49,500 (1.24)
2.1×10^{-3}	1.04×10^{-3}	0.506	0.118	39,000	34,100 (1.18)
2.5×10^{-3}	1.00×10^{-3}	0.372	0.113	40,200	44,900 (1.18)
2.8×10^{-3}	0.87×10^{-3}	0.419	0.109	52,000	53,800 (1.11)
3.9×10^{-3}	0.87×10^{-3}	0.475	0.097	59,000	50,600 (1.17)
5.9×10^{-3}	0.81×10^{-3}	0.438	0.113	46,800	50,600 (1.17)

[TPhE] (M)	$M_n(\text{PS})(\text{calc})$	$M_n(\text{PS})(\text{OsO}_4)$	$M_n(\text{PS})(\text{NMR})$
0.87×10^{-3}	9000	7100	5900
1.8×10^{-3}	9400	8800	8100
2.1×10^{-3}	11,800	9500	9150
2.5×10^{-3}	11,700	9700	9300
2.8×10^{-3}	13,000	14,700	16,400
3.9×10^{-3}	11,700	11,800	12,000
5.9×10^{-3}	11,700	11,100	11,100

(PB) Representing the polybutadiene block and (PS) the polystyrene block of the triblock copolymers calculated using the ratio of the monomer and the initial amount of initiator ($M_n(\text{calc})$) and the ones measured with SEC ($M_n(\text{SEC})$), [B] and [Sty] are the concentrations of butadiene and styrene used.

with durene or hexamethylbenzene. We could therefore be certain there was no problem during the synthesis of the triblock copolymer.

3.5.3. Effect of TPhE on the microstructure of the polybutadiene block

Because of the strong dissociating power of TPhE it could be thought that the influence of the additive was too intense to leave the 1,4-microstructure of the polybutadiene block intact. But Fig. 10 proves the opposite. There was no change of the microstructure even with the highest concentrations of TPhE used.

In view of the very strong effect of tetraphenylethylene (TPhE) we wanted to check also 2,2-diphenylpropane (DPhP). They both have the possibility to complex with the Li^+ -cation between two phenyl rings, although the angle between the rings is not the same in both species. Moreover in the case of TPhE we have phenyl groups attached to a sp^2 -carbon atom and in the case of DPhP to a sp^3 -carbon.

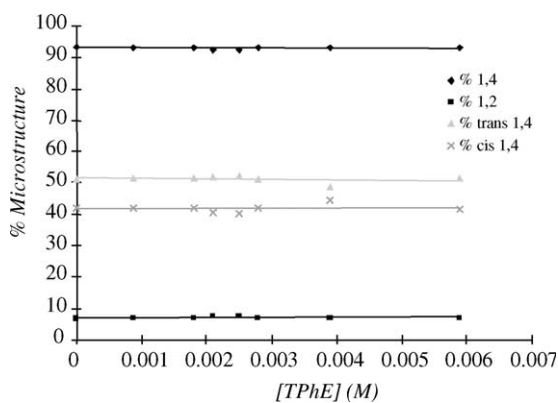


Fig. 10. Microstructure of the polybutadiene middle block as a function of the concentration of TPhE.

3.6. 2,2-Diphenylpropane as additive

In this paragraph we looked in more detail at 2,2-diphenylpropane (DPhP) as a possible additive in our system to synthesize Li-DIB. For a comparison with TPhE, it seemed interesting to perform a detailed study of it in our system, although there are quite some differences between its fundamental structure and that of TPhE.

The goal of this study is to examine the interaction of Li^+ with the two phenyl groups. We have chosen 2,2-diphenylpropane instead of diphenylmethane, because the latter has two acidic protons and these would react with the very strong basic carbanions, such as *t*-BuLi, PBuLi or PStLi. Apart from the above mentioned accelerating effect and the fact that the microstructure of the polybutadiene formed again remained the same as in pure cyclohexane up to the highest concentrations of DPhP, the results of the triblock copolymer synthesis looked rather unfavorable.

We started with an amount of about 1.25×10^{-3} M *t*-BuLi and half of this amount *m*-DIB in the presence of about 2×10^{-3} M DPhP up to 300×10^{-3} M. In all the experiments the concentration of [Li-DIB] was much too low compared to [*t*-BuLi] and a complete mismatch of [PBuLi] and [Li-DIB] was observed. On top of that the measured M_n -values were much higher than the calculated ones, without there being a trend in the differences. In view of all the anomalies observed when using DPhP we did not retain DPhP as a possible π -complexing agent in the synthesis of triblock copolymer since we got much better results with other additives.

3.7. Double 1,1-diphenylethylene as precursor

Different research groups have studied precursors based on double 1,1-diphenylethylene, most of the work was done

by researchers of Dow Chemical. 1,3-di(1-phenylethenyl)-benzene (PEB) gave the best results although still polar additives had to be added, the seeding technique had to be used or oligomeric PStLi had to be used as initiator to get well-defined soluble bifunctional initiator systems.

It has been reported that butyllithium adds readily to 1,1-diphenylethylene (DPE) in hydrocarbon solvents [29,30]. The product could initiate isoprene and butadiene to form copolymers with DPE. Because of the bulkiness of the phenyl groups, DPE did not homopolymerize. The addition of butyllithium to compounds containing two DPE groups should produce dilithium initiators. A 5% excess of *s*-BuLi was used in the experiments to counteract the estimated amount of impurities still existing in the system. The addition reaction was completed in about 3 h. The fine dispersion formed for all four double DPE compounds was found to initiate the polymerization of butadiene [31]. The precursor is not commercially available.

3.7.1. *t*-BuLi as initiator with PEB

In a first series of experiments *t*-BuLi was chosen to add to PEB, in a 2/1 molar ratio *t*-BuLi/PEB. In two experiments we added 6×10^{-3} M TPhE to the reaction mixture and in two others 0.8 M durene was used as additive. These were the concentrations of additive at which the best results were obtained with *m*-DIB as a precursor. To know the concentration of the precursor engaged in the reaction, we used UV/Vis-spectroscopy. We obtained the extinction coefficient by a series of standard solutions. We found a maximum in absorbance at 236 nm with $\epsilon = 36,000 \text{ M}^{-1} \text{ cm}^{-1}$, which was in agreement with the one obtained by McGrath et al. [32]. For the final anion (Li-PEB) we used $\epsilon = 13,000 \text{ M}^{-1} \text{ cm}^{-1}$ at 435 nm per anionic center in the dilithium-compound. This value of ϵ was based on data from an earlier PhD-thesis made in our laboratory [33]. In this work the reactivity was studied of 1,1-diphenyl-*n*-hexyllithium (1,1-DFHLi), 1,1,3-triphenyloctyllithium (1,1,3-TFOLi) and 2-polystyryl-1,1-diphenylethyllithium (PDFELi) with styrene in benzene and cyclohexane at 22 °C. All these species are diphenylmethylanion-compounds and should be comparable with the anion in this research. The concentrations of Li-PEB obtained were much too low and the measured molecular weights were too high.

The results indicated that the reaction with *t*-BuLi was incomplete, which might be explained by steric hindrance due to the voluminous diphenyl-compound on one hand and the more voluminous *t*-BuLi compared to *s*-BuLi on the other.

3.7.2. *s*-BuLi as initiator with PEB

In this experiment we used *s*-BuLi instead of *t*-BuLi and made a blank experiment (without durene as additive) and one in the presence of 0.8 M durene. In both cases the increase up to the final plateau level of the dilithium compound Li-PEB was qualitatively as well as quantitatively much more satisfactory than the results obtained with *t*-BuLi. Also the molecular weights in the case with durene were satisfactory although not completely correct, but as described in the literature this compound is very difficult to purify. The numerical results of both experiments are given in Table 6.

The main difference between the experiment with and the one without durene is the formation of a fine suspension of Li-PEB in the experiment without durene when the reaction was approaching completion, a macroscopic observation we did not see in the samples with durene present. The increase of absorbance was measured at λ_{max} , namely 435 nm. The plateau level was reached in less than 5 h, which is much faster than the reactions with *m*-DIB. This is not surprising in view of the higher reactivity of the PEB-precursor.

The numeric data indicate a positive result. Indeed the concentration of the initial amount of *s*-BuLi was almost the same as the resulting concentration for the Li-PEB component, only the concentration of PBuLi was a little higher. This could be due to the absorption of some remaining initiator, although it seemed improbable that there was still some bifunctional initiator in view of the relatively low molecular weight distribution and the final agreement of the polystyryllithium concentration. However, due to its very high extinction coefficient, the smallest amount of unreacted precursor results in a strong absorbance, and the λ used to determine the concentration of PBuLi is in the same UV-region. Therefore it could be possible that the high concentration of PBuLi which is calculated from the

Table 6
Results of the SBS-blockcopolymer with PEB as precursor

Without durene	With durene (0.8 M)	
[<i>s</i> -BuLi] = 1.16×10^{-3} M	[<i>s</i> -BuLi] = 1.07×10^{-3} M	
[Li-PEB] = 1.04×10^{-3} M	[Li-PEB] = 0.86×10^{-3} M	
Very fine suspension of precipitate	[PBuLi] = 1.31×10^{-3} M (not completely decolorized)	
	[PStLi] = 0.96×10^{-3} M	
	$M_n(\text{PB})(\text{calc}) = 21,200$	$M_n(\text{PS})(\text{calc}) = 9500$
	$M_n(\text{PB})(\text{SEC}) = 17,200$ (1.25)	$M_n(\text{PS})(\text{SEC/NMR}) = 12,700$
		$M_n(\text{PS})(\text{OsO}_4/\text{SEC}) = 13,150$

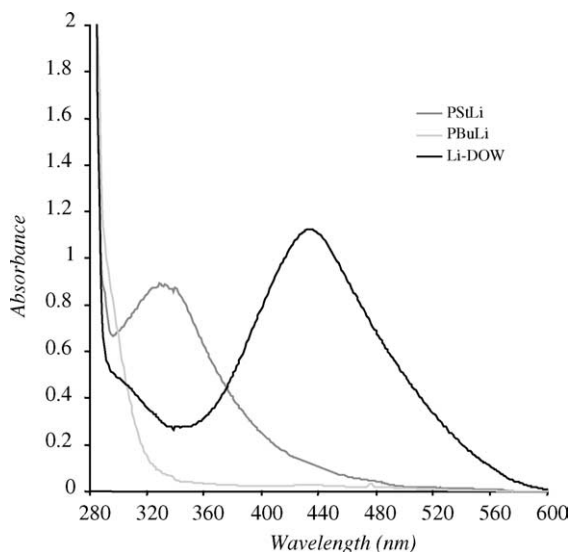


Fig. 11. Spectral evolution of the synthesis of triblock copolymers based on the reaction of *s*-BuLi with 1,3-di(1-phenylethenyl)benzene.

absorbance at 277 nm was partly due to some remaining precursor.

The shift of the λ_{\max} when going from Li-PEB to PBuLi and subsequently to PStLi is given in Fig. 11 and confirmed the positive results. From the qualitative point of view all the maxima in absorbance were the same as the ones described in the literature. The quantitative results of the concentrations are summarized in Table 6.

4. Conclusion

In the experiments concerning the synthesis of triblock copolymers, based on the initiation of a bifunctional initiator synthesized from *t*-BuLi and *m*-DIB, addition of the π -complexing agents mesitylene, hexamethylbenzene and 2,2-diphenylpropane resulted in a mixture of different products, which was caused by side reactions. Only addition of durene and tetraphenylethylene resulted in well-defined SBS-triblock copolymers and these two π -complexing agents seemed to be the only additives that can be recommended for the synthesis of these copolymers. It should also be noted that tetraphenylethylene is a much stronger π -complexing agent than durene. The experimental conditions to be recommended for the synthesis of well-defined SBS-triblock copolymers emerging from this work are therefore 10^{-3} M *t*-BuLi and 5×10^{-4} M *m*-DIB at 45 °C in the presence of at least 0.5 M durene or 6×10^{-3} M TPhE. The reaction of this mixture was over after about 24–30 h and resulted in a strictly bifunctional initiator, i.e. a dilithium compound (Li-DIB).

Benzene and TME seemed to be weak π -complexing agents as shown in previously reported work [8]. None of

the π -additives used resulted in a microstructure different from that of polybutadiene synthesized in the absence of the additive, i.e. pure non-polar solvent. This is a main advantage of these additives in contrast to polar additives as used in the literature by other research groups, resulting always in substantial contents of vinyl units. Thus the triblocks contain a central polydiene block with more than 90% 1,4 content so the elastomeric properties should be optimal. This is proof that the interaction between the Li^+ cation and the propagating diene monomer estimated necessary for the formation of primarily 1,4-microstructure can still occur in the presence of these additives.

In a final stage 1,3-di(1-phenylethenyl)benzene (PEB) was used as a precursor instead of 1,3-diisopropenylbenzene although they are very similar, i.e. a divinyl compound on a central phenyl ring. Also in this system of *s*-BuLi and PEB, durene and tetraphenylethylene seemed to have a positive influence on the synthesis of a SBS-triblock copolymer comparing it with some experiments in the absence of any additive.

Acknowledgements

We wish to thank Asahi Chemical Ind. for the financial support. In particular we want to thank Mr. Morita for the interest he took in our work and for the information, which he kindly provided us with.

References

- [1] Hsieh HL, Quirk RP. Anionic polymerization. New York: Marcel Dekker; 1996.
- [2] Yu YS, Jérôme R, Fayt R, Teyssié Ph. *Macromolecules* 1994;27: 5957.
- [3] Yu YS, Dubois Ph, Jérôme R, Teyssié Ph. *Macromolecules* 1996;29: 1753.
- [4] Yu YS, Dubois Ph, Jérôme R, Teyssié Ph. *Macromolecules* 1996;29: 2738.
- [5] Yu YS, Dubois Ph, Jérôme R, Teyssié Ph. *Macromolecules* 1996;29: 6090.
- [6] O'Driscoll K, Patsiga R. *J Polym Sci Part A* 1965;3:1037.
- [7] Bywater S, Worsfold DJ. *Can J Chem* 1962;40:1564.
- [8] Hofmans J, Maesele L, Wang G, Janssens K, Van Beylen M. *Polymer* 2003;44:4109.
- [9] Wang G, Van Beylen M. *Polymer* 2003;44:6205.
- [10] Yakimansky A, Wang G, Janssens K, Van Beylen M. *Polymer* 2003; 44:6457.
- [11] Yamagishi A, Szwarc M, Tung L, Lo GY-S. *Macromolecules* 1978; 11:607.
- [12] Tung LH, Lo GY-S, Beyer DE. *Macromolecules* 1978;11:616.
- [13] Quirk RP, Ma J-J. *Polym Int* 1991;24:197.
- [14] Bredweg CJ, Gatzke AL, Lo GY-S, Tung LH. *Macromolecules* 1994;27:2225.
- [15] Lo GY-S, Otterbacher EW, Gatzke AL, Tung LH. *Macromolecules* 1994;27:2233.
- [16] Lo GY-S, Otterbacher EW, Pews RG, Tung LH. *Macromolecules* 1994;27:2241.
- [17] Gatzke AL, Green DP. *Macromolecules* 1994;27:2249.

- [18] Schulz GG, Höcker H. *Makromol Chem* 1977;178:2589.
- [19] Kolthoff IM, Lee TS, Carr CW. *J Polym Sci* 1946;1:429.
- [20] Lutz P, Beinert G, Rempp P. *Makromol Chem* 1982;183:2787.
- [21] Beinert G, Franta E, Rempp P. *Makromol Chem* 1978;179:551.
- [22] Lutz P, Franta E, Rempp P. *Polymer* 1982;23:1953.
- [23] Lutz P, Beinert G, Franta E, Rempp P. *Eur Polym J* 1979;15:1111.
- [24] Gatzke AL. *J Polym Sci, A1* 1969;7:2281.
- [25] Wang LS, Favier JL, Sigwalt P. *Polym Commun* 1989;30:248.
- [26] Ohlinger R, Bandermann F. *Makromol Chem* 1980;181:1935.
- [27] Johnson AF, Worsfold DJ. *Makromol Chem* 1965;85:273.
- [28] Wang G, Janssens K, Van Oosterwijck C, Yakimansky A, Van Beylen M. *Polymer* 2004 in press.
- [29] Evans AG, George DB. *J Chem Soc* 1961;4653.
- [30] Yuki H. *Prog Polym Sci Jpn* 1972;3:141.
- [31] Tung LH, Lo GY-S. *Macromolecules* 1994;27:1680.
- [32] Broske AD, Huang TL, Hoover JM, McGrath JE. In: Hogen-Esch TE, Smid J, editors. *Recent Advances in Anionic Polymerization*. New York: Elsevier; 1987.
- [33] Dils J. Ph.D. Thesis, K.U. Leuven; 1976.