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Anionic polymerization of isoprene, butadiene and styrene with 3-dimethylaminopropyllithium

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The synthesis of dimethylaminopropyllithium (DMAPLi), from the corresponding chloride and lithium metal, by using high-vacuum techniques, is described. DMAPLi was purified by crystallization under vacuum. Gas chromatography–mass spectrometry analysis of the purified product, after neutralization with degassed methanol, showed the existence of $\sim 2\%$ impurities. The most important of these impurities ($\sim 1.5\%$) were tetramethylhexamethylenediamine and dimethylaminohex-1-ene. By using DMAPLi as initiator, several polymerizations of isoprene, butadiene and styrene were carried out in benzene, under high-vacuum conditions. The molecular-weight range of the polymers obtained was from about 3×10^3 to 4×10^4. The polydispersity index ($I = M_w/M_n$) of the polydienes was similar ($I < 1.1$) to those obtained with the classical initiator s-butyllithium, but the vinyl content was higher. It was found that the lower the molecular weight of the polydienes, the higher the vinyl content. In the case of styrene, the polydispersity index of the polystyrenes produced was relatively high ($I = 1.2$ to 1.5), but by adding small amounts of tetrahydrofuran or by using unpurified initiator, which contains polar impurities, the polydispersity index recovers the usual values, for molecular weights higher than $\sim 1 \times 10^4$.

(Keywords: 3-dimethylaminopropyllithium; anionic polymerization; polydispersity)

INTRODUCTION

ω-Functionalized polymers are a valuable class of materials. Owing to the ability of the functional groups to participate in a variety of physical (e.g. reversible ionic association) and chemical (e.g. chain extension, cross-linking) reactions, these materials are of both academic[1] (e.g. model networks) and commercial[2,3] (liquid rubbers) interest.

In principle any type of addition polymerization can be employed to prepare ω-functionalized polymers[4,5], but if near-monodisperse polymers are desired the choice is restricted to termination-free polymerizations[6]. This technique generates near-monodisperse living polymer chains with stable carbanionic ends, which can be easily converted into a variety of functional groups, by reaction with an appropriate electrophilic terminating agent[7].

Functional groups can also be introduced on the chain ends by using functional initiators[8]. In this case the influence of the functional group on the polydispersity and microstructure of the resulting polymers should be considered.

A way to incorporate the dimethylamino functional group at the chain end is to initiate the polymerization by 3-dimethylaminopropyllithium (DMAPLi). Eisenbach *et al.*[9] first reported the synthesis of DMAPLi and the results obtained using this initiator to polymerize α-methylstyrene, styrene and butadiene[10]. The synthesis of the initiator (in tetrahydrofuran (THF) and cyclopentane) and the polymerizations were carried out in an inert atmosphere. The initiator was used as prepared without purification. In the case of α-methylstyrene the polymers obtained had much higher number-average molecular weights than the stoichiometric ones and high polydispersity ($M_w/M_n > 1.5$). For polystyrenes and polybutadienes, not enough characterization data were given.

Worsfold[11] also prepared DMAPLi in heptane and used this initiator in order to synthesize ω-functionalized polystyrenes and polyisoprenes. The main goal of this work was to study the influence of the position of the functional group in a polymeric chain on the reactivity of the group.

Stewart *et al.*[12] have used DMAPLi prepared in hexane, after purification, to prepare low-molecular-weight polybutadienes ($M_n < 1500$) under argon. Some results on the variation of the microstructure of the polymers with respect to the amount of polar impurities in the initiator solution were given.

Fetters and coworkers[13] by using this initiator prepared amine-capped polyisoprenes, having predictable

