On the Anionic Polymerization of (Dialkylamino)isoprenes. 2. Influence of the Tertiary Amino Group on the Polymer Microstructure

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ABSTRACT: The anionic polymerization of 5-(*N*,*N*-dialkylamino)isoprenes carrying various alkyl substituents was studied in nonpolar (benzene, hexane) and polar solvents (tetrahydrofuran, dioxane, triethylamine). The microstructure is found to be strongly dependent on the bulkiness of the tertiary amino group. All polymerizations in nonpolar solvents occur by a 4,1-addition of the monomer to the anionic chain end. In THF no polymerization occurs. The results are discussed with respect to the stereoelectronic situation at the growing chain end. For monomers with the most bulky branched side groups (isopropyl, isobutyl, and 2,6-*cis*-dimethylpiperidyl) the addition is not only regioselective but also stereoselective, giving rise to the formation of stereoregular polymers with cis-4,1-repeating units. In the case of monomers with linear, less bulky alkyl substituents (e.g. ethyl, propyl, butyl, or piperidyl), the polymer contains a mixture of cis- and trans-4,1-units (until about 70%). In all cases the amount of 4,3-units is less than in the anionic polymerization of isoprene, despite the fact that the aminoisoprenes have a polarity comparable to triethylamine.

Introduction

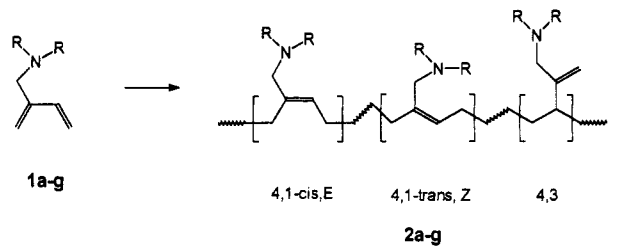
The anionic polymerization of 1,3-dienes has been widely used for the synthesis of defined homo- and block copolymers. Addition of 2(*R*)-1,3-dienes to carbanionic species may occur at position 1 or 4, resulting in 1,4- and 1,2- or 4,1-, and 4,3-addition. The stereochemistry of the anionic polymerization of dienes depends on the type of counterion as well as on the nature of the solvent. The polymerization of isoprene in hydrocarbon solvents by lithium-based initiators gives a polymer with a high content of cis-4,1-units, while in polar solvents or even in the presence of small quantities of highly basic ethers such as THF or tertiary amines polymers having various amounts of 4,3- and 1,2-units are formed.[1–4] To our knowledge only diene monomers with nonpolar side groups have been used in anionic polymerizations so far.

Recently we reported on first experiments of the anionic polymerization of (diisopropylamino)isoprene **1a**,[5] a 1,3-diene with a tertiary amino group linked to carbon C-5 of 2-methyl-1,3-butadiene (isoprene). Owing to the presence of the tertiary amino group we expected a polymer microstructure similar to what is known for the anionic polymerization of dienes in the presence of amines.[6] As the most surprising result, a highly stereoregular partially crystalline polymer **2a** was formed. From the analogy of the ^{1}H- and ^{13}C-NMR spectra to polyisoprene we assigned a cis-4,1-microstructure ("cis" with respect to the polymer backbone, i.e., an *E*-structure according to IUPAC nomenclature) to the polymer (Scheme 1).

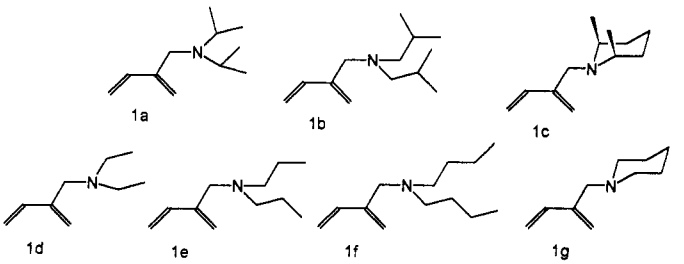
The stereoregular polymerization proceeded without any special precaution. The formation of the stereoregular polymer has been attributed to steric as well as electronic effects related to the intramolecular complexation between the Li^+ counterion, the carbanion, and the diisopropylamino groups.

The present contribution reports on the anionic polymerization of a series of *N*,*N*-dialkyl-2-vinylallylamines

Scheme 1



Scheme 2



1a–g [trivial names: 5-(*N*,*N*-dialkylamino)isoprene, 3-[(*N*,*N*-dialkylamino)methyl]-1,3-butadiene) (Scheme 2)] to elucidate the factors controlling the polymer microstructure in more detail.

Experimental Section

Monomer Synthesis. The monomers were prepared via a potassium *tert*-butoxide mediated rearrangement of the corresponding *N*,*N*-dialkyl-*O*-allyl acetals in dimethyl sulfoxