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Dienes polymerization in the presence of metal hydrides and triethylaluminum

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Abstract

Butadiene and isoprene can be polymerized by potassium hydride in aromatic hydrocarbons at various temperatures and in short times. A first additive, triethylaluminum, is needed to favour the homogeneity of the initiating system in the solvent of reaction. The importance of a second additive, a potassium alkoxide, is discussed in terms of activation of the polymerization. Experimental parameters like temperature, initiator concentration, activator/initiator ratio and monomer concentration are also investigated with the aim to reach a high content of 1,4 units. Transfer reactions occur for isoprene even though a good control of the polymerization is obtained for butadiene.

Keywords: Dieres; Alkali metal hydride; Trialkylaluminum

1. Introduction

It has been reported in previous studies that lithium and sodium hydride when associated to some metal alkyl derivatives yield soluble 'ate' complexes [1,2] that can initiate the anionic polymerization of styrene in hydrocarbons at high temperature. Such initiating systems find their interest for their low cost and the possibilities to control the anionic styrene polymerisation at temperature higher than 100 °C, even in conditions close to the bulk monomer. The preparation of 1,3-butadiene/styrene and isoprene/styrene random and block copolymers using such systems could be also of great interest in particular if the diene units can be incorporated preferentially in a high 1,4-cis proportion. As generally admitted the reference anionic system to reach such a high 1,4-cis insertion involves polymerisation of dienes in non-polar media with lithium as counter-ion [3]. The use of sodium and potassium-based initiators remained so far extremely limited for several reasons including the insolubility of most metal alkyl derivatives in hydrocarbon media and their low selectivity towards 1,4 insertion. 2-Ethylhexylsodium [4,5] and bimetallic systems such as Bu_3SnNa [6] that are reported to be soluble in hydrocarbons can initiate isoprene polymerization but yield polyisoprene with a low amount of 1,4 units. Patterson and Halasa have investigated the polymerization of butadiene with a series of potassium-based catalysts obtained by the association of potassium alkoxides and alkyl-magnesium [7] or alkyl-lithium [8]. Metal-to-metal ligand exchange reactions generates in situ an alkylpotassium, which polymerizes anionically butadiene in high yields with a predominant selectivity in 1,4-trans unit at low temperature (10 °C). Similar systems made from the combination of barium alkyls and Lewis acids like zinc or aluminum alkyls were also reported to be very efficient for the formation of polybutadiene with a high content of 1,4 units [9,10].

The purpose of this work was to examine the capacity of alkali metal hydride/trialkylaluminum complexes for the polymerization of isoprene and butadiene in hydrocarbon media at elevated temperature. The contribution as third component to the initiating system of alkali metal alkoxides, as well as the influence of the reaction temperature and the initiator and monomer concentrations on the control of the polymerization and on the polydiene microstructure is also investigated.

2. Experimental

2.1. Materials

Isoprene (99% from Aldrich) and butadiene (99% from Aldrich) were stored over *n*,*s*-dibutylmagnesium (1 M in

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heptane from Aldrich) and distilled before use. Triethylaluminum (Et_3Al, 1.9 M/25 wt% in toluene or 1.0 M in hexanes from Aldrich) and 2-methylbutan-2-ol (99% from Aldrich) were used as received. Potassium hydride (30–35% in mineral oil from Lancaster) and potassium metal (98% chunk in mineral oil from Aldrich) were stored under argon atmosphere in a glove box. Lithium hydride (95% in mineral oil from Aldrich) and sodium hydride (60% in mineral oil from Chemmetal) were stored under argon atmosphere in a glove box and used without any purification. Toluene (98% from Baker), benzene (98% from Baker), *tert*-butylbenzene (99% from Aldrich) and cyclohexane (99% from Baker) were purified with polystyryllithium, distilled under vacuum and stored in graduated glass tubes under vacuum.

KH/Et_3Al solution was prepared by reaction of potassium hydride with triethylaluminum either in toluene, benzene or *tert*-butylbenzene. Typically, cyclohexane-washed KH (0.290 g, 7.25×10^{-3} mol) was placed in a glass flask fitted with PTFE stopcocks and degassed under vacuum before adding 25 mL of dry toluene. Then, a known amount of Et_3Al solution was added with a syringe under nitrogen flow to reach a ratio [Al]/[Na] = 1. The final solution was let under stirring at room temperature, until KH was completely solubilized, in general after about 3–4 h.

Potassium *t*-amyloxide solution was prepared by reaction of 2-methylbutan-2-ol with cyclohexane-washed potassium metal dispersed in toluene or in cyclohexane. The mixture was reacted at 80 °C for about 2 days and stored over an excess of potassium metal at room temperature. The solution concentration was 0.05 mol/L. A similar procedure was carried out for sodium *t*-amyloxide in the presence of sodium metal.

2.2. Polymerizations

All polymerizations were performed under dry nitrogen in a high pressure glass reactor flamed under vacuum and equipped with a magnetic stirrer and fitted with PTFE stopcocks. Typically, cyclohexane (12 mL) and isoprene (3 mL, 0.03 mol) (or butadiene) were introduced under vacuum through connected glass tubes. Then, the initiating system KH/Et_3Al (1/1) (4×10^{-5} mol) and the activator *t*-AmOK (8×10^{-6} mol) were added via syringes under nitrogen. The mixture was maintained under stirring in a thermostated bath at 80 °C and MeOH/THF was added to stop the reaction. Remaining monomer and solvent were evaporated under vacuum and the polymer was dried under vacuum to constant weight.

2.3. Analysis

Polyisoprene and polybutadiene molar masses were measured by SEC at 20 °C using THF as eluent on a Varian apparatus equipped with a JASCO HPLC-pump type 880-PU and a dual refractive index/UV Varian detector and fitted with one TSK column (PL Poly Pore $7.5\times300\ \mathrm{mm}^2$, 5 μm), calibrated with polystyrene standards, at an elution rate of 1 mL/min. A 0.6 corrective factor was then applied for the estimation of the polyisoprene and polybutadiene experimental $\bar{M}_n$'s [11]. ^1H and ^{13}C NMR were performed on a Bruker 400 ultra shield spectrometer in $CDCl_3$ and at room temperature. The MALDI-TOF mass spectroscopy (matrix-assisted laser desorption/ionisation time-of-flight) measurements were performed on a BIFLEX III instrument (Bruker Daltonik GmbH, Bremen): polymers were dissolved at a concentration of 10 g/L in THF and in a dithranol(1,8,9-trihydroxyanthracene) matrix at 20 g/L. Polymer and matrix solutions were then mixed in a 1:1 ratio (i.e. 20 μL each). Five volume percent (2 μL) of AgTFA (silver trifluoroacetate, 0.02 M in THF) was added as cationizing agent, and this mixture was then spotted on the sample holder.

3. Results and discussion

Alkali metal hydrides are readily available products that found important applications in organic synthesis as reducing agents and more recently as hydrogen source for battery cells. They can be found either as powder or as dispersion in mineral oil but are insoluble in non-polar solvents. This is probably the reason why their use as anionic polymerisation initiator remained for long extremely limited. Addition of trialkylaluminum to sodium hydride was found to yield soluble complexes able to initiate the anionic styrene polymerisation at high temperature [2]. This approach was extended to other alkali metal hydrides in order to form the corresponding hydrocarbon soluble aluminate complexes, which were then examined as potential initiators for the high temperature anionic polymerisation of dienes.

For potassium hydride (KH), addition of 1 equiv of Et_3Al is sufficient to get in toluene, after a few hours mixing, at 20 °C, a completely soluble and transparent system, corresponding to the formation of a 1:1 KH:Et_3Al complex. A similar behaviour is observed with NaH in presence of Et_3Al or *i*-Bu_3Al [2] although complete solubilization requires several days at 20 °C. Heating the mixture at 50 °C allows to reduce the necessary reaction time to a few hours. Solubilization of LiH is more difficult and requires higher proportions of trialkylaluminum ($Al/Li>1$) and high mixing temperature (80 °C) to break the LiH aggregates. Even in these conditions, solubilization of LiH is not complete.

For KH and NaH, at ratios $0.8<[Al]/[Mt]<1$, corresponding to a slight excess of the metal hydride with respect to trialkylaluminium, the initial MtH particles are already destroyed yielding a turbid solution. This was explained by the concomitant formation of a soluble 1:1 complex and of an insoluble 2:1 (NaH:Et_3Al) complex in which is involved the excess of metal hydride with respect to the alkylaluminum. It is worthy noting that for styrene polymerization initiated with NaH:*i*-Bu_3Al the best compromise between efficiency and activity was found for the stoechiometry 1:0.9 [2]. At ratio lower than 1:0.8, the initiator efficiency was low because of the heterogeneity of the system and at the 1:1 ratio or in the presence of an excess of trialkylaluminum with respect to the metal hydride the propagation rate was too slow or the system even inactive. This led us to postulate the active contribution of 2:1 complexes in the polymerization process.

Table 1
Isoprene polymerization initiated by MtH/Et_3Al (1:1)+*t*-AmOMt ([*t*-AmOMt]/[MtH]=0.2) at different temperatures in cyclohexane, [MtH]=0.0026 M, [isoprene]=2 M

MtH	Additive	T (°C)	Time (h)	Conv (%)	$\bar{M}_{n\ theo}$ [a] (g/mol)	$\bar{M}_{n\ exp}$ (g/mol)	PDI	Microstructure (%)		
								1,4 (cis/trans)	3,4	1,2
LiH	*t*-AmOK[b]	80	16	76	37,400	11,200	2.5	70 (36/34)	27	3
LiH	*t*-AmONa[b]	80	15	70	34,000	25,700	2.9	51 (26/25)	44	5
NaH	*t*-AmONa	80	24	32	15,800	19,800	2.2	54 (27/27)	41	5
NaH	*t*-AmOK	120	6	69	34,900	35,100	2.1	65 (32/33)	32	3
KH	*t*-AmOK	80	6	79	39,500	23,100	2.2	70 (35/35)	27	3
KH	*t*-AmOK	100	4	100	50,000	6700	2.7	73 (36/37)	24	3

[a] Theoretical molar masses at given conversion.
[b] [*t*-AmOMt]/[MtH]=1.

Table 2
Isoprene polymerization initiated by KH/Et_3Al (1:1)+*t*-AmOK ([*t*-AmOK]/[KH]=0.2) at different temperatures in cyclohexane (+ε toluene), [KH]=0.0026 M, [isoprene]=2 M

T (°C)	Toluene ($\%_{vol}$)	Time (h)	Conv (%)	$\bar{M}_{n\ theo}$ [a] (g/mol)	$\bar{M}_{n\ exp}$ (g/mol)	PDI	N[b]	Microstructure (%)		
								1,4 (cis/trans)	3,4	1,2
20	3.5	23.5	19	9500	13,600	1.7	0.7	48 (20/28)	46	6
40	2.1	16.5	58	29,000	20,800	1.9	1.4	60 (29/31)	36	4
60	1.1	6	68	34,000	15,700	2.1	2.2	65 (31/34)	31	4
80	2.1	6	82	40,100	9300	2.6	4.4	74 (36/38)	23	3
100	2.1	4	100	50,000	7100	2.7	6.8	73 (36/37)	24	3
120	2.1	4	100	50,000	6700	2.7	6.7	74 (37/37)	23	3

[a] Theoretical molar masses at given conversion.
[b] Number of chains formed per initial KH molecule.

$MtH:R_3Al$ systems (Mt=Li, Na, K) were first investigated as such as initiating systems for isoprene and butadiene polymerization in hydrocarbons at elevated temperature. The $LiH:Et_3Al$ system was found almost inactive even at 100 °C. For NaH:*i*-Bu_3Al systems at the stoechiometry (1:1) as well as for [Na]:[Al] ratios lower or higher than one, very slow rates of isoprene polymerisation, corresponding to a few percent conversion in 24 h, are observed in toluene or cyclohexane at 80 °C. Polymerization experiments carried out in similar conditions with the $KH:Et_3Al$ (1:1) complex shows a slightly higher reactivity at 80 °C and about 18% of low molar mass polyisoprene is formed after 30 h. These first results led us to conclude that $MtH:R_3Al$ initiating systems used as such are of very limited interest for dienes polymerization.

The influence of various additives including metal alkoxides to $MtH:R_3Al$ systems on the isoprene polymerization and the polyisoprene molar mass and microstructure was then investigated. Among the various compounds checked, the addition of sodium and potassium *tert*-amyloxides, which are soluble in cyclohexane, was found to yield a significant activation of the polymerization both for the LiH, NaH and KH trialkylaluminum-based systems. Results are collected in Table 1.

For $LiH:Et_3Al$ an active homogeneous polymerization system, is obtained at 80 °C, after addition of 1 equiv of *t*-AmONa or *t*-AmOK. As it may be seen in Table 1 the polyisoprene microstructure observed in the presence of *t*-AmONa or *t*-AmOK as additive are close to those found with NaH and KH systems, respectively, suggesting a direct contribution of these metal cations in the isoprene insertion process likely through LiH-*t*-AmONa and LiH-*t*-AmOK alkali metal interchange reactions [7,8].

A much lower amount of such additives (0.2 equiv with respect to NaH) is required to get a significant activation effect with $NaH:Et_3Al$. Replacement of *t*-AmONa by *t*-AmOK and raising the reaction temperature to 120 °C improves the polymerization rate and increases the amount of 1,4 insertion in the polymer up to 65%, a value close to the one found for KH based systems suggesting also alkali metal exchanges between NaH and *t*-AmOK. Best results in terms of rate enhancement and 1,4 microstructure are obtained with $KH:Et_3Al$ (1:1) associated to *t*-AmOK (0.2 equiv): about 80% isoprene conversion is achieved in 6 h at 80 °C in cyclohexane.

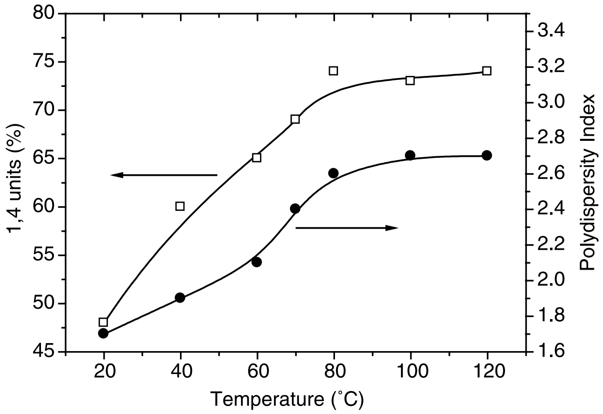


Fig. 1. Influence of temperature on the microstructure and polydispersity of polyisoprene initiated by KH/Et_3Al (1:1)+*t*-AmOK ([*t*-AmOK]/[KH]=0.2), [KH]=0.0026 M, [I]=2 M, cyclohexane (+ε toluene).

Table 3
Isoprene polymerization initiated by KH/Et$_3$Al (1:1)+t-AmOK seeds at different [t-AmOK]/[KH] ratios, cyclohexane, [isoprene]=2 M et [KH]=0.0026 M, T=80 °C

[t-AmOK]/[KH]	Toluene (%$_{vol}$)	Time (h)	Conv (%)	$\bar{M}_{n\ theo}$ [a] (g/mol)	$\bar{M}_{nexp}$ (g/mol)	PDI	1,4 (%)
0	1.1	30	18	9000	7300	2.4	74
0.2	2.1	6	82	41,000	9300	2.6	74
0.6	0.0[b]	2	82	41,000	18,800	3.0	68
1	0.0[c]	3	78	39,000	24,000	2.7	67
1.2	0.0[b]	2	87	44,000	22,300	2.7	66

[a] Theoretical molar masses at given conversion.

[b] KH/TEA solution 0.25 M in benzene.

[c] Toluene evaporated.

Furthermore, this system yields a polyisoprene with the higher 1,4 unit content (about 70%). These results led us to investigate the KH:Et$_3$Al:t-AmOK in more detail.

In order to determine the influence of the temperature on isoprene polymerization, experiments were carried out using KH:Et$_3$Al (1:1) associated with 0.2 equiv of potassium t-AmOK at temperatures ranging from 20 to 120 °C (Table 2), while the composition and concentration of the initiating system and the isoprene concentration were kept constant. As expected the temperature affects strongly the reactivity of the propagating species and polymerization yields go from 19% in 23 h at 20 °C to 100% in less than 4 h at 100 °C. However, the increase of reaction temperature and reactivity is accompanied by a significant increase of transfer reactions as indicated by the low experimental molar masses compared to theoretical values calculated assuming the formation of one polyisoprene chain per potassium hydride. This number of chain goes from 0.7 at 20 °C to almost seven at 100 °C and above. The different chain transfer mechanisms involved in these systems will be discussed later in this manuscript. Examination of the polyisoprene microstructure as a function of the reaction temperature, Fig. 1, reveals a continuous increase of the proportion of 1,4-units from 20 to 80 °C. At higher temperatures, in the 80–120 °C range, a plateau corresponding to the formation of polyisoprene with about 74% of 1,4 units is then reached. In the same time, the cis–trans ratio (50/50) remains constant whatever the temperature. A rather similar situation was reported for isoprene polymerisation in presence of Li counter-ion [3], although in

Table 4
Isoprene polymerization initiated by KH/Et$_3$Al (1:1)+t-AmOK (0.2 equiv) seeds at different monomer concentrations, at 80 °C in cyclohexane

[Isoprene] (mol/L)	[KH] (mol/L)	1,4 (%)
0.3	2.1×10^{-4}	81
2	2.1×10^{-4}	86
1	5.3×10^{-4}	74
2	5.3×10^{-4}	74
2.4	5.3×10^{-4}	77
1	6.5×10^{-3}	64
4	6.5×10^{-3}	66

Table 5
Isoprene polymerization initiated by KH/Et$_3$Al (1:1)+t-AmOK (0.2 equiv) seeds at different initiator concentrations, at 80 °C in cyclohexane, [isoprene]=2 M

[KH] mol/L	% 1,4	Proportion of 1,4 cis (%)	Proportion of 1,4 trans (%)
5.2×10^{-4}	74	51	49
2.6×10^{-3}	70	49	51
2.7×10^{-2}	54	39	61

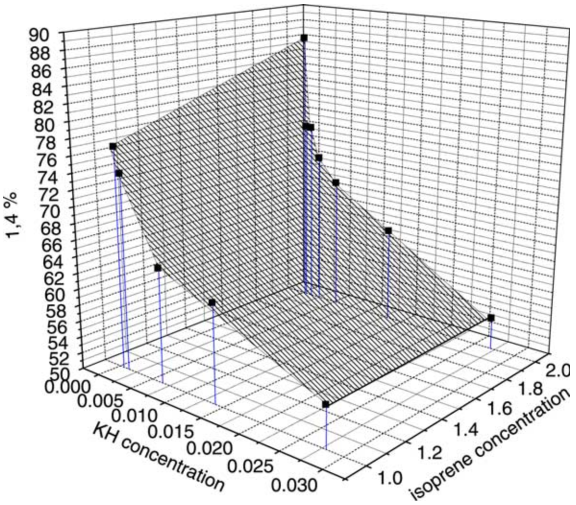


Fig. 2. Influence of initiator and monomer concentrations on polyisoprene microstructure, KH/Et$_3$Al (1:1)+t-AmOK ([t-AmOK]/[KH]=0.2), [KH]=0.0026 M, [I]=2 M, cyclohexane, T=80 °C.

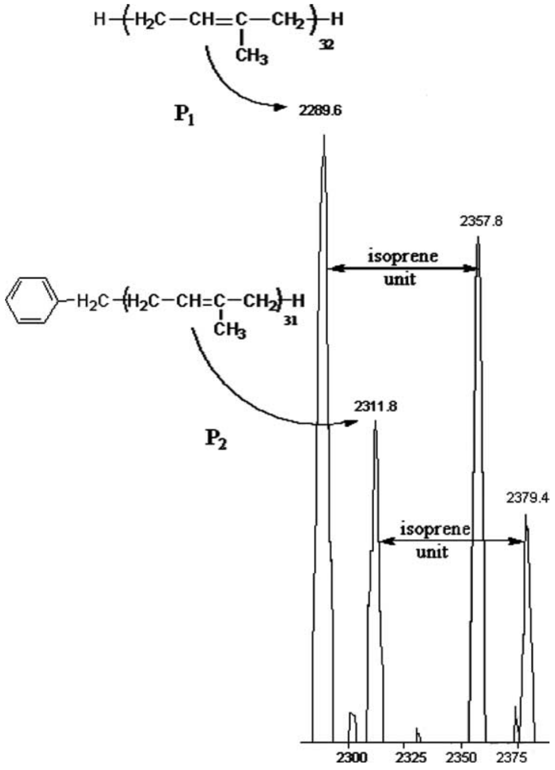
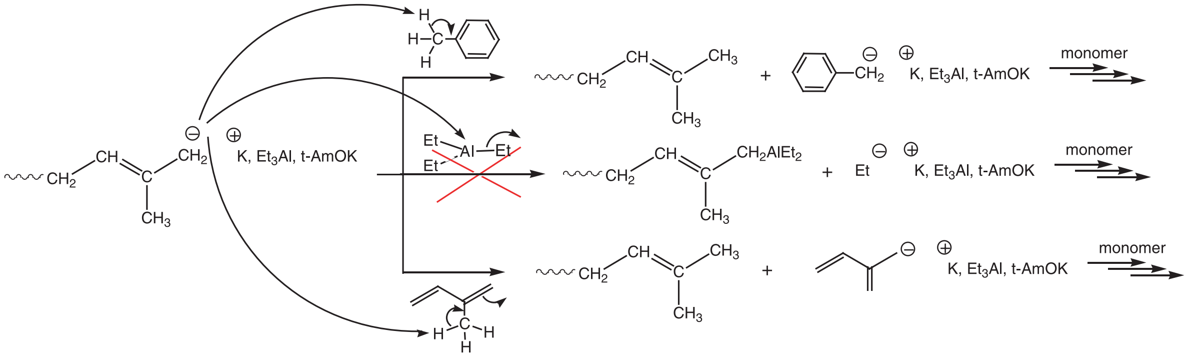


Fig. 3. MALDI-TOF spectrum of polyisoprene oligomers ($\bar{M}_n$exp=2800 g/mol) obtained in the presence of KH/Et$_3$Al (1:1)+t-AmOK ([t-AmOK]/[KH]=0.2) as initiating system in cyclohexane in presence of toluene (5.6%) at 80 °C.



Scheme 1.

this case the proportion of cis units was higher (70%). Literature data on isoprene polymerization involving a potassium counter-ion in non-polar solvents reports the formation of 1,4-cis isoprene units in proportion varying from 20 to 37% at temperature ranging from 20 to 120 °C [3]. It may thus be concluded that complexation of potassium by triethylaluminum significantly improves the 1,4 incorporation. It is believed in our case that monomer insertion proceeds into a polyisoprenyl K:Et_3Al:*t*-AmylOK complex, which remains relatively stable up to 80 °C. At higher temperature destabilization of the complex as well as a more important contribution of other reaction processes might explain the level off in the stereoregulation.

Besides the temperature effect, the influence of an increasing proportion of potassium *t*-amyloxide onto the KH:Et_3Al activity was examined. Results of experiments performed in the presence of [*t*-AmOK]/[KH] ratio ranging from 0 to 1.2 are given in Table 3. At ratio [*t*-AmOK]/[KH] = 1.2, at 80 °C in cyclohexane, isoprene conversion reach 87% in 2 h. However, the rate increase is accompanied by a noticeable decrease in the relative proportion of 1,4 units, which goes down to 66%.

The influence of monomer and active centre concentration on the polyisoprene microstructure can be figured out from data collected in Tables 4 and 5, respectively. The combined effect of these two parameters on the microstructure can be seen also in Fig. 2. Change in isoprene concentration, keeping constant the concentration of KH, exerts a very limited influence on the polyisoprene microstructure. On the contrary at almost constant isoprene concentration variation of initiator concentration from 2.7×10^{-2} to 2.1×10^{-4} mol/L results in an important modification of the 1,4 to 3,4 + 1,2 ratio. Low KH:Et_3Al concentrations lead to the higher fraction in 1,4 units. For example, going from [KH] = 2.7×10^{-2} to 1.3×10^{-3} mol/L results in an increase of 1,4 units from 54 to 74%. With even lower initiator concentrations, 2.7×10^{-4} or 5.2×10^{-4} mol/L, polyisoprene with 1,4 content in the range 80–90% were obtained. However, at these initiator concentrations polymerization times are long and final yields do not exceed 10–15%, likely because of an important deactivation of the small amount of active species by impurities remaining in the system. Besides, results reported in Table 5 show that at high KH concentration the formation of 1,4-trans units is favoured to the detriment of 1,4-cis. This is in line with data reported earlier by Worsfold and Bywater [12] for lithium systems, who proposed a mechanism involving competitive monomer addition/chain end isomerization reactions and in which, at high active species concentration, isomerization yielding 1,4-trans units readily occurs before next monomer insertion takes place.

As already noticed in this paper, the polydispersity of the polymers are broad and experimental molar masses are generally much lower than theoretical values calculated assuming the formation of one chain per KH molecule, suggesting the presence of transfer reactions. Fig. 3 presents the Maldi-Tof mass spectroscopy analysis of polyisoprene oligomers obtained with the KH:Et_3Al:*t*-AmOK initiating system at 80 °C in cyclohexane, in the presence of a small amount of toluene (5.6%$_{\text{vol}}$) coming from the trialkylaluminum solution. The first peak series (P_1) corresponds to polyisoprene chains, with two hydrogen as termini ($P_1 = M_{\text{Ag}} + n(M_{\text{isoprene}}) + 2$ g/mol), in agreement with the expected initiation by an hydride group and termination by a proton from methanol used as terminating agent. The second population (P_2) corresponding to about 35% of the total polymer matches isoprene chains with a benzyl group and an hydrogen at the chain ends, $P_2 = M_{\text{Ag}} + (n-1)(M_{\text{isoprene}}) + (M_{\text{benzyl}}) + 2$ g/mol. The presence of benzyl is indicative of a transfer reaction to toluene, see Scheme 1. To avoid this reaction toluene-free alkylaluminum

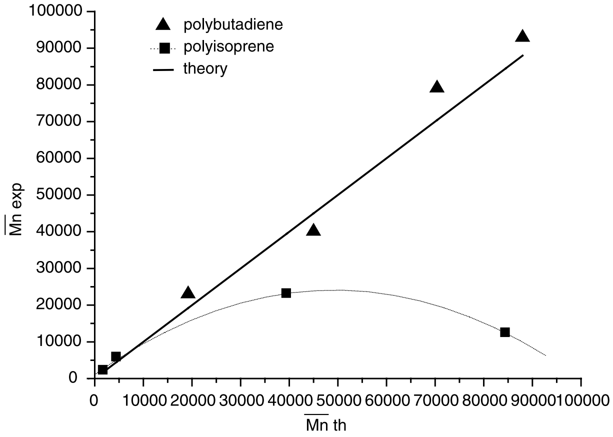


Fig. 4. Experimental molar mass vs. theoretical molar mass, cyclohexane, [Monomer] = 2 M, [*t*-AmOK]/[KH] = 0.2, T = 80 °C.

Table 6
Butadiene polymerisation initiated by KH/Et$_3$Al[a] (1:1)+*t*-AmOK ([*t*-AmOK]/[KH]=0.2) at 80 °C in cyclohexane, [butadiene]=2 M

[KH] (mol/L)	Time (h)	Conv (%)	$\bar{M}_{n\ theo}$[b] (g/mol)	$\bar{M}_{n\ exp}$ (g/mol)	PDI	*f* (%)	Microstructure (%)	
							1,4	1,2
5.5×10^{-3}	3	96	19,200	23,000	1.4	83	60	40
2.2×10^{-3}	4	90	45,000	40,100	1.5	112	64	36
1.4×10^{-3}	4	88	70,400	79,100	1.6	89	67	33
1.1×10^{-3}	4	88	88,400	92,900	1.8	95	69	31

[a] KH/Et$_3$Al solution 0.25 M in *tert*-butylbenzene.

[b] Theoretical molar masses at given conversion.

solutions were prepared and used for the preparation of the initiating system. Although polyisoprene with higher molar mass were obtained, see Table 3, the experimental molar masses remained lower than the theoretical ones, see Fig. 4. Since transfer to triethylaluminum, characterized by the incorporation of an ethyl group at one of the chain end was not observed by Maldi-Tof, the possibility of a transfer reaction to isoprene monomer was further investigated, see Scheme 1. Indeed polyisoprene series bearing an hydride end or an isoprenyl end only differ in molar mass by 2 g/mol and are difficult to distinguish. According to a theoretical study reported by Litvinenko et al. the isoprene-like terminus resulting from the transfer to monomer process, should be able to participate in the polymerization as a macromonomer [13]. As a consequence a branched polymer should form. The rather low polyisoprene molar masses obtained and their unimodal distribution suggest that contribution of this process is not so significant suggesting a low reactivity of the bulkyl isoprenyl-end as compared to isoprene. In order to investigate the contribution of transfer to isoprene a series of polymerization experiments was performed with butadiene in similar reaction conditions using *t*-butyl benzene as solvent. Results collected in Table 6 shows that polybutadienes can be prepared in a few hours at 80 °C whereas the chain microstructure reveals a predominant 1,4 butadiene insertion, between 60 and 70%. With this monomer, a good agreement between polybutadiene experimental molar masses and theoretical ones, up to 100,000 g/mol, is observed, see Fig. 4, while polydispersities are improved.

4. Conclusion

New ternary initiating systems based on alkali metal hydride, trialkylaluminum and alkali metal alkoxides have been used for the polymerization of isoprene and butadiene in non-polar solvents. Best results were obtained with the association of potassium hydride, triethylaluminum and potassium *tert*-amyloxide, which allows the polymerization of isoprene and butadiene in hydrocarbon media at 80 °C in short reaction time. Lithium and sodium hydrides are also efficient initiators but much less active. In these systems, metal hydrides behave as the anionic initiator. The identified roles of the aluminum derivative and of the metal alkoxide are, respectively, to form a soluble aluminate complex and to activate this complex towards dienes polymerization. The three constituents of the initiating systems likely also contribute in a more subtle and complex way through ligand exchanges and reorganization of the aluminate complexes to the design of active species and to the polymerisation process, which makes difficult to understand the mechanisms, which govern the stereochemistry of the reaction.

One limitation of these initiating systems concerns isoprene polymerization and the important transfer reaction to monomer, which strongly limits the polyisoprene molar masses. However, in the case of polybutadiene, a good control of the polymerization is obtained and polybutadiene with predominant 1,4 monomer units and high molar masses can be synthesized in a few hours.

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