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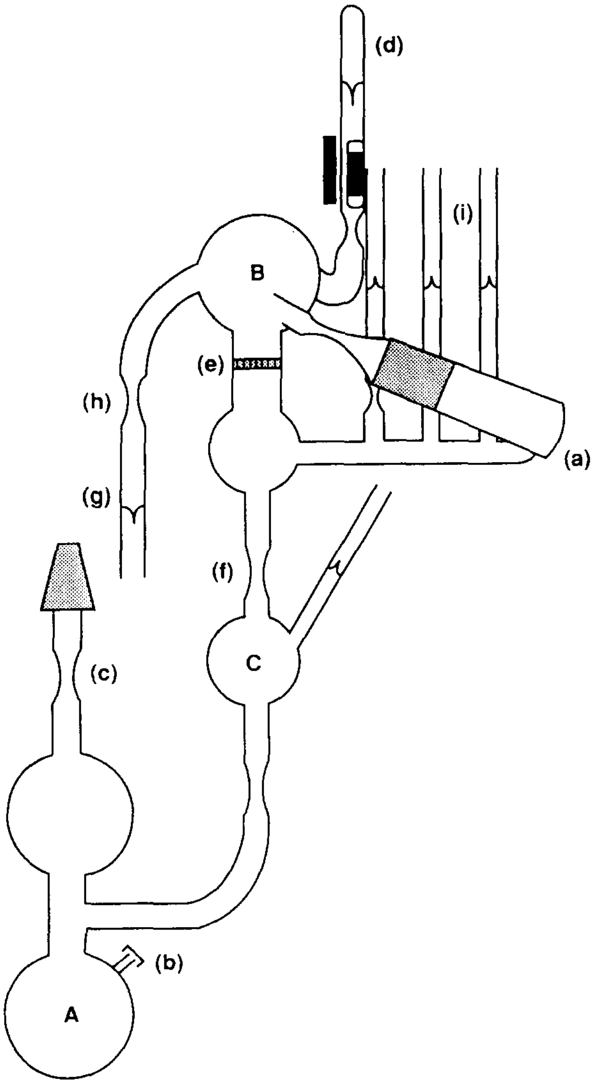

Figure 1 Apparatus for the synthesis of 3-dimethylaminopropyllithium (see text for details)

molecular weights and low polydispersity. They studied the variation of microstructure with the molecular weight for the range 1.5×10^4 to 1.85×10^5.

In this paper we study the influence of DMAPLi on the polydispersity and the microstructure of the polymers obtained from isoprene, butadiene and styrene in benzene under high-vacuum conditions (molecular-weight range $\sim 3 \times 10^3$ to 4×10^4). The functional initiator was synthesized by using high-vacuum techniques and analysed by gas chromatography–mass spectrometry (g.c.-m.s.). This study elucidates, refines and complements the previous ones.

EXPERIMENTAL

Synthesis of the initiator

The synthesis of 3-dimethylaminopropyllithium was carried out in a specially designed all-glass apparatus (*Figure 1*). Sixfold excess of lithium metal was used. 3-Dimethylaminopropyl chloride (DMAPCl) was dried over CaH_2 for two days on the vacuum line, degassed several times during this period and finally distilled into a calibrated ampoule, which was then attached to the main reactor.

The reactor was attached to the vacuum line, checked for pinholes and flame-dried. After pumping for sufficient time the appropriate amount of lithium dispersion in hexane, containing about 2% sodium, was placed in ampoule (a) by breaking the vacuum for a short time. Then the hexane was evaporated. About 4 ml of n-BuLi solution in hexane was subsequently introduced through septum (b) by a syringe, for purging of the reactor. Then purified hexane ($\sim$ 30 ml) was distilled into flask A. The reactor was sealed at (c) and removed from the line. Ampoule (a) was washed with hexane in order to transfer Li^0 to flask B and cut off. The whole apparatus was rinsed with the n-BuLi solution and then washed by condensing hexane on the walls. Finally hexane was distilled from flask A to flask B and the purge section was cut off.

Flask B was immersed in a water bath maintained at 20°C. Afterwards break seal (d) was ruptured and small amounts of DMAPCl were added for a period of 2 h to the Li^0 dispersion under stirring. When addition was completed, ampoule (d) was removed. Reaction was allowed to proceed for another 3 h. At the end of this period the bath temperature was lowered to 0°C. The insoluble DMAPLi precipitated, while the by-products (mainly Wurtz coupling product) were still soluble in hexane. The mixture was filtered through glass filter (e) and hexane was distilled to B in order to extract all the remaining by-products. Then the hexane solution was removed in flask C by sealing at (f). The reactor was attached to the vacuum line again through break seal (g) and sufficient amount of purified benzene was distilled into flask B. By sealing at (h) the reactor was free again and immersed in a water bath at 25°C. DMAPLi was allowed to dissolve with continuous stirring (solubility 0.35 M). When dissolution was accomplished the DMAPLi solution was separated from unreacted Li^0 by filtering through filter (e) and divided into ampoules (i) for subsequent use.

Analysis of initiator

Determination of the active concentration. The reactivity of the initiator solution was determined by two methods. In the first, a known amount of the solution was hydrolysed and the resulting amine was removed by distillation. The remaining base was titrated with aqueous HCl solution to a phenolphthalein endpoint. In the second method, a known amount of purified styrene was polymerized using a known amount of initiator solution, and the active concentration was calculated by means of the equation:

$$\text{moles initiator} = \text{grams of monomer}/M_n$$

where M_n is the number-average molecular weight of polystyrene formed, determined by s.e.c. Good agreement between the two methods was obtained.

Determination of impurities. In a specially designed glass apparatus, the initiator solution was concentrated about seven times, neutralized with degassed methanol and transferred to a vial. All these operations were carried out under vacuum. G.c.-m.s. analyses were performed using a Carlo Erba model 5300 GC connected to a Hewlett-Packard model 5988 quadrupole mass spectrometer in electron impact ionization (e.i., 70 eV) and positive chemical ionization (p.c.i., methane reagent gas) modes.

Conditions. Low-boiling impurities: injection, splitter (200°C); column, CPSIL 8CB 50 m ×0.32 mm i.d., 5.0 μm thickness film (Chrompack); oven temperature programmed from 70°C to 200°C at 10°C min^{-1}. High-boiling impurities: injection, cold on column; column, CPSIL 5CB 25 m × 0.32 mm i.d., 1.2 μm thickness film (Chrompack); oven temperature programmed from 70°C to 200°C at 10°C min^{-1}.

Polymer synthesis

All polymerizations were carried out under high vacuum, in all-glass sealed and n-BuLi rinsed apparatus at room temperature. Solvents (benzene, tetrahydrofuran, anisole), monomers (isoprene, butadiene, styrene) and terminating agent (methanol) were purified using standard high-vacuum anionic polymerization techniques[14]. Benzene was the principal solvent used throughout this work. For diene polymerizations only DMAPLi, which was previously separated from by-products present in the preparation mixture, was used. In the case of styrene, DMAPLi recovered from the reaction mixture without further purification was also used as a hexane solution, in two cases. For the preparation of low-molecular-weight polystyrene, THF and anisole were also used as modifiers of the polymerization kinetics. THF was added at a portion of 0.3% (v/v) in benzene ([THF]/[Li]> 3) and anisole in such a quantity that [anisole]/[Li]= 10 (~ 0.5% v/v).

Polymer characterization

Molecular-weight distributions along with weight- and number-average molecular weights were obtained by s.e.c. No correction for instrumental spreading was applied. A Waters model 510 pump and Waters model 401 differential refractometer in series with a set of four μ-Styragel columns, having a continuous porosity range from 500–10^5 Å, was used. THF was the carrier solvent at 30°C at a flow rate of 1 ml min^{-1}. The instrument was calibrated with narrow-distribution polystyrene standards covering the range of the molecular weights studied.

Number-average molecular weights were obtained by membrane osmometry (m.o.) in a Wescan model 231 membrane osmometer at 37°C. RC-51 membranes were used. Toluene distilled over CaH_2 was the solvent. For the low-molecular-weight samples a UIC model 070 vapour-pressure osmometer (v.p.o.) was used. H.p.l.c.-grade benzene was the solvent at 40°C. The instrument was calibrated with benzil. The M_n values from m.o. were obtained from the corresponding $(\pi/c)^{1/2}$ vs. c plots, where π is the osmotic pressure. In the case of v.p.o. the M_n values were obtained from the $(\Delta R/c)$ vs. c plots (ΔR is the change in the resistance of the thermistors), using the relation $(\Delta R/c)_{c=0} = k_v/M_n$ where k_v is the calibration constant. In all cases the correlation coefficient was better than 0.98.

The microstructure of polydiene homopolymers was determined by ^1H and ^{13}C n.m.r. spectroscopy[15–17] in $CDCl_3$ at 30°C using a Bruker AC200 spectrometer.

Table 1 The most important impurities of 3-dimethylaminopropyllithium found by g.c.-m.s.

Impurity	ppm/initiator
$(CH_3)_2N(CH_2)_4CH{=}CH_2$	5200
$(CH_3)_2N(CH_2)_3CH(OH)CH(OH)CH_3$	1800
$(CH_3)_2N(CH_2)_3CH(OH)CH(OCH_3)CH_3$	1720
$(CH_3)_2N(CH_2)_6N(CH_3)_2$	8650

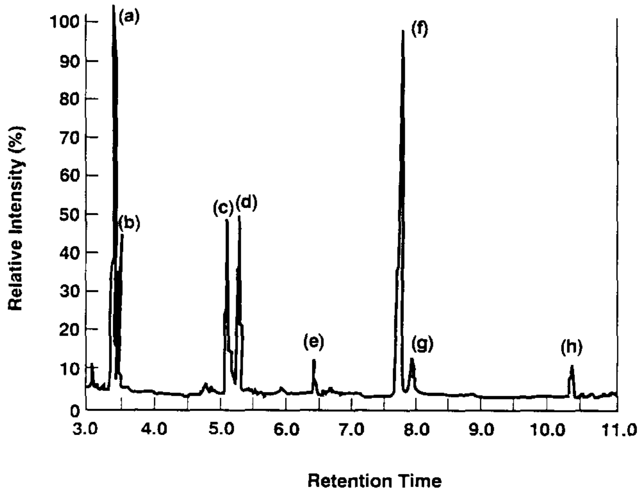

Figure 2 Gas chromatogram of the high-boiling compounds found in the solution of purified DMAPLi: (a) $(CH_3)_2N(CH_2)_4CH{=}CH_2$; (b) $(CH_3)_2N(CH_2)_3N(CH_3)_2$; (c) $(CH_3)_2N(CH_2)_4CH(OH)CH_3$; (d) $(CH_3)_2N(CH_2)_3CH(OH)CH(OCH_3)CH_3$; (e) $(CH_3)_2N(CH_2)_6CH_2OH$; (f) $(CH_3)_2N(CH_2)_6N(CH_3)_2$

RESULTS AND DISCUSSION

Purity of the initiator

The g.c.-m.s. analysis has not shown any low-boiling-point compounds except dimethylaminopropane, which is the product of the reaction of DMAPLi with methanol. The high-boiling impurities, about 2 wt%, were essentially tertiary amines. The most important are given in *Table 1*. Tetramethylhexamethylenediamine (TMHDA), formed by the coupling reaction between DMAPLi and DMAPCl (Wurtz reaction), was the predominant one. Dimethylaminohex-1-ene (DMAH) was probably obtained by reaction of DMAPLi with allylic chloride present in the reaction mixture[9,18]. The oxygenated compounds given in *Table 1*, and other less important oxygenated compounds found, were probably produced, during the termination of DMAPLi with methanol, from TMHDA and CH_3OLi or the small amount of oxygen present in methanol. In *Figure 2* the gas chromatogram of the high-boiling impurities is given.

Isoprene polymerization

Several polymerizations of isoprene were carried out using purified DMAPLi. Molecular weights ranged from 4300 to 40 000 and the concentration of DMAPLi was between 1.83×10^{-3} M and 2.17×10^{-2} M. After mixing the reagents the appearance of the yellowish colour of polyisoprenyllithium was slow compared to s-BuLi polymerizations. However, s.e.c. analysis revealed that the polymers had narrow molecular-weight distributions ($I < 1.1$) and there is good agreement between stoichiometric molecular weight, M_s, and number-average

