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The synthesis of a hydrocarbon-soluble organolithium anionic initiator. A gas–liquid chromatography study of the efficiency of the reaction of *s*-butyllithium with *p*-divinylbenzene

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Abstract

The extent of conversion of the reaction between *sec*-butyllithium and *p*-divinylbenzene was evaluated by quantitative gas–liquid chromatography. The reaction of stoichiometric amounts of ultra-high purity *sec*-butyllithium with pure *p*-divinylbenzene at 0°C produces an anionic initiator, 1,4-bis(1-lithio-3-methylpentyl)benzene, **2**, in essentially quantitative yields, with low concentrations of monofunctional impurities. Upon the addition of 10 mol% excess of triethylamine to *sec*-butyllithium, the reaction of *sec*-butyllithium with *p*-divinylbenzene at 0°C yielded a homogeneous product with composition of 96% difunctionality and 4% monofunctionality, with the total disappearance of *p*-divinylbenzene as observed by GLC.

The high purity 1,4-bis(1-lithio-3-methylpentyl)benzene initiator, **2**, is an effective initiator for 1,3-butadiene polymerizations in hydrocarbon solvents and allows the synthesis of polybutadienes with microstructures ranging from 13% to 16% 1,2-vinyl content, as observed by ^{1}H NMR analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Anionic polymerization; 1,4-Bis(1-lithio-3-methylpentyl)benzene; Gas–liquid chromatography

1. Introduction

Living anionic polymerization initiated by alkyllithium compounds provide a powerful method for the synthesis of styrene and diene polymers of predictable molecular weight, narrow molecular weight distribution, controlled chain-end and in-chain functionality, copolymer composition, microstructure, stereochemistry and molecular architecture [1–5]. However, many anionic syntheses produce a complex mixture of functionalized and unfunctionalized species with controlled molecular architecture, including dimers and trimers [6,7].

The development of efficient hydrocarbon-soluble, difunctional organolithium compounds for simple, reproducible initiation in the living anionic synthesis of telechelic oligomers and polymers with controlled polymer properties was well documented. Specifically, polydienes with high 1,4-microstructure and optimal elastomeric properties are obtained [8–18]. A variety of aromatic divinyl compounds have been evaluated as precursors for the quantitative formation of hydrocarbon-soluble dilithium initiators [8–18]. The criteria for the selection of suitable dilithium compounds for the initiation of diene polymerization include (a) the rapid, quantitative reaction of stoichiometric amounts of the diolefin with organolithium compounds such as *sec*-butyllithium, (b) the low-cost preparation of precursor diolefins and dilithio initiators, (c) high solubility of the dilithium compound in hydrocarbon solvents, and (d) the rapid initiation of diene polymerization in hydrocarbon solvents to form polymers with predictable molecular weights, narrow molecular weight distribution, high 1,4-diene microstructure and quantitative difunctionalization upon reaction with electrophiles. In addition, difunctional organolithium initiators are essential for the two-step synthesis of A–B–A triblock copolymers, when the living anion of monomer A is unable to initiate the polymerization of monomer B [1–5].

High purity *p*-divinylbenzene can be employed as a precursor for the formation of difunctional organolithium initiators in anionic polymerization procedures. However, many reports discuss the reactions of *s*-butyllithium with mixed isomers of divinylbenzene, consisting of 71% of

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m-divinylbenzene and 15% *p*-divinylbenzene. Rempp and coworkers [14] found that the stoichiometric reaction of two moles of *sec*-butyllithium with mixed isomers of divinylbenzene (71% *m*-divinylbenzene, 15% *p*-divinylbenzene) in benzene produced a pure, useful, hydrocarbon-soluble, dilithium initiator for diene polymerizations. The observed rate of reaction of the *m*-isomer was greater than that of the *p*-isomer and no trifunctional and tetrafunctional impurities were formed. In contrast, Bandermann and coworkers [12] reported that oligomerization reactions predominate when *sec*-butyllithium is added to *m*-divinylbenzene at room temperature in hydrocarbon media in the absence of polar additive. Bifunctional initiator formation, containing some oligomers, results and an initiator system with functionality greater than two is formed. In addition, Foss and coworkers [19] reported the formation of a difunctional initiator, with overall functionality of greater than two, by the addition of *sec*-butyllithium to divinylbenzene in the presence of excess triethylamine (4/1 = TEA/Li), with concomitant increase of the 1,2-microstructure of polydienes.

The synthesis of 1,4-bis(1-lithio-3-methylpentyl)benzene from *sec*-butyllithium and *p*-divinylbenzene entails the use of ultra-high-purity reagents and high vacuum apparatus. For the formation of high purity initiator, the separation of *m*- and *p*-isomers is essential, since the *m*-isomer has higher reactivity in the preparation of the initiator in hydrocarbon media. In general, the separation and purification of *p*-divinylbenzene by chemisorption and distillation from commercially available divinylbenzene, which is a mixture of ethylvinylbenzene, *m*- and *p*-divinylbenzene with traces of diethylbenzene, gave a mixture of the *m*- and *p*-divinylbenzene in less than quantitative yields. This communication describes the quantitative synthesis of *p*-divinylbenzene and the low-temperature synthesis of an anionic initiator, 1,4-bis(1-lithio-3-methylpentyl)benzene for initiation of 1,3-butadiene polymerization using ultrapure reagents and high vacuum techniques.

2. Experimental

2.1. Chemicals

Initiator preparations, kinetic studies and butadiene polymerizations were conducted using standard high vacuum techniques with breakseals, and in an argon atmosphere glovebox [20]. Toluene was purified as described previously [20]. 1,3-Butadiene (Fluka, 98%) was stirred over freshly crushed calcium hydride at −78°C, degassed and distilled onto a succession of sodium mirrors at −23°C. The diene monomer was then freshly distilled from *n*-butyllithium at −6°C into calibrated ampoules kept at −78°C immediately before use. Triethylamine was purified by distillation from *n*-butyl-*sec*-butylmagnesium purged into calibrated ampoules prior to use.

2.2. Characterization

^{1}H NMR spectra of samples in $CDCl_3$ were recorded on Varian XL-80, Varian XL-100, Varian HA-60IL and Hitachi Perkin-Elmer R24A Spectrometers. Mass spectra were recorded on Varian MAT 311A and EAI-MS 902 Mass Spectrometers. Qualitative and quantitative separations of reaction products and purification of starting materials were carried out on a PYE Model 105 Preparative Gas Chromatograph, a Perkin-Elmer 990 Analytical Chromatograph, a Waters Liquid Chromatograph with dual U6k Injection Model 660 Programmer and a Waters Preparative Liquid Chromatograph System 500. Molecular weights of polymers were determined on a Knauer Vapour Pressure Osmometer. Infrared spectra were recorded on a Beckman Acculab 2 Infrared Spectrophotometer.

2.3. Preparation of s-butyllithium

Owing to the presence of non-initiating basic impurities

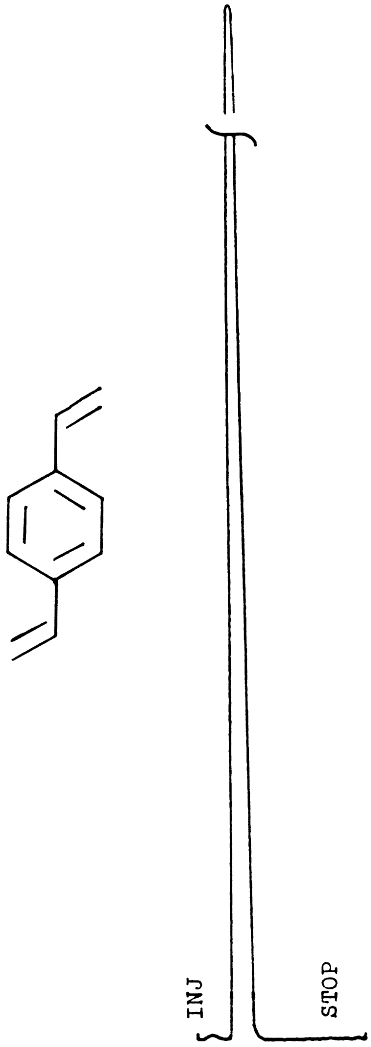
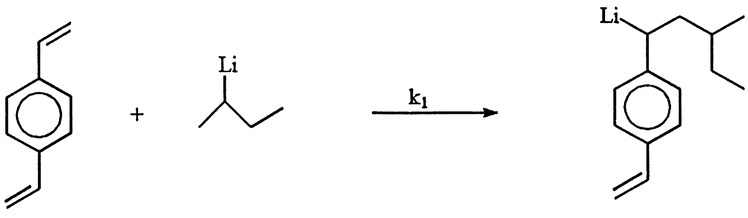


Fig. 1. The gas–liquid chromatogram for high purity *p*-divinylbenzene. Retention time: 3.76 s.

such as peroxides, alkoxides, hydroxides and hydrides which affect initiation and propagation rates and reduce *cis*-1,4 content [13], commercially available *sec*-butyllithium (Alfa Inorganics, 2.0 M in hexane) was purified to 100% purity by distillation under reduced pressure as previously described [11]. The initiator solution was subdivided into calibrated ampoules and the concentration of *sec*-butyllithium was determined by the double-titration method with 1,2-dibromoethane [21].

2.4. Isolation and purification of p-divinylbenzene

p-Divinylbenzene was isolated from commercially available 50% solution of divinylbenzene (Merck) in ethylvinylbenzene containing diethylbenzene and *m*-divinylbenzene according to the procedure outlined by Papov and Schwachula [22] with modifications. Divinylbenzene (Merck, 100 mL), toluene (100 mL), methanol (BDH, 2 mL) and hydroquinone (BDH, 0.1 g) were heated to 80°C. Anhydrous cuprous chloride (Merck, 70 g) was added to the reaction mixture, with stirring, followed by slow cooling to 25°C over a period of 4 h. The solid residue of copper–*p*-isomer complex was immediately filtered at 25°C and washed several times with toluene. The complex was decomposed by heating to 80°C in the presence of toluene (50 mL). The reaction temperature was maintained for 30 min followed by hot filtration. Concentration of the filtrate *in vacuo* gave a clear mixture with the *p*-isomer content enriched to about 90% purity. *p*-Divinylbenzene was purified by multi-step preparative gas–liquid chromatography and stabilized with *t*-butylcatechol. A 10% solution of *p*-divinylbenzene was prepared by distillation from *n*-butyl-*s*-butylmagnesium into calibrated ampoules, diluted with the appropriate solvent and stored at −23°C. Although storage at −22°C was recommended [23], polymerization was observed after 3 days at −22°C. Consequently, the



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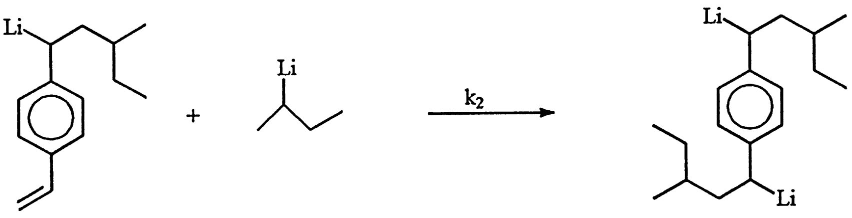

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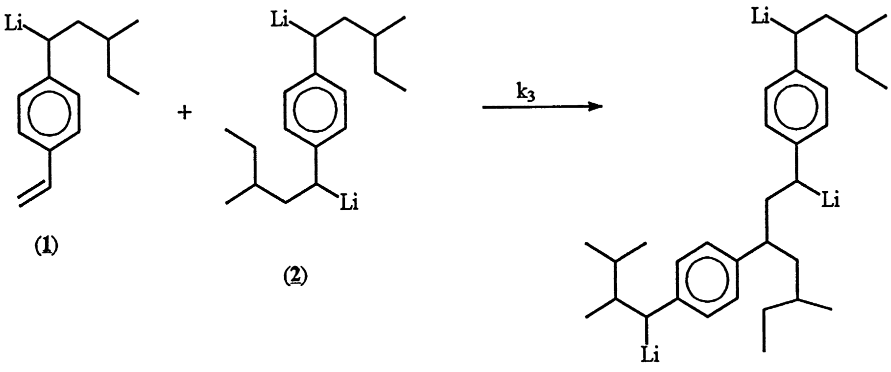

