Difunctional Initiator Based on 1,3-Diisopropenylbenzene. 2. Kinetics and Mechanism of the sec-Butyllithium/ 1,3-Diisopropenylbenzene Reaction†

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ABSTRACT

Kinetics of the addition of s-butyllithium (*s*-BuLi) to 1,3-diisopropenylbenzene (1,3-DIB) has been studied, and the activation energy has been found to be 17.5 kcal/mol. Addition of *s*-BuLi to 1,3-DIB in a 2/1 molar ratio results in an oligomer rather than the desired diadduct. This observation has to be compared to the anionic polymerization of 1,3-DIB (hydrocarbon solvent at 50 °C) which leads to a polymer bearing ca. one double bond per monomeric unit. Li-NMR analysis of the addition of *s*-BuLi to 1,3-DIB (2/1 molar ratio) confirms the nonequivalence of the lithium cations and shows that ca. 30% *s*-BuLi remains unreacted when 1,3-DIB has been completely consumed. In the early stage of the addition, the propagation rate is faster than depropagation and the average molecular weight increases. When a depropagation-propagation quasi-equilibrium is reached, the oligomer molecular weight remains constant. It finally decreases when no DIB is left, as a result of depropagation. When the *s*-BuLi/1,3-DIB adduct is used as an initiator for styrene polymerization in the presence of a polar solvent, such as THF, initiation by monofuntional, difunctional, trifunctional, and tetrafunctional species is observed. In an apolar solvent, however, polystyrene of a narrow molecular weight distribution and a functionality of 2 is formed. This experimental observation more likely indicates that depolymerization of the 1,3-DIB oligomers occurs upon the addition of styrene. A mechanism which accounts for this propagation-depropagation process has been proposed and experimentally supported.

Introduction

An efficient difunctional anionic initiator soluble in apolar solvents is a prerequisite for the two-step synthesis of rubbery telechelic polydienes and thermoplastic elastomers of the ABA type where the central block B is a polydiene of a high cis-1,4 content. Considerable effort has been devoted for many years to the synthesis of well-defined hydrocarbon soluble difunctional orga-nolithium initiators.[2-11] 1,3-Diisopropenylbenzene (1,3-DIB) was earlier proposed as a potential precursor, but rapidly neglected when it was observed that the reaction of 1,3-DIB with *s*-BuLi in a 1/2 molar ratio led to a mixture of di- and polyfunctional compounds rather than to the expected pure diadduct.[12] Recently, Hogen-Esch et al. have revised this reaction, in benzene at 50 °C and claimed the formation of a well-defined difunc-tional initiator, that allowed them to block copolymerize butadiene (BD) and methyl methacrylate (MMA).[13]

A previous paper from this laboratory has reported on the synthesis of poly(styrene-*b*-butadiene-*b*-polystyrene) (SBS) thermoplastic elastomers in cyclohexane or benzene solution by using the 2/1 *s*-BuLi/DIB adduct as an initiator.[1] Although the molecular weight distribution of both the PBD central block and the final copolymer was narrow and the molecular weight matched the expected value, in agreement with the observations by Hogen-Esch et al., the final copolymers proved to be diblocks rather than the expected triblock copolymers. It was concluded that even though the stoichiometric reaction of *s*-BuLi with 1,3-DIB in a nonpolar medium resulted in a diadduct, this organolithium compound did not behave as

a difunctional anionic initiator in a hydrocarbon solvent, but rather as a monofunctional one.[1] This general conclusion was based on the extremely poor mechanical properties of final copolymers compared to commercially available thermoplastic elastomers, on the molecular weight of the PS blocks released by the selective degradation of the PBD block, and on synthesis initiated by the *s*-BuLi/1,3-DIB addition product prepared with a molar excess of *s*-BuLi.

All these apparent contradictions about the actual structure of the 2/1 *s*-BuLi/DIB reaction product (di- or polyfunctional adducts) and the number of active an-ionic sites (mono-, di-, or polyfunctional initiator) have prompted us to revise that reaction in a nonpolar medium.

Experimental Section

Chemicals. Styrene (Janssen) was dried over CaH_2 for 2 days, then added with fluorenyllithium, and distilled just before use. Butadiene (Air Liquid Co.) was condensed after passing through a column filled with freshly crushed CaH_2 and then distilled over *n*-BuLi prior to use. 1,3-Diisopropen-ylbenzene (Aldrich) was dried over CaH_2 for 1 day, distilled from fluorenyllithium, and then diluted with dry cyclohexane. Diphenylethylene (Aldrich) was dried over *n*-BuLi and diluted with dry cyclohexane. This solution was added with (diphenylmethyl)Li and distilled before use. Commercially available *sec*-butyllithium (Janssen) was titrated with 1,2-dibromobu-tane.[14] Tetrahydrofuran (THF) was purified by refluxing over a Na-benzophenone complex. Cyclohexane and benzene were refluxed over CaH_2 for several days. All solvents were added with living Li polystyryl oligomers and distilled prior to use.

s-BuLi/1,3-DIB Addition Reaction. Solvent, *s*-BuLi, and then 1,3-DIB were added under an inert atmosphere into a previously flamed glass reactor equipped with rubber septa connected through tight stopcocks. Syringes and stainless steel capillaries were used in order to transfer liquid chemicals. The reaction temperature was controlled in a thermostated water bath, and the reaction mixture was mixed with a magnetic stirrer. The reaction was terminated by addition of methanol (previously flushed with nitrogen).

Kinetic Experiments. Kinetics of the *s*-BuLi/1,3-DIB reaction was studied in cyclohexane or benzene solution, by using the *s*-BuLi to 1,3-DIB (2/1 molar ratio) reaction product in a temperature range from 20 to 70 °C. Samples were picked from the reaction medium at various times. The organo-lithium species were analyzed by GC with a Perkin-Elmer 8600 gas chromatograph by using nitrogen as a carrier and 1,3-diisopropylbenzene in cyclohexane as a reference.

Figure 1. SEC analysis of 1,3-DIB oligomers initiated by *s*-BuLi (*s*-BuLi/1,3-DIB = 1/10 molar ratio; 50 °C; cyclohexane).
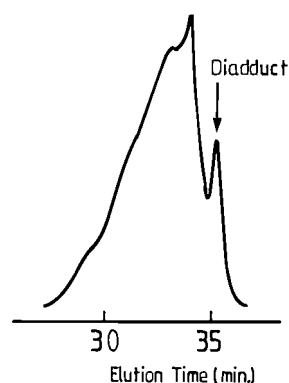
Polymerization and Characterization. A well-known amount of monomer was slowly added to the initiator solution of a known concentration at 0 °C, under nitrogen. The reaction mixture was kept at 50 °C for 4 h when styrene was polymerized or overnight for the butadiene polymerization.

Size exclusion chromatography (SEC) was carried out in THF at 40 °C with a Hewlett-Packard 1090 liquid chromato-graph equipped with four columns (10^5, 10^3, 500, and 100 Å) and a HP 1037 A refractive index detector. Polystyrene standards were used for calibration. All NMR spectra were recorded with a Bruker AM 400 superconducting magnet system operating in the FT mode at 100.6 MHz (^1H) and 155.5 MHz (^7Li), using a deuterium lock. ^1H chemical shifts were referred to $(CH_3)_4Si$, and ^7Li NMR shifts, to a 0.2 M LiCl solution in D_2O. *s*-BuLi and 1,3-DIB solutions in cyclohexane were added with ca. 10% C_6D_6 as an internal lock under nitrogen at a low temperature, then transferred into NMR tubes, and degassed by freeze-thaw cycles before sealing the tubes under vacuum. GC-MS data were recorded with a HP 5890-VGAUTOSPEC Q.

Figure 2. ^{1}H-NMR analysis of 1,3-DIB oligomers initiated by *s*-BuLi (*s*-BuLi/1,3-DIB = 1/10 molar ratio; 50 °C; cyclohexane).
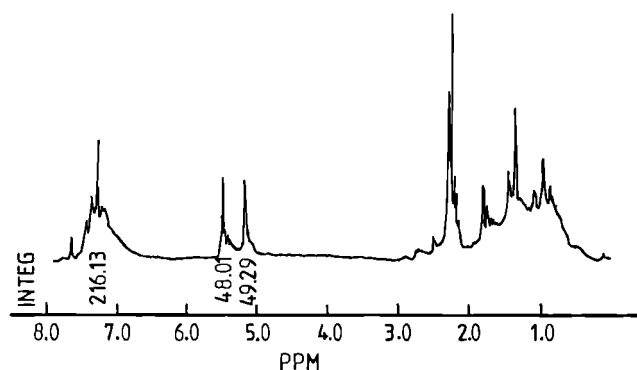
Results and Discussion

Ceiling Temperature of 1,3-Diisopropenylben-zene. The anionic polymerization of 1,3-DIB in THF at a low temperature has been reported by Rempp et al.[15] who claimed a reversible propagation with a ceiling temperature close to room temperature. This reversibility was advantageously used for the synthesis of a supposedly difunctional anionic initiator.[6,9] However, it has been observed in this study that the anionic polymerization of 1,3-DIB takes place even at 50 °C in cyclohexane, which indicates that the ceiling temperature of 1,3-DIB is higher. Actually, when 1,3-DIB is added with an anionic initiator, such as *s*-BuLi (1,3-DIB/*s*-BuLi in a 10/1 molar ratio), in cyclohexane solution at 50 °C, the reaction mixture turns red and the viscosity gradually increases, although no gel is formed even after 20 h. The reaction product is recovered after deactivation by solvent evaporation and drying at 100 °C under high vacuum for 48 h in order to remove the possibly unreacted 1,3-DIB. A precipitation technique is disregarded because low molecular weight compound might be lost. A poly(1,3-DIB) sample withdrawn after 20 h of reaction shows an SEC trace and an ^{1}H-NMR spectrum comparable to the sample withdrawn after 1 h, as shown in Figures 1 and 2. SEC analysis shows a markedly broad molecular weight distribution, which indicates that the propagation rate is not slower than the initiation rate. The ^{1}H-NMR spectrum exhibits resonance peaks at 5.10 and 5.40 ppm, characteristic of the vinylidene protons of the pendant isopropenyl groups. From the relative intensities, it is concluded that there is an average of one double bond per monomeric unit (0.9 per monomeric unit). This result is in agreement with the observation by Rempp et al. in THF at -30 °C.[15]

SEC and ^{1}H NMR analysis shows that the MW of the oligomers and the amount of unreacted vinyl groups do not change beyond 1 h of reaction, even for a long period of time. This observation indicates that the active oligomers do not react with the pendant olefin groups and that no grafting reaction takes place in cyclohexane. Gelation is never observed even though the reaction is performed overnight, stating that the reactivity of the pendant double bonds in cyclohexane is lower than in THF where gelation occurs when the reaction mixture is kept at -30 °C for some time.[15] That one isopropenyl group per 1,3-DIB molecule is left unreacted also confirms that the reaction rate of *s*-BuLi with the pendant isopropenyl group is much smaller than the initiation and propagation rates. In the case of 1,4-DIB, the reaction rate constant of the pendant double bond is smaller by ca. 3-4 orders of magnitude than the propagation rate constant of the monomeric analogue.[16] Reaction of ca. 10 mol % of a second isopropenyl group is thought to be consistent with the formation of a diadduct rather than the reaction of pendant double bonds of oligomers for steric hindrance reasons (Figure 1).

As a first piece of information, 1,3-diisopropenylben-zene can be anionically polymerized even at 50 °C in cyclohexane. The formed poly(1,3-DIB) is substituted by ca. one double bond per monomeric unit, and the ceiling temperature must be somewhat higher than 50 °C, in agreement with the reported T_c value for the 1,4-isomer (49.0 ± 5 °C).[16]

Copolymerization of 1,3-DIB with Styrene. Co-polymerization of styrene and 1,3-DIB has been initiated by *s*-BuLi at room temperature in cyclohexane (styrene/1,3-DIB = 1/1 in volume). The originally yellow

color of the reaction medium turns to red during polymerization, which might be the signature for a sequential polymerization. This expectation is confirmed by the lack of unsaturated vinylidene groups in the polymer formed in the early stages of the reaction. The characteristic NMR signals of the vinylidene protons of the isopropenyl group are only detected in samples withdrawn from the reaction mixture after the color has changed, i.e. after quantitative styrene conversion. The SEC trace of these samples (Figure 3) shows that a coupling reaction of the growing chains occurs as a result of the difunctionality of 1,3-DIB. The molecular weight of the longest chains is 3 times as high as the shortest chains, which would indicate that three-arm star-shaped macromolecules are formed as a result of a grafting reaction on DIB oligomers. This reaction would be restricted to a few pendant double bonds because of steric hindrance effects. When copolymerization of styrene and 1,3-DIB is performed in a sequential way, i.e., addition of 1,3-DIB after complete styrene polymerization, a trace of star-shaped or branched molecule is formed in the early stage of copolymerization (Figure 4).

Figure 3. SEC analysis of the styrene/1,3-DIB polymerization product recovered 30 min after the color change (styrene/1,3-DIB = 1/1 (v/v); styrene/*s*-BuLi molar ratio = 20; room temperature; cyclohexane).
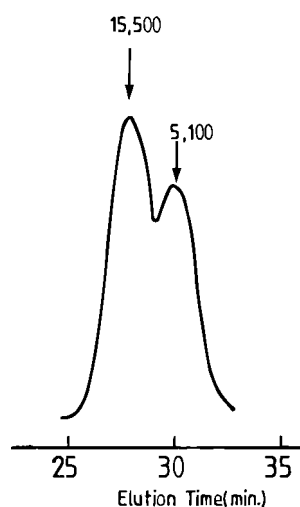

Figure 4. SEC analysis of the styrene/1,3-DIB polymerization product (styrene/1,3-DIB = 1/1 (v/v); room temperature; cy-clohexane): (a) PS before 1,3-DIB addition; (b) 5 min after 1,3-DIB addition.
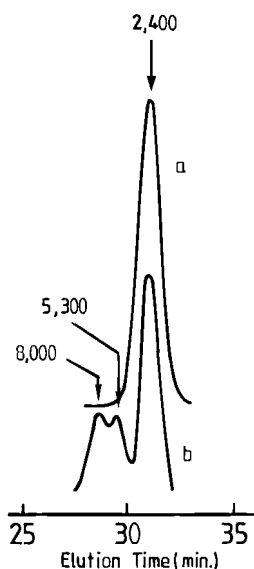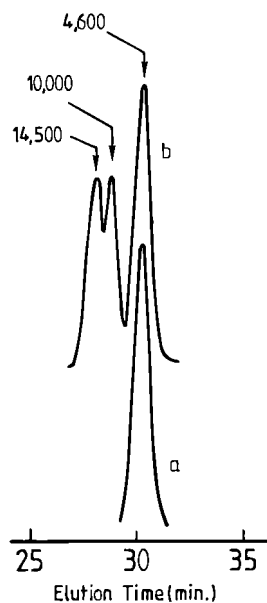

Figure 5. SEC analysis of coupled polystyrene (1,3-DIB/PS-Li molar ratio = 1/2; 60 °C, 1 h in cyclohexane): (a) original PS; (b) coupled PS.

According to Rempp et al.[6] only few star-shaped macromolecules are formed, i.e. less than 5% when a solution of monofunctional "living" polystyrene in benzene is added with 1,3-DIB and kept for 2 h at 40 °C. These authors claimed the restricted propensity of 1,3-DIB to polymerization under these conditions. Similar experiments have been carried out in cyclohexane for 1 h at 60 °C, and the final polymer has been characterized by SEC. Figure 5 shows elution peaks that correspond to chains of a molecular weight 2 and 3 times higher than the parent "living" polymer; at least 50% PS-Li are involved in coupling reactions (based on relative SEC peak areas).

Kinetics of the Addition Reaction of *s*-BuLi onto 1,3-DIB. The addition reaction of *s*-BuLi onto 1,3-DIB is quite complex, since the two double bonds of 1,3-DIB are reactive in anionic polymerization, the propagation rate of which is comparable with the initiation rate, as previously mentioned. Rempp et al.[17] have reported on the kinetics of this addition reaction and proposed a scheme which does not take into account the consumption of 1,3-DIB during propagation, since it is assumed that a pure diadduct is the main product of the addition reaction. In this study, the conversion of 1,3-DIB has been measured by gas chromatography by using 1,3-diisopropylbenzene as a reference. Several experiments have been carried out under the conditions used for the synthesis of difunctional initiator, i.e. mixing of 1,3-DIB and *s*-BuLi in a 1/2 molar ratio, in cyclohexane or benzene, at a concentration of ca. 10^{-2} mol,L^{-1} and in the temperature range from 20 to 70 °C. Figure 6a shows the time dependence of the 1,3-DIB conversion. The reaction of 1,3-DIB and *s*-BuLi is very slow at room temperature in cyclohexane, and no precipitation is observed. Raising the temperature increases the reaction rate, which is much higher in benzene than in cyclohexane. Figure 6b shows ln $[M]/[M]_0$ vs time plots at various temperatures (20-70 °C) in cyclohexane. The rate constant k is calculated from the slope of the straight lines and plotted as ln k vs $1/T$. Figure 6c is linear and leads to a reasonable activation energy of 17.5 kcal/mol.

Structure of the *s*-BuLi/1,3-DIB Adduct. The actual structure of the BuLi/DIB adduct is a matter of controversy.[6,12,13] Rempp and co-workers report that the addition of 2 mol of *s*-BuLi onto 1 mol of 1,3-DIB contains one pendant double bond per aromatic ring.[6] Thus, the monoadduct would be formed rather than the expected diadduct, and the second *s*-BuLi molecule would react only when the monomer is added to the initiator solution. In sharp contrast, Cameron et al.[12] have not detected an NMR signal for residual unsat-urations in the isolated products. Even when equimolar amounts of 1,3-DIB and *s*-BuLi are reacted, no olefin signal is observed in the final product. Conversely, higher molecular weight materials are detected by SEC, which indicates that oligomerization occurs during the addition reaction. In addition to these oligomers, small amounts of compounds of a molecular weight smaller than the Bu_2-DIB diadduct (particularly when the molar 1,3-DIB/*s*-BuLi ratio is 1) are observed and assigned to unreacted 1,3-DIB and to the monoadduct. Cameron et al.[12] have proposed the following structure for the oligomers:[12]
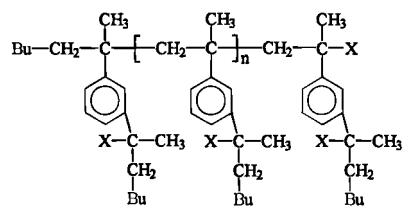
where X = Li or H.

Hogen-Esch et al.[13] have reported similar results; i.e. no olefin bond is detected by ^{1}H-NMR for product formed when *t*-BuLi is added to 1,3-DIB in a 2/1 molar ratio in benzene at 50 °C for 1 h. These authors do not, however, mention formation of oligomers.

Figure 6. (a) Kinetics of the addition reaction of *s*-BuLi onto 1,3-DIB (2/1 molar ratio), in cyclohexane at 70 °C($\triangle$), 50 °C (○) , 35 °C(□), and 20 °C(▲)and in benzene at 20 °C(●). (b) Plot of ln [M]/[M]$_0$ vs time at 20, 35, 50, and 70 °C, in cyclohexane. (c) Plot of ln k vs 1/T (solvent: cyclohexane).
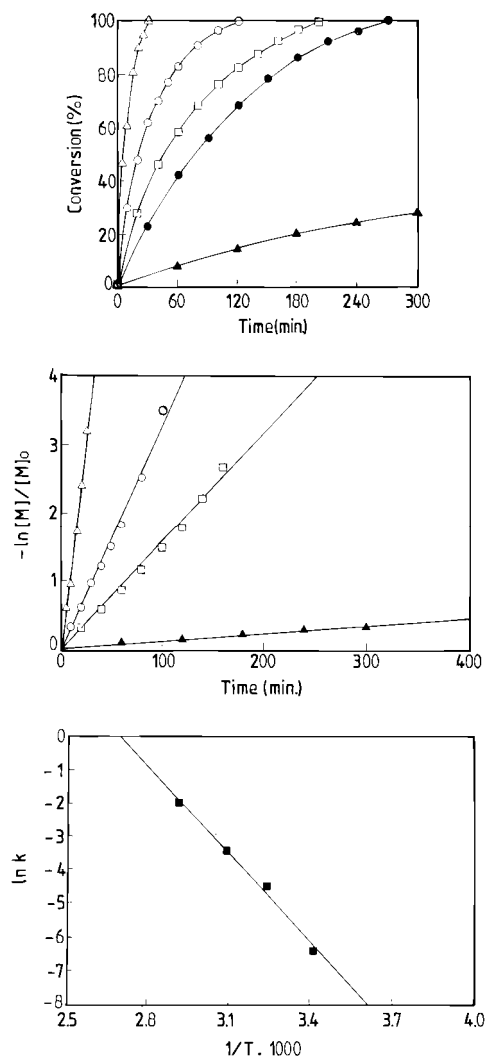
Due to the lack of consistency in the experimental observations reported up to now the addition reaction has to be reexamined. Thus, 2 equiv of *s*-BuLi has been reacted with 1,3-DIB at 20 °C in cyclohexane, and

the products withdrawn at different time intervals have been characterized by SEC, as shown in Figure 7. Oligomerization occurs in the very early stages of the reaction. On the basis of a calibration with polystyrene standards, the apparent molecular weights for each peak in Figure 7 are in good agreement with the diadduct, the dimer, the trimer, and the hexamer, respectively. After 5 min, the reaction product is a mixture of diadduct, dimer, and trimer, whereas the hexamer is detected for a longer reaction time. The reaction rate of *s*-BuLi with 1,3-DIB is very slow at 20 °C in cyclohexane, since ca. 10 mol % 1,3-DIB are consumed after 1 h (Figure 6a). Figure 7 shows that the molecular weight of the *s*-BuLi/1,3-DIB adduct increases up to a maximum value as 1,3-DIB is consumed. After an overnight reaction, the molecular weight remains essentially constant although most of 1,3-DIB has reacted (Figure 7c,d). This observation suggests that a quasi equilibrium is reached under these conditions.

The same development is observed when the reaction is carried out at 50 °C, since the molecular weight increases within 10 min up to a constant value. When 1,3-DIB is completely consumed (after 2 h), the molecular weight starts to decrease. Figure 8 shows that after 20 h at 50 °C, the high molecular weight component tends to disappear and the reaction product mainly consists of the diadduct and a dimer. The oligomer depolymerization is faster when the temperature is increased.

When 1,3-DIB is added to 2 mol equiv of *s*-BuLi at -30 °C in a dilute toluene solution, the molecular weight increases with time. If, 3 h later, the reaction temperature is increased to 20 °C and kept constant for an additional 1 h, the hexamer essentially disappears. When the temperature is further increased up to 50 °C for 1 h, the molecular weight continues to decrease and the relative content of the trimer is significantly reduced (Figure 9). A parallel ^{1}H-NMR analysis shows that vinylidene groups remain unreacted in the early stages of the reaction, although their relative content is much less than one per aromatic unit. If the reaction time is long enough, these double bonds are no longer detected. Unreacted olefin bonds are also observed by ^{1}H-NMR when equimolar amounts of *s*-BuLi and 1,3-DIB are reacted even for 1 day at 20 °C. In contrast, no unsaturated olefin group is detected in the addition product of 1.5 mol *s*-BuLi/mol of 1,3-DIB. In these two experiments where the *s*-BuLi/1,3-DIB molar ratio is less than 2, oligomerization is the dominant reaction.