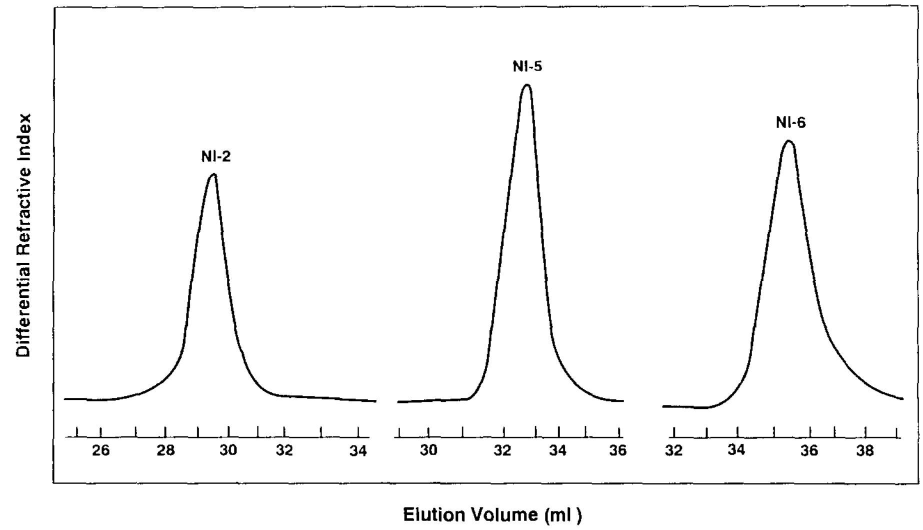

Figure 3 S.e.c. chromatograms of samples NI-2, NI-5 and NI-6 (purified DMAPLi; solvent, benzene)

Table 2 Molecular characteristics of polyisoprenes prepared by DMAPLi

Sample	M_s $\times 10^{-4}$	$M_n{}^a$ $\times 10^{-4}$	I^b (M_w/M_n)	1,4 (wt%)	3,4 (wt%)	1,2 (wt%)
NI-2	3.8	3.82	1.07	85	15	–
NI-7	2.32	2.37	1.07	84	16	–
NI-3	1.62	1.66	1.07	83	17	–
NI-4	1.07	1.15	1.07	81.5	18.5	–
NI-5	0.85	0.88^c	1.07	80	20	–
NI-8	0.49	0.6^c	1.1	72	28	–
NI-6	0.35	0.43^c	1.28	59	38	3

[a] By membrane osmometry
[b] By s.e.c.
[c] By v.p.o.

molecular weight, M_n, measured by osmometry. Examples are given in *Figure 3*. The only exception is the lower-molecular-weight sample ($M_n = 4300$), which has $I = 1.28$ but M_s is close to M_n (*Table 2*). Some broadening of the distribution is expected as the molecular weight decreases[19].

Apparently all the initiator is consumed although the molecular-weight distribution is somewhat higher compared with s-BuLi polymerizations at the same molecular-weight range. It seems that the slower initiation rate is overshadowed by the slower propagation rate[20,21] (and in comparison with that of styrene[22]).

The presence of the dimethylamino group on the initiator affects the microstructure of the polyisoprene (PI). The typical microstructure of PI produced by s-BuLi is[19]: ~ 10 wt% 3,4, ~ 70 wt% *cis*-1,4, ~ 20 wt% *trans*-1,4. There is an increase of 3,4 content on decreasing the molecular weight and consequently increasing the concentration of the functional initiator in the polymerization mixture. This is not surprising having in mind the modifying effect that tertiary amines exert on diene polymerization[6,23]. There is no evidence of 1,2 enchainment except again for sample NI-6 with the lower molecular weight where the 1,2 content is ~ 3 wt%.

Butadiene polymerization

The molecular weights of the polybutadienes (PBd) prepared by DMAPLi cover the range between 5600 and 36 000 and the concentration of the initiator was between 7.5×10^{-4} M and 7×10^{-3} M. There is always good agreement between M_s and M_n measured by osmometry. This is direct evidence that DMAPLi is an efficient initiator for butadiene. The polydispersity index is almost the same as that obtained for polybutadienes prepared with s-BuLi as initiator. *Figure 4* shows characteristic s.e.c. chromatograms for the DMAPLi-initiated polybutadienes. The values obtained by s.e.c. are between 1.05 and 1.07. The molecular characteristics of the PBd samples measured by membrane osmometry, vapour-pressure osmometry and s.e.c. are given in *Table 3*. These results show that there is no great difference between s-BuLi and DMAPLi for the polymerization of butadiene. The reason for this is again the low propagation rate relative to initiation[24].