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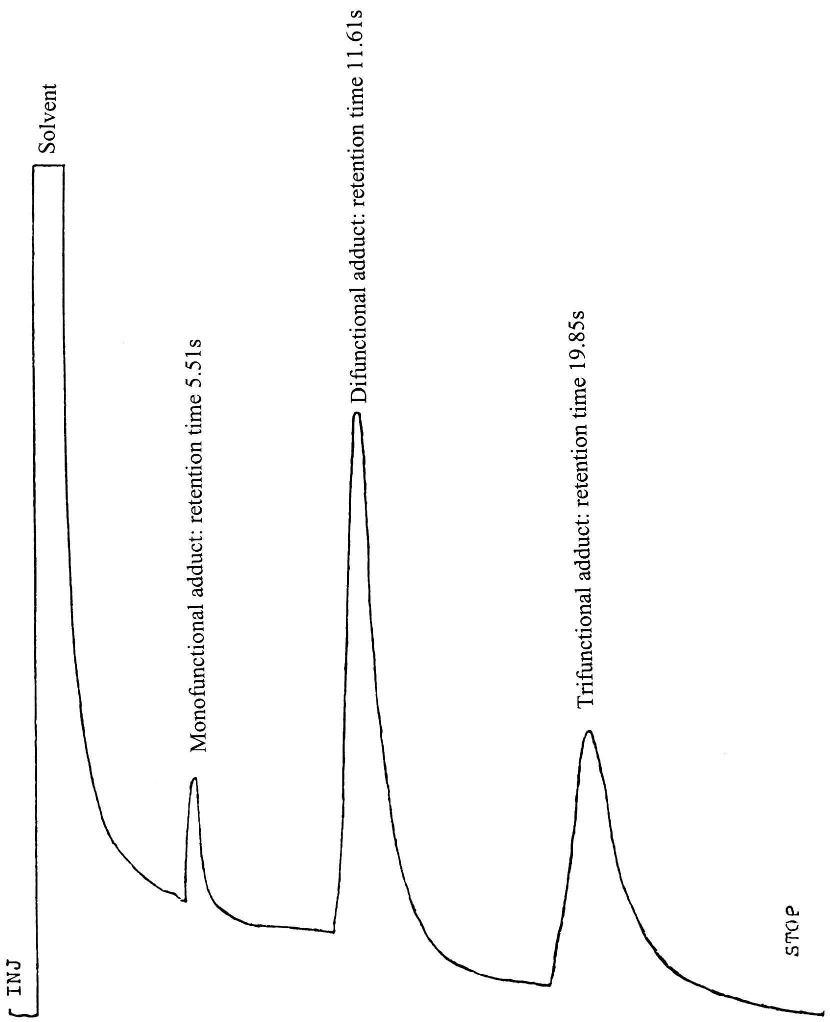

Fig. 2. The gas–liquid chromatogram of the methanolysis products of the reaction of *sec*-butyllithium with *p*-divinylbenzene in toluene at 60°C.

p-divinylbenzene was ampoulized immediately before use. GLC: one peak, retention time = 3.76 s (Fig. 1); density of *p*-divinylbenzene = 0.913 g/mL at 40°C.

2.5. Synthesis and analysis of difunctional initiator

Initiator synthesis for butadiene polymerization were performed using standard high vacuum techniques with breakseals. The addition reactions of *sec*-butyllithium with *p*-divinylbenzene in hydrocarbon media were carried out at low temperature by considering the effect of added triethylamine. The reactions were quenched with degassed methanol under nitrogen atmosphere and the products characterized by GLC. Retention times were recorded for *p*-divinylbenzene, the mono- and di-adducts as well as polyfunctional components and the peak areas and percentage composition evaluated by a HP 3380A integrator.

2.6. Polymerization

Butadiene polymerizations were carried out using standard high vacuum techniques with breakseals. In a typical procedure, high purity anionic initiator, 1,4-bis(1-lithio-3-methylpentyl)benzene, **2**, was prepared by the addition of *sec*-butyllithium to *p*-divinylbenzene in the presence of 10% molar excess of triethylamine in toluene at 0°C. Butadiene was added to the anionic initiator and the reaction was allowed to proceed for 12 h at 0°C. The yellowish colour of the polybutadienyllithium end disappears immediately after quenching the reaction mixture with dry degassed methanol. The polymer was precipitated into methanol and dried under vacuum.

3. Results and discussion

3.1. Initiator synthesis: formation of 1,4-bis(1-lithio-3-methylpentyl)benzene

In principle, since the two vinyl groups of *p*-divinylbenzene are activating groups and in conjugation with each other, the reaction of two moles of *sec*-butyllithium with *p*-divinylbenzene should proceed efficiently to produce

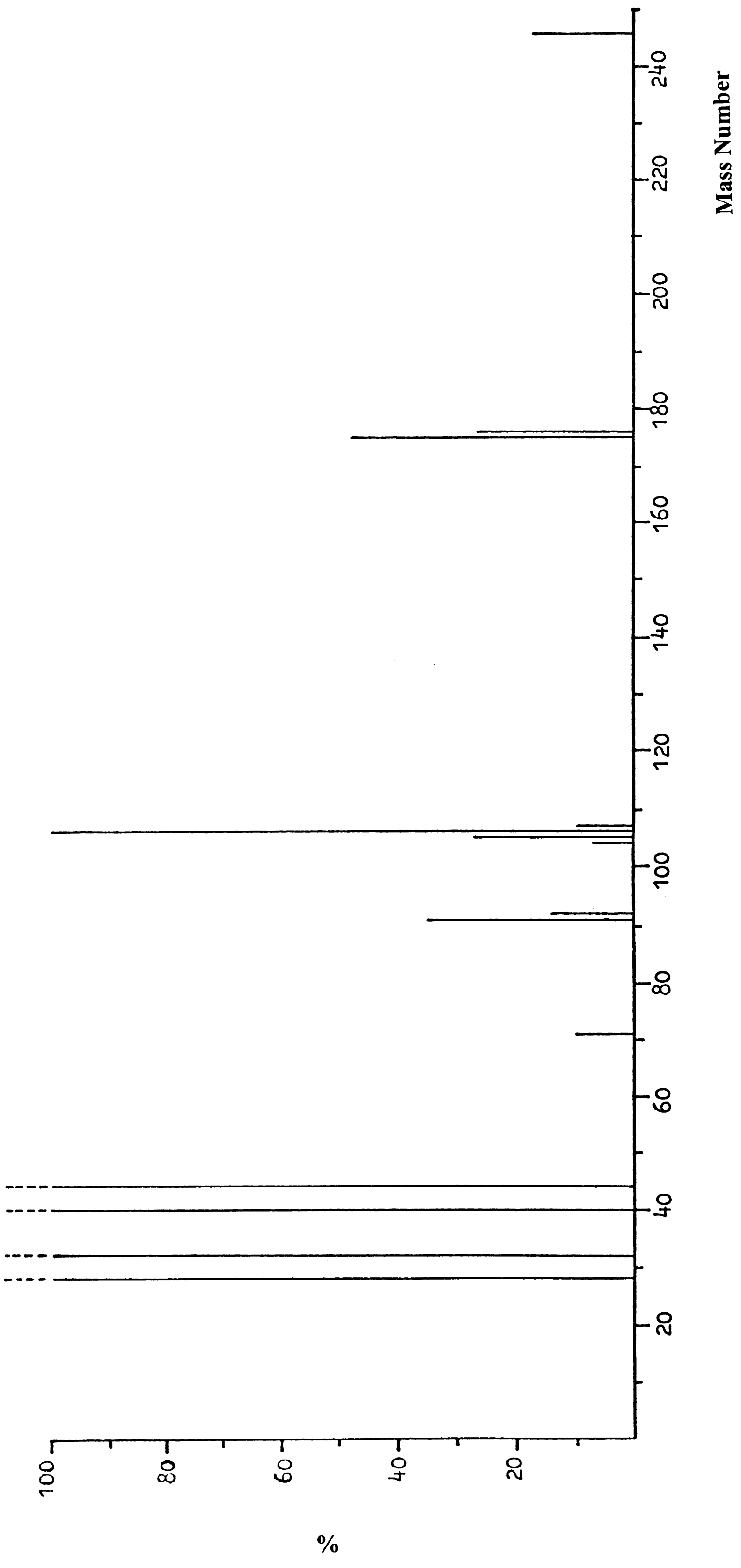

Fig. 3. Mass spectrum of the methanolysis product of **2**.

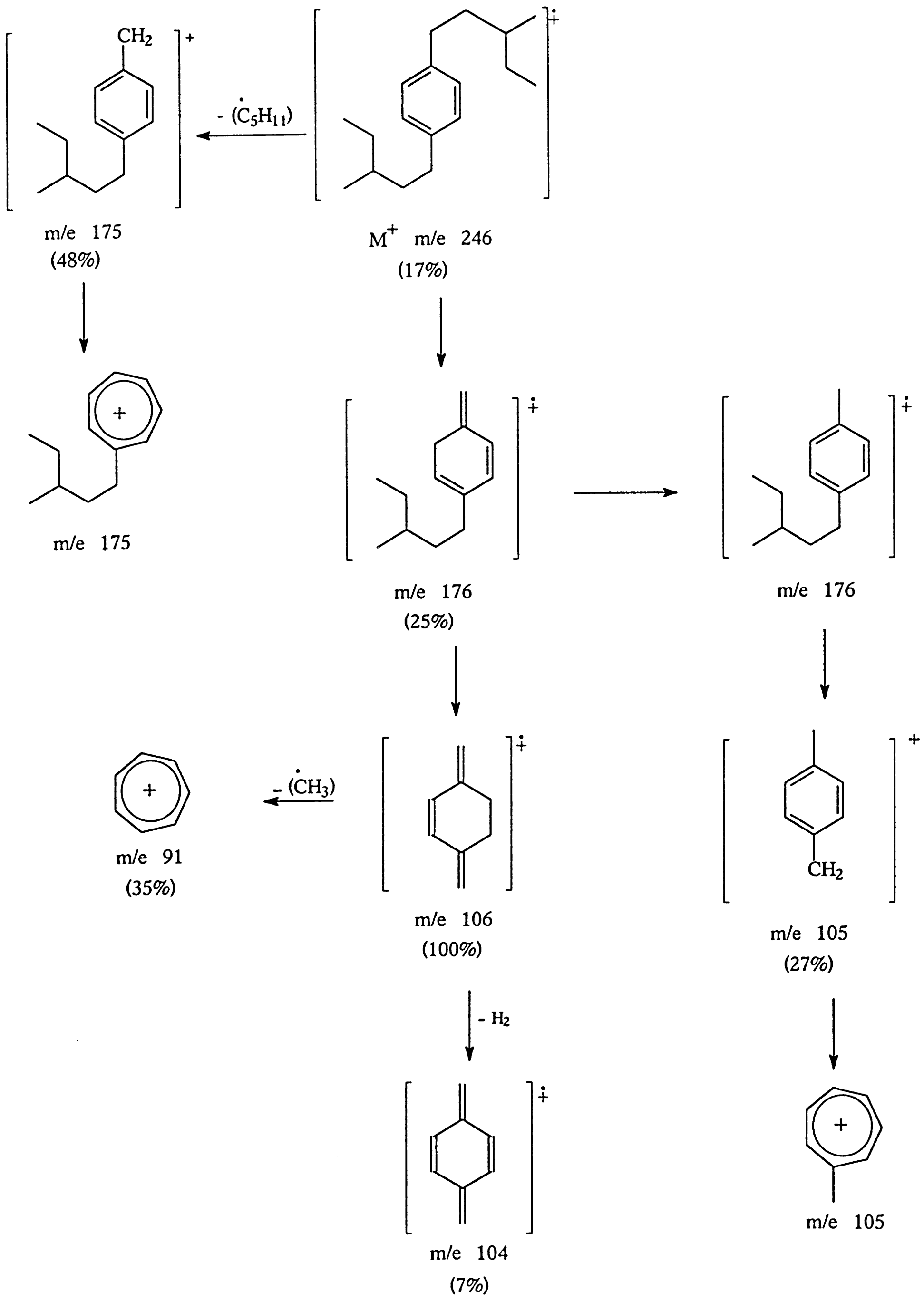

Fig. 4. Mass spectral fragmentation pattern of the methanolysis product of **2**.

the corresponding dilithium species (Eqs. (1) and (2)). Because of the resonance stabilization of the monofunctional adduct, the rate constant for the first addition, k_1, is significantly higher than the rate constant for the second addition, k_2, in hydrocarbon medium [11,14]. However, side reactions such as trifunctional initator formation is possible (Eq. (3)).

The extent of difunctional anionic initiator formation, in the absence of added polar additive, was determined by the addition of stoichiometric amounts of *sec*-butyllithium to *p*-divinylbenzene, at different temperatures, and studied by gas–liquid chromatography. The reactions were followed by the disappearance of *p*-divinylbenzene and the appearance of the methanolysis products of (a) the monofunctional species, *p*-1-lithio-3-methylpentylvinylbenzene, **1**, formed by the addition of one mole of *sec*-butyllithium to *p*-divinylbenzene, and (b) the difunctional species, 1,4-bis(1-lithio-3-methylpentyl)benzene, **2**, formed by the addition of two moles of *sec*-butyllithium to *p*-divinylbenzene. In the reaction of *sec*-butyllithium with *p*-divinylbenzene in toluene at

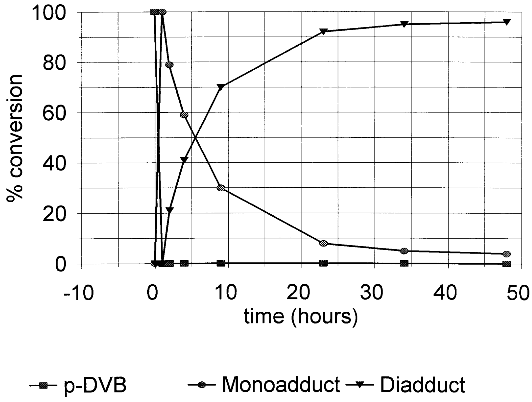

Fig. 5. Percent conversion versus time for the reaction of *sec*-butyllithium with *p*-divinylbenzene in toluene at 0°C in the presence of 10 mol% triethylamine to *sec*-butyllithium.

0°C, the onset of reaction was characterized by the development of a deep red colour. However, since aromatic benzylic lithium compounds tend to crystallize in hydrocarbon media [24], the expected formation of a red precipitate was observed after 6 h at 0°C. At this point, 100% of *p*-divinylbenzene had reacted. After reaction of 12 days at 0°C, GLC analysis of the reaction products after quenching with methanol show the methanolysis product of the monoadduct **1** and the diadduct **2**. The dilithium species was obtained in 83% yield as observed by integration of the peak areas and 5% of the trifunctional side reaction product was formed at this temperature. However, at the reaction temperature of 60°C, the formation of significant amounts of the trifunctional impurity was observed by GLC analysis (Fig. 2). The methanolysis product of **2** was extracted with chloroform and the structure and purity of the dilithium adduct were confirmed by ^{1}H NMR and mass spectroscopic analysis (Fig. 3). The mass spectrum shows the molecular ion at *m*/*e* M^+246 (17%) and the peaks at *m*/*e* 176 (25%) and *m*/*e* 106 (100%) for ions resulting from successive McLafferty rearrangements, that is, the loss of an isopentene unit which is consistent with the formation of the dilithium adduct. The peak at *m*/*e* 91 (25%) is a attributed to the formation of the resonance stabilized cycloheptatrienyl cation (Fig. 4).

In conclusion, in the absence of activators, the reaction of *sec*-butyllithium with *p*-divinylbenzene at low temperature to form the anionic initiator, 1,4-bis(1-lithio-3-methylpentyl)benzene proceeds to high levels of difunctionality, but with traces of monofunctional and trifunctional impurities. Thus, because of side reactions and the long reaction time, this method of synthesis of a difunctional initiator for initiation of 1,3-butadiene polymerization does not constitute a practical synthetic step.

3.2. Initiator synthesis: effects of added triethylamine

Studies show that the addition of small amounts of bases such as ethers and amines drastically affects the rate of reaction of organolithium compounds [25,26]. In particular, when triethylamine is employed as a polar modifier in the anionic polymerization of diene monomers, a marked increase in the formation of the undesirable 1,2-microstructure in the addition product was observed [1,27]. Moreover, it has been reported that low concentrations of triethylamine are relatively effective in promoting organolithium initiated polymerization of dienes in hydrocarbon medium, with limited reduction in the *cis*-1,4-microstructure of the resulting diene polymers [11]. In addition, the reaction between *sec*-butyllithium and divinylbenzene in the presence of high concentrations of triethylamine increased the reaction rate, but the formation of large amounts of trifunctional impurities was observed [19,25].

In this study, the effect of triethylamine on dilithium initiator formation, which is produced from the reaction of *sec*-butyllithium and *p*-divinylbenzene in toluene at 0°C, was examined by GLC with a 10 mol% of triethylamine to *sec*-butyllithium (Fig. 5). At the beginning of the reaction, the solution developed a deep red colour. The rapid, linear complete disappearance of *p*-divinylbenzene with respect to time is observed with concomitant quantitative formation of the monofunctional species according to GLC analysis data of a methanolysis aliquot. The quantitative formation of the monofunctional adduct and the absence of the difunctional species at the beginning of the reaction is attributed to the extensive charge delocalization in the monofunctional species, leading to a relatively stable intermediate and the absence of the activating effect of the *p*-vinyl group towards the nucleophilic addition reactions by the second *sec*-butyllithium molecule. The reaction medium remained homogeneous for 1 h at 0°C, whereafter traces of precipitate was observed. The coordination of triethylamine with the lithium ion weakens the coordination bonds in the insoluble adducts and also renders the *sec*-butyllithium molecules more reactive. The effect of the addition of triethylamine was to facilitate the complete solubilization of the precipitate, thereby increasing the rate of formation of the difunctional adduct, as compared to the reaction in the absence of polar additive. After several days of reaction at 0°C, only difunctional initiator (96%) and monoadduct (4%) were observed with no traces of tri- and tetrafunctional impurities. However, significant amounts of trifunctional species are obtained at higher temperatures, even at low concentrations of triethylamine. The absence of trifunctional adduct in the reaction at low triethylamine concentration could be attributed to the greater activating effect of the amine, by onium–ate complexation, on the *sec*-butyllithium tetramer, thereby promoting addition reaction of *sec*-butyllithium with the monofunctional adduct. Thus, for difunctional initiator synthesis from the reaction of *sec*-butyllithium with *p*-divinylbenzene in the presence of polar additive, the optimum ratio of triethylamine was determined as 10% molar ratio to organolithium for the efficient promotion of the rapid addition of the organolithium compound to the second

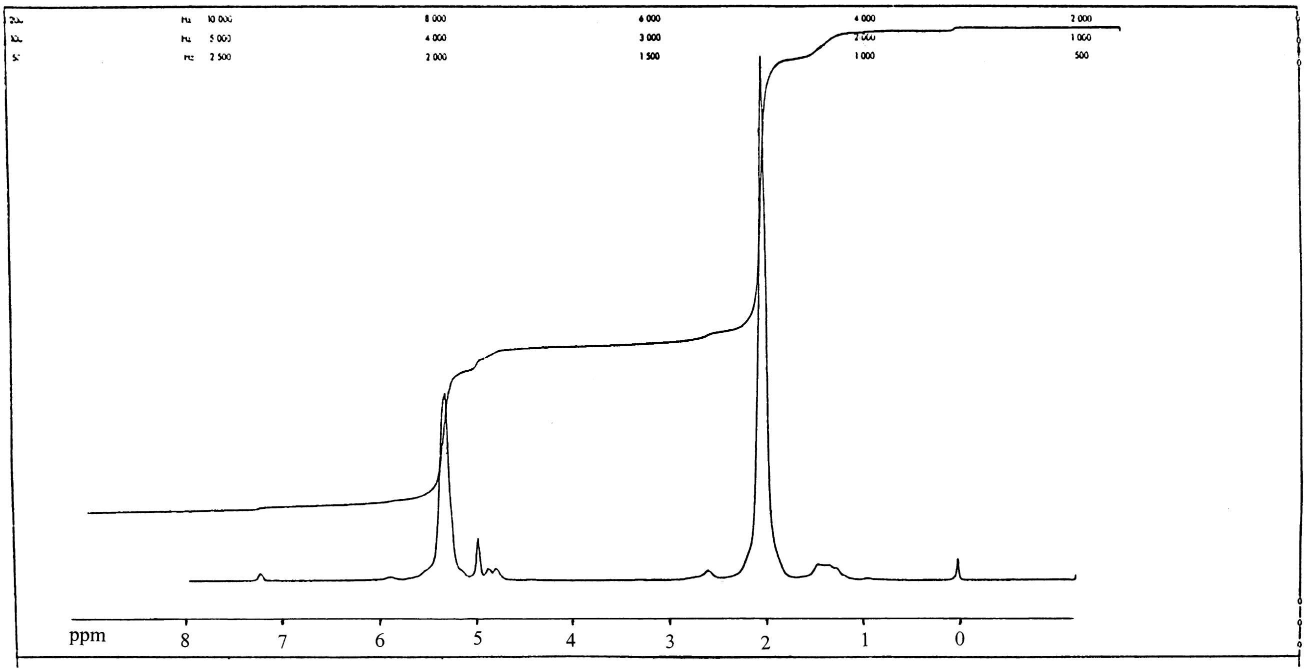

Fig. 6. ^{1}H NMR spectrum of polybutadiene synthesized using the diadduct, **2**, in toluene at 0°C in the presence of 10 mol% triethylamine.

vinyl group, with no significant occurrence of side reactions.

3.3. Butadiene polymerization

High purity anionic initiator, 1,4-bis(1-lithio-3-methylpentyl)benzene, with overall functionality of 1.97 as measured by methanolysis product analysis, was used as the initiator for butadiene polymerization in the presence of 10% molar excess of triethylamine in toluene. The polybutadienes formed had polydiene microstructures ranging from 13 to 16% 1,2-vinyl content, as observed by ^{1}H NMR analysis [28] (Fig. 6). The increased vinyl enchainment in the presence of 10% ratio of triethylamine to organolithium is much less than the 34% 1,2-enchainment found by Kamienski [26]. The higher 1,2-content was owing to the presence of triethylamine which increased the ionicity of the alpha carbon-lithium bond and favoured a more stable allylic-type chain end.

4. Conclusion

As the reaction medium remains homogeneous for a limited period, these results show that the extent of formation of dilithium initiator involving the reactions of *sec*-butyllithium with *p*-divinylbenzene and the resultant intermediate, *p*-1-lithio-3-methylpentylvinylbenzene, can be monitored by gas–liquid chromatography. The reaction of equimolar amounts of *sec*-butyllithium and *p*-divinylbenzene, in the absence of polar modifier, yielded about 85% diadduct, 1,4-bis(1-lithio-3-methylpentyl)benzene. However, when triethylamine was added, essentially quantitative diadduct formation was obtained at 0°C, with low concentration of monofunctional adduct, but no polyfunctional impurities. In addition, the presence of a 10% ratio of triethylamine to lithium does not appreciably affect the microstructure of the polybutadiene formed using anionic initiator **2**. Experimental evidence to show the quantitative synthesis of **2** as well as detailed characterization of the telechelic polymer formed using the difunctional initiator **2** will be the subject of a future publication.

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