Figure 7. SEC analysis of 1,3-DIB oligomers (*s*-BuLi/1,3-DIB molar ratio = 2; 20 °C; in cyclohexane): (a) after 5 min; (b) after 30 min; (c) after 60 min; (d) overnight reaction.
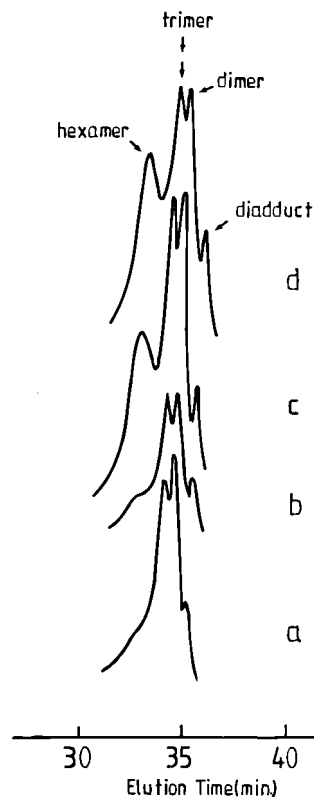

Figure 8. SEC analysis of 1,3-DIB oligomers (*s*-BuLi/1,3-DIB molar ratio = 2; 50 °C; in cyclohexane): (a) after 1 h; (b) after 20 h.
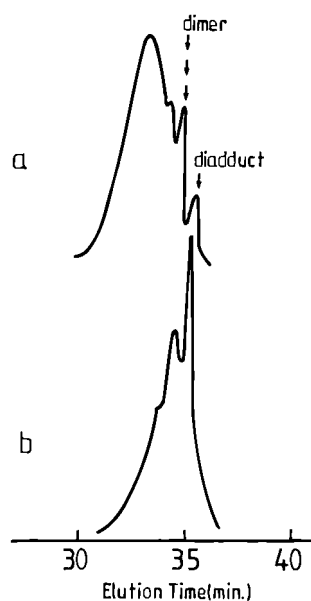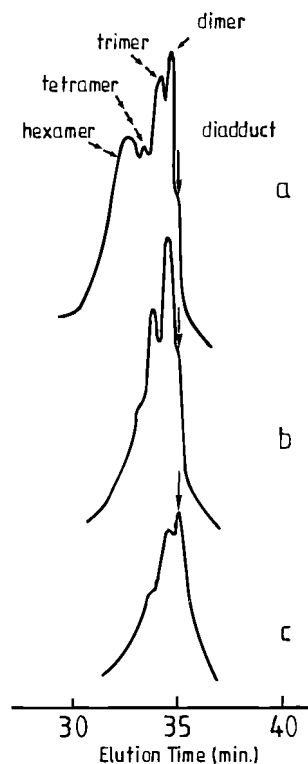
Figure 9. SEC analysis of 1,3-DIB oligomers (*s*-BuLi/1,3-DIB molar ratio = 2; toluene): (a) after 3 h at -30 °C; (b) one additional hour at room temperature; (c) one additional hour at 50 °C.


⁷Li-NMR Spectrum of the *s*-BuLi/1,3-DIB Adduct.

If oligomerization occurs when 2 mol of *s*-BuLi are reacted with 1 mol of 1,3-DIB, there should be as many unreacted *s*-BuLi molecules as 1,3-DIB molecules in the oligomers. Although the oligomer formation has been confirmed by SEC, no evidence has been reported yet for unreacted *s*-BuLi. For this purpose, reaction of *s*-BuLi with 1,3-DIB in a 2/1 molar ratio in cyclohexane, at room temperature and 50 °C, respectively, has been analyzed by ⁷Li-NMR. The ⁷Li-NMR spectrum of *s*-BuLi shows a sharp peak at -1.0 ppm, and a new set of resonances appears when 1,3-DIB is added (Figure 10). These additional signals are consistent with polymetalated oligomers. The relative peak area for these oligomers increases with reaction time at the expense of the *s*-BuLi signal. However, even when 1,3-DIB has been completely consumed, ca. 30% of the original *s*-BuLi remains unreacted.

Mechanism of the BuLi/1,3-DIB Reaction. The experimental results indicate that the complex reaction of *s*-BuLi with 1,3-DIB proceeds through three main steps. After an initial increase in molecular weight, a mixture of diadduct and oligomers is formed, the average molecular weight of which remains essentially unchanged until the complete consumption of 1,3-DIB. Then, the molecular weight decreases with reaction time.

The formation of oligomers may be sketched out as follows:
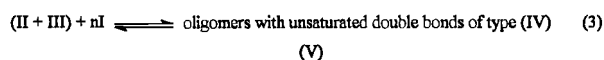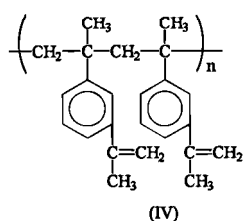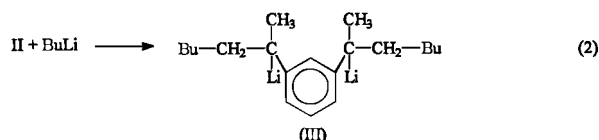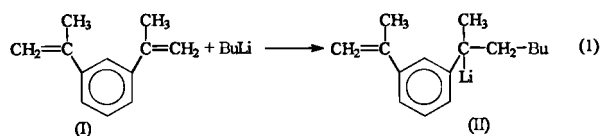
Reaction 3 predominantly occurs when 1,3-DIB is used in excess. Reactions 2 and 4 become dominant in the case of an excess of *s*-BuLi. Under the conditions used for the synthesis of the dilithium adduct, reactions 1 and 3 are faster than reactions 2 and 4 in the early stage, so that vinylidene groups are detected in the ^{1}H- NMR spectrum of the reaction product. When most 1,3-DIB is consumed, reactions 1 and 3 become slower than reactions 2 and 4, which accounts for a small content in unsaturated double bonds for the products formed in the later reaction stage.

α-Methylstyrene (AMS) is also known for a living equilibrium polymerization, which releases a monomer prone to be again polymerized. In contrast, depolymerization of poly(1,3-DIB) is expected to release a lithium monoadduct (II) instead of the monomer. The monoadduct can either initiate the 1,3-DIB polymerization or add *s*-BuLi to form a diadduct (III) or react with a multimetalated oligomer or with a lithium diadduct with formation of another oligomer or a dimer. On the whole, the addition reaction of 1,3-DIB and *s*-BuLi is a quasi equilibrium process. In the early stages, the propagation rate is faster than depropagation, which leads to an increase in molecular weight. When a quasi equilibrium is reached between the depropagation releasing a monoadduct and the propagation of the 1,3-DIB monomer, the molecular weight of the oligomers remains constant. After all 1,3-DIB monomer has been consumed, the molecular weight of oligomers decreases, as controlled by the depropagation alone.

Figure 10. ^{7}Li-NMR analysis of organolithium compounds in cyclohexane: (a) *s*-BuLi at room temperature; (b) *s*-BuLi/1,3-DIB in 2/1 molar ratio at 25 °C for 8 days; (c) *s*-BuLi/1,3-DIB in 2/1 molar ratio at 50 °C for 2 h.
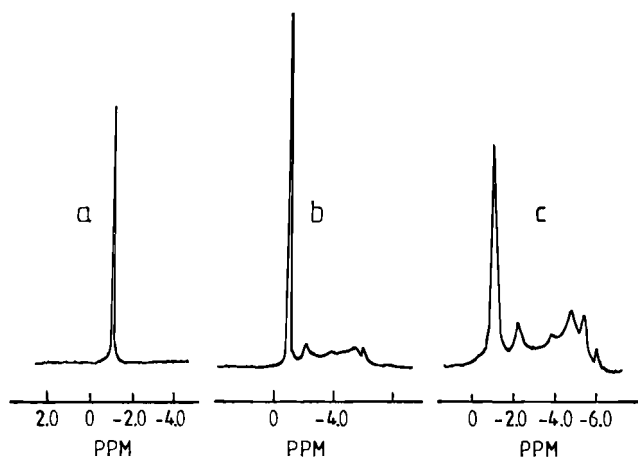

Figure 11. SEC analysis of polystyrene initiated by a *s*-BuLi and (α-methylstyryl)Li mixture in a 1/1 molar ratio, in cyclohexane, at 25 °C ($M_n = 2900$; $M_w/M_n = 1.05$).
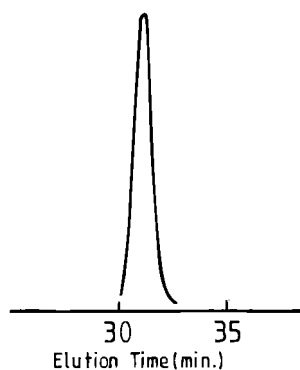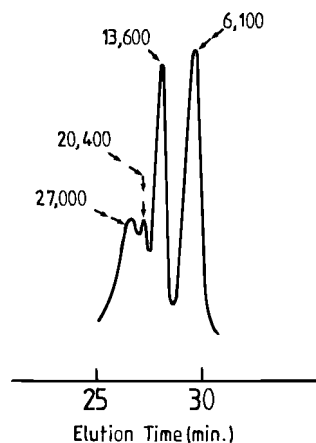

Figure 12. SEC analysis of polystyrene initiated by *s*-BuLi/ 1,3-DIB in a 2/1 molar ratio (in THF at -78 °C).

Initiation Mechanism of Butadiene Polymerization by the *s*-BuLi/1,3-DIB Adduct. Although it is clear that the *s*-BuLi/1,3-DIB adduct solution is a mixture of unreacted *s*-BuLi, diadduct, and oligomers, the anionic polymerization of, e.g., polybutadiene leads to chains of a low polydispersity, in apolar solvents.[1] Rempp et al.[9] have claimed that the "diadduct solution" could be used to initiate anionic polymerization as soon as 60% of the double bonds of 1,3-DIB have reacted with *s*-BuLi. In spite of the presence of oligomers, the "diadduct solution" behaves as if it only contains a pure diadduct. These authors have not explained why, upon the monomer addition, the oligomers rapidly disappear and quantitatively contribute to the initiation process as diadducts. Cameron et al.[12] have proposed that the initiation by *s*-BuLi would be faster compared to species lithiated at a benzyl position and that initiation by polyfunctional materials

would be as slow as the degree of polymerization would be high for reasons of steric hindrance. Thus a marked inverse relationship between functionality and initiation rate would explain a narrow molecular weight distribution. In order to give credit to this hypothesis, we have prepared a mixture of *s*-BuLi and species lithiated at the benzyl position, i.e. the reaction product of *s*-BuLi and α-methylstyrene used in a 1/1 molar ratio. This mixture has been used to initiate anionic polymerization of styrene in cyclohexane. If the initiation by *s*-BuLi is faster than that by the (benzyl)-Li species, a bimodal or at least a broad molecular weight distribution should be observed. Actually, the distribution is unimodal and narrow (Figure 11), in complete disagreement with the hypothesis by Cameron et al.

As an additional piece of information, a multimodal distribution is observed when polymerization is initiated by the *s*-BuLi/1,3-DIB adduct in a polar solvent such as THF. Figure 12 shows well-resolved elution peaks that correspond to species of regularly increasing molecular weights (relative ratios of 1, 2, 3, and 4). They would correspond to oligomers initiated by monofunc-tional, difunctional, trifunctional, and tetrafunctional species, thus present in the *s*-BuLi/1,3-DIB adduct solution. This observation supports that all these initiating species have the same initiation rate independently of possible steric hindrance.

Rempp et al. have also proved a functionality of 2 for the "living" chains initiated by the "*s*-BuLi/1,3-DIB adduct solution" in benzene.[9] Hogen-Esch et al. have reached a similar conclusion.[13] A reasonable explanation of the fact that a mixture of multifunctional initiators selectively forms difunctional living chains is that the 1,3-DIB oligomers are rapidly depolymerized upon the monomer (e.g. butadiene) addition. This addition would thus have an effect quite comparable to that of an increasing reaction time or temperature. In order to strengthen this explanation, butadiene was added to an "adduct solution" in cyclohexane at room temperature, and samples have been withdrawn after 30 min and 20 h, respectively, and deactivated by acidified methanol. SEC analysis (Figure 13) shows that, after 30 min, the high molecular weight components in the original adduct have disappeared, indicating that the oligomer depolymerization is much faster than the butadiene propagation at 25 °C. Furthermore, the experimental molecular weight of the final polybutadiene is in good agreement with the theoretical value calculated from the relative amounts of butadiene and 1,3-DIB. The additional observation of a unimodal and narrow molecular weight distribution for polybutadiene strongly supports that the diadduct is selectively responsible for the initiation reaction.

It might be argued that the low molecular weight peak observed after the monomer addition results from initiation by *s*-BuLi and propagation. As a convincing evidence of the oligomer depolymerization, diphenyl-ethylene (DPE), i.e. a nonpolymerizable monomer, has been added to the "adduct solution" instead of butadiene, all the other experimental conditions being the same. Figure 14 clearly shows the complete disappearance of the high molecular weight components and the formation of a unique low molecular weight species as a result of the DPE addition. In contrast to the ^{1}H-NMR spectrum of the *s*-BuLi/1,3-DIB adduct, which shows very broad resonance signals, consistent with a nonmonomeric structure, much narrower resonance signals are observed for the product formed after the DPE addition (Figure 15).

If the *s*-BuLi/1,3-DIB diadduct is formed as a result of the oligomer depolymerization, then the reaction of this diadduct with DPE results in a monomeric compound, which may have structure I or II after deactivation, depending on the addition of one or two DPE molecules.

We have previously reported[1] that the diadduct behaves as a monofunctional initiator in apolar solvents.
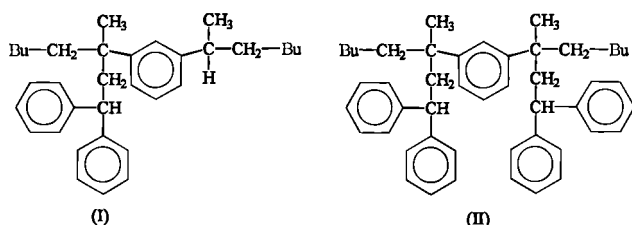
If it is so, the monomeric compound would display structure I. The ^{1}H-NMR spectrum of the product recovered after the DPE addition exhibits four resonance groups. Group A in the range 6.8-7.2 ppm is asssigned to the aromatic protons of DIB and DPE. Signal B at 3.9 ppm corresponds to the benzylic proton of DPE. Signal C at 2.5 ppm is attributed to the methylene protons of DPE. Group D in the range 0.4-2.2 ppm corresponds to the aliphatic protons of DIB and the butyl group. If the monomeric compound corresponds to structure I, the proton ratio for these four resonance groups should be A/B/C/D = 14/1/2/29 and for structure II A/B/C/D = 12/1/2/14. The experimental ratio turns out to be A/B/C/D =

15.3/1.0/2.2/29.2, which strongly supports structure I. This structure has been further confirmed by GC-MS. Figure 16 leads to a molecular mass of 454, in line with structure I.

Figure 13. SEC analysis of the *s*-BuLi/1,3-DIB adduct in cyclohexane, after butadiene addition at 25 °C: (a) *s*-BuLi/ 1,3-DIB adduct; (b) 30 min after BD addition; (c) 20 h after BD addition (MW$_{cal}$ = 1400, MW$_{exp}$ = 1500).
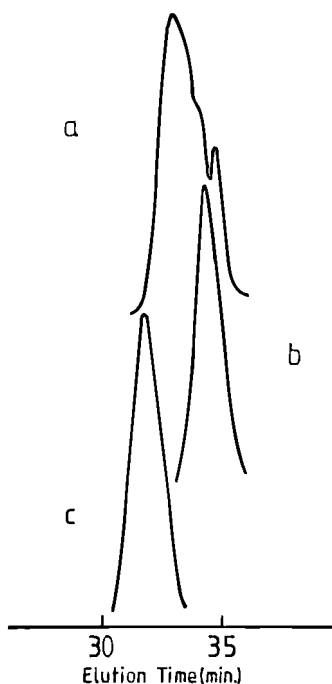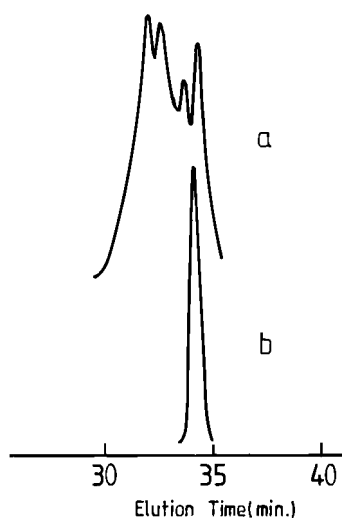

Figure 14. SEC analysis of the addition product of *s*-BuLi onto 1,3-DIB in a 2/1 molar ratio at 50 °C in toluene for 2 h and of the reaction product with DPE at 50 °C for 20 h: (a) *s*-BuLi/1,3-DIB adduct; (b) reaction product with DPE.

A comparable behavior can be observed for α-meth-ylstyrene oligomeric anions, which depolymerize upon the addition of styrene. α-Methylstyrene has been first added with *s*-BuLi (AMS/*s*-BuLi = 6) in THF at -78 °C for 30 min. Upon addition of styrene, the color of the solution changed at once from deep red (characteristic of the α-methylstyrene anion) to yellow (characteristic of the styryl anion). After ca. 10 min, the deep red color is again observed. This change in color has been repeated 7 times upon addition of styrene. Since this phenomenon can be repeated so many times, even for an initial α-methylstyrene/BuLi molar ratio as low as 6, the hypothesis of residual α-methylstyrene monomer has to be disregarded. In this respect, Worsfold and Bywater have indicated that α-methylstyrene is completely converted into polymer at -78 °C.[18] According to these observations (see also refs 19 and 20), it must be assumed that the α-

methylstyrene that end-caps the living (polystyryl)Li chains around -78 °C results either from the partial conversion of α-methylstyrene when added with *s*-BuLi or from the depropagation of the oligo(R-methylstyrene) anion in agreement with the observations reported for the *s*-BuLi/1,3-DIB adduct in this study.

Figure 15. ^{1}H-NMR analysis of the addition product of *s*-BuLi onto 1,3-DIB in a 2/1 molar ratio at 50 °C in toluene for 2 h and of the reaction product with DPE at 50 °C for 20 h: (a) *s*-BuLi/1,3-DIB adduct; (b) reaction product with DPE.
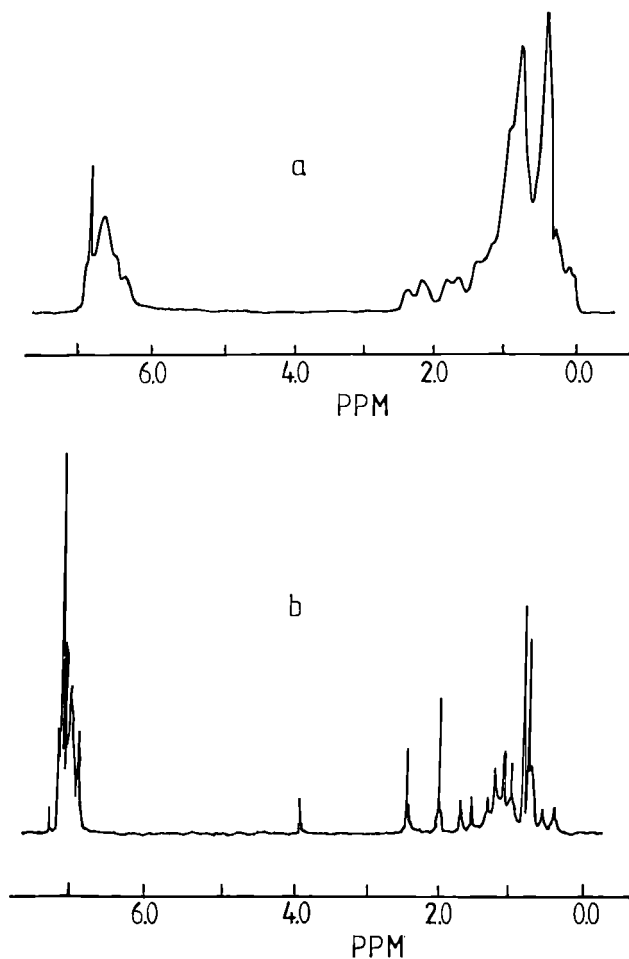

Conclusion

The ceiling temperature of 1,3-DIB is somewhat higher than 50 °C, since it can be anionically polymerized at 50 °C in cyclohexane, with formation of an oligomer that approximately bears one double bond per monomeric unit. Under the conditions used for the synthesis of a difunctional initiator, i.e. by mixing 1,3-DIB and *s*-BuLi in a 1/2 molar ratio in cyclohexane, ^{1}H NMR signals for unreacted vinylidene groups are detected for samples withdrawn in the early stage of the reaction. When the reaction time is long enough, these signals are no longer observed. ^{7}Li-NMR analysis confirms that the lithium-organic compound formed is a mixture of multilithiated species. It also shows that even when 1,3-DIB has been completely consumed, ca. 30% of *s*-BuLi remains unreacted.

The addition reaction of *s*-BuLi onto 1,3-DIB is very complex, as a result of the difunctionality of 1,3-DIB and the occurrence of competing polymerization and depolymerization reactions, that lead to a quasi-equilibrium state. In the early stage, propagation is faster than depropagation and the molecular weight increases. When the depropagation that releases a monoadduct and propagation of 1,3-DIB counterbalance each other, the average molecular weight of the oligomers is practically constant. Beyond the complete consumption of 1,3-DIB, the molecular weight decreases, since depropagation then

dominates.

Figure 16. GC-MS analysis of the reaction product of the *s*-BuLi/1,3-DIB adduct with DPE in toluene at 50 °C for 20 h.
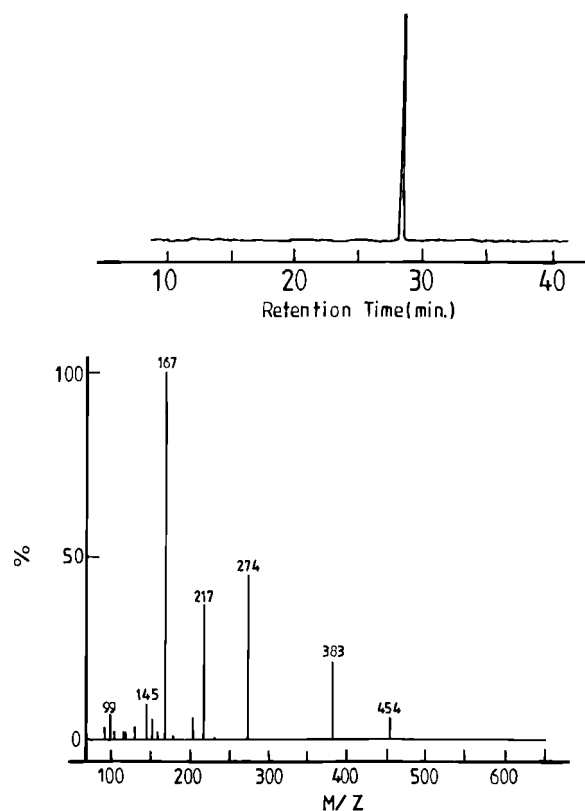
When the *s*-BuLi/1,3-DIB adduct is used as an initiator of anionic polymerization in polar solvents, such as THF, initiation by at least monofuntional, difunctional, trifunctional, and tetrafunctional species is observed. Surprisingly enough, this mixture yields polymers of a low dispersity and of a functionality of 2 in apolar solvents. A reasonable explanation is that the 1,3-DIB oligomers rapidly depolymerized upon monomer (e.g. butadiene) addition. This hypothesis has been confirmed by additional experiments with the nonpolym-erizable diphenylethylene. In an apolar solvent, a monomeric compound is formed, which is the monoaddition product of DPE to the diadduct. This conclusion agrees with our previous observations that the diadduct behaves as a monofunctional initiator in apolar solvent.[1] Activation of the second anionic site of the 1,3-DIB-Li_2 diadduct by polar additives and the perfectly controlled synthesis of triblock copolymers will be reported in the near future.[21]

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