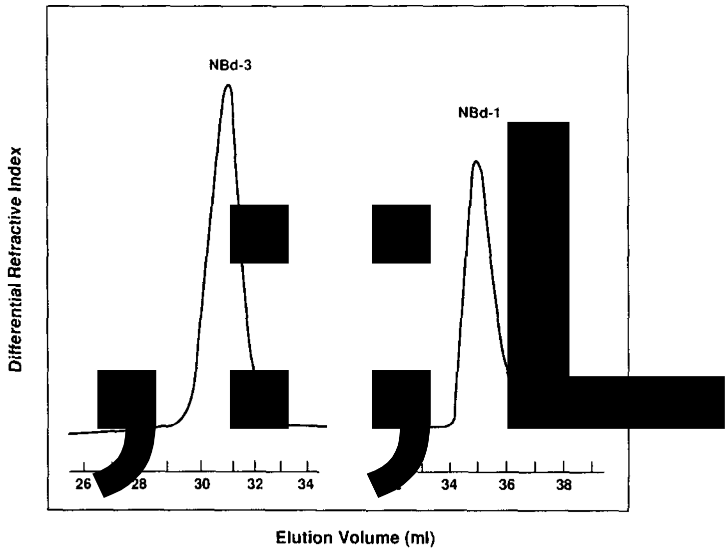

Figure 4 S.e.c. chromatograms of samples NBd-3 and NBd-1 (purified DMAPLi; solvent, benzene)

The effect of the use of DMAPLi as initiator is more pronounced in the change of microstructure. The polymerization of butadiene initiated by s-BuLi in benzene leads mainly to the 1,4 structure rather than

Table 3 Molecular characteristics of polybutadienes prepared by DMAPLi

Sample	M_s $\times 10^{-4}$	$M_n{}^a$ $\times 10^{-4}$	I^b	*cis* 1,4 (%)	*trans* 1,4 (%)	1,2 (%)
NBd-1	0.6	0.56^c	1.07	27.1	40.9	32.0
NBd-2	1.35	1.26	1.06	29.2	44.8	26.0
NBd-3	1.4	1.31	1.06	29.0	44.0	27.0
NBd-4	3.3	3.49	1.05	33.8	47.1	19.1
NBd-5	3.7	3.56	1.05	36.5	51.2	12.3

[a] By membrane osmometry
[b] By s.e.c.
[c] By v.p.o.

the 1,2 structure (the typical microstructure is[25]: ~ 7 wt% 1,2, ~ 36 wt% *cis*-1,4, ~ 57 wt% *trans*-1,4). However, the addition of polar compounds, such as ethers or amines, increases the amount of 1,2 enchainment.[26] The n.m.r. spectra of amine-capped polybutadienes show an increase of 1,2 content with decreasing molecular weight (*Table 3*). The situation is analogous to isoprene polymerizations. This is reasonable if we consider the increased initiator concentration needed to prepare low-molecular-weight polymers. The results are given in *Table 3*.

It is interesting to note that the *trans*/*cis* ratio remains almost stable and equal to 3/2 for polymers with different vinyl contents.

Styrene polymerization

In this case, DMAPLi in hexane, which was not separated from the by-products of the synthesis, was also used as initiator for two polymerizations. The polystyrenes obtained exhibited low molecular-weight distributions ($I = 1.09$, *Figure 5a*), although initiation was slow and the appearance of the orange colour of the living polymer was gradual over a period of a few minutes (*Table 4*). This is probably due to the presence of the tertiary amines, which can act as chelating agents, decreasing the propagation rate of the polymerization of styrene[27].

When purified DMAPLi was used for the preparation of polystyrenes having $M_s > 12\,000$, initiation rate was slow, resulting in relatively high polydispersity ratios ($I = 1.23-1.27$), but presumably consumption of initiator was complete because M_n was close to M_s and subsequent addition of isoprene gave diblocks having narrow molecular-weight distributions as determined by s.e.c.

The situation is different when $M_s < 9300$. In this case polymers having high molecular-weight distributions with long tails in the low molecular-weight region of the chromatogram were obtained (*Figure 6a*). Additionally, molecular weights measured by s.e.c. were considerably higher than the stoichiometric ones, with the difference being lower as M_s increased. Obviously the initiation reaction was incomplete and appreciable amounts of initiator remained unreacted. Subsequent addition of isoprene to the mixture resulted in polymers having bimodal distributions (*Figure 6b*). The new peaks are relatively narrow. The one corresponding to higher molecular weights can be attributed to the diblock formed by reaction of PSLi living chains with part of the isoprene added. The low-molecular-weight peak may correspond to polyisoprene homopolymer formed by reaction of the remaining initiator with the isoprene monomer. There seems to be a similarity between the behaviour of DMAPLi and t-BuLi towards the styrene initiation[28,29]. The results do not change with the addition of anisole ([anisole]/[Li] = 10) to the polymerization solution before the initiation reaction takes place (*Table 4*).

When THF was added to the mixture of styrene and DMAPLi ([THF]/[Li] $\geqslant$ 3) the appearance of the red-orange colour was immediate and certainly faster than in the absence of THF. The polymers had still relatively high molecular-weight distributions but good agreement

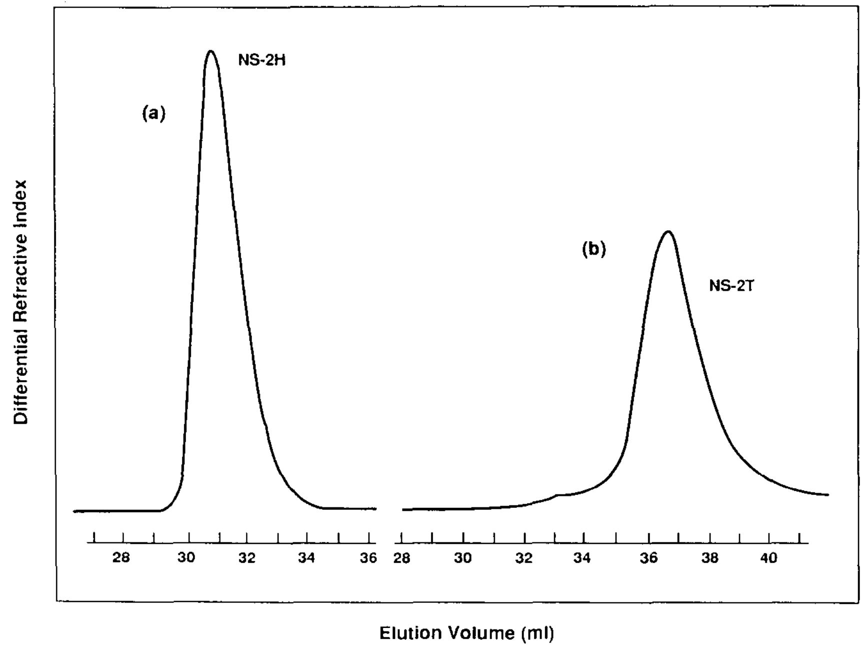

Figure 5 S.e.c. chromatograms of samples (a) NS-2H (unpurified DMAPLi, solvent benzene) and (b) NS-2T (purified DMAPLi; solvent, benzene and THF)

Table 4 Molecular characteristics of polystyrenes prepared by DMAPLi

Sample[a]	M_s $\times 10^{-4}$	M_n[b] $\times 10^{-4}$	I[b]
NS-1B	0.26	0.98	1.46
NS-2B	0.3	0.99	1.32
NS-3B	0.63	1.51	1.35
NS-4B	0.93	1.13	1.44
NS-5B	1.9	1.97[c]	1.23
NS-6B	1.23	1.37	1.28
NS-7A	0.92	1.2	1.40
NS-8T	0.33	0.35[d]	1.46
NS-9T	0.45	0.44[d]	1.42
NS-10T	0.54	0.5[d]	1.21
NS-11T	0.71	0.79[d]	1.14
NS-12T	1.08	1.07[d]	1.09
NS-13H	3.41	3.5	1.09
NS-14H	3.96	4.05	1.09

[a] Capital letters that accompany samples denote: B, purified DMAPLi in pure benzene was used; A, anisole was added as a cosolvent; T, THF was added as a cosolvent in the polymerization mixture; H, DMAPLi in hexane solution was used as prepared

[b] By s.e.c.

[c] By membrane osmometry

[d] By v.p.o.

between M_s and M_n was accomplished (*Figure 5b*). After addition of isoprene, relatively narrow molecular-weight distribution diblocks were prepared. In the presence of THF the polydispersity ratio decreased when the molecular weight increased (*Table 4*).

Since at this low molecular-weight region end-group effects can play an important role in s.e.c. experiments (polar groups can be adsorbed on the columns), low-molecular-weight polystyrenes, polyisoprenes and polybutadienes were run through the g.p.c. with the carrier solvent being a mixture of 95% THF and 5% tetramethylethylenediamine (TMEDA). The distributions obtained were the same for polydienes but were 5–10% lower for polystyrenes probably due to the higher affinity of polystyrene for the column packing when TMEDA is not present.

The behaviour of DMAPLi (which seems to have similarities with that of diethylamide[30]) as an anionic initiator for isoprene, butadiene and styrene can be explained by the higher degree of association and presumably the lower constant of dissociation for DMAPLi in hydrocarbons compared to s-BuLi, factors that affect reactivity of initiator molecules towards monomer molecules. This assumption is consistent with the insolubility of DMAPLi in hexane and also the low solubility (0.35 M) in benzene. The amine group on the initiator molecule makes it more polar but also decreases the reactivity of the C–Li bond, stabilizing the carbanion by withdrawing charge from C1 to nitrogen. Also complexation of the amine moiety to Li cation accompanied with the formation of a stable five-membered ring cannot be ruled out. Such a complexation can influence the mode of addition of monomer molecules to the growing chain, especially at the beginning of polymerization. The phenomenon must be more pronounced in the stage of initiation than in the propagation reaction for stereochemical reasons. So, the differences in behaviour towards different monomers can be a result of differences in the stage of initiation. It is important to have in mind that in the stage of propagation there may be two kinds of complexation between amine groups and Li^+. The first one is an intramolecular complexation, the magnitude of which is independent of initiator concentration in the system, and the second an intermolecular complexation that depends on concentration. This feature of the propagation reaction may play a decisive role in the microstructure of the polydienes prepared with DMAPLi.

These may account for the slower rate of initiation observed in both isoprene and styrene polymerizations. In the case of styrene, the proximity of the aromatic ring to the polymerizable double bond makes it less reactive and more sterically hindered towards complexation with the active centre. Isoprene and butadiene are expected to be more susceptible to complexation due to their 1,3 olefinic structure. The presence of the weak coordinating ether anisole seems to make no difference at all to the whole situation. On the contrary, when the stronger coordinating ether THF is present, initiation is much faster, indicating increased reactivity of DMAPLi molecules resulting from breakage of the aggregates and formation of DMAPLi–THF complexes that are more reactive[31,32]. However, these etherates must be less reactive than the corresponding n-BuLi–THF species and even than s-BuLi[33] itself judging from the high molecular-weight distributions of the low-molecular-weight polystyrenes prepared in this fashion. It seems that the presence of tertiary amines (bidentate chelating

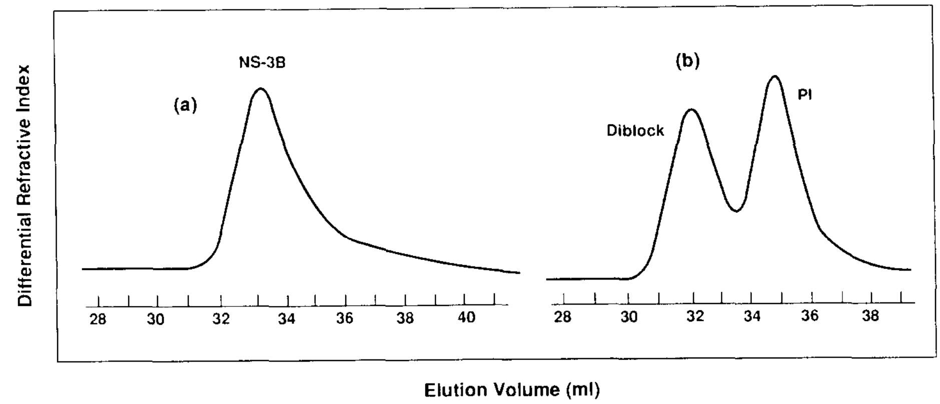

Figure 6 S.e.c. chromatograms of (a) NS-3B (purified DMAPLi; polymerization in pure benzene) and (b) NS-3B after the addition of isoprene (first peak, diblock formed; second peak, homopolyisoprene formed by reaction of isoprene with unreacted DMAPLi)

agents) from the preparation reaction of the initiator has a similar but less pronounced effect on the kinetics of polymerization[34].

CONCLUSIONS

DMAPLi is an effective initiator for the synthesis of polybutadienes and polyisoprenes with dimethylamino end-groups. These polymers have narrow molecular-weight distributions and predictable molecular weights but the microstructure depends on the molecular weight. Vinyl content increases by decreasing molecular weight.

In the case of styrene DMAPLi gives polymers with higher polydispersity index and when the molecular weight is lower than about 10 000 initiation is incomplete. The presence of strongly coordinating ethers, like THF, or bidentate tertiary amines facilitates complete initiation and lower polydispersity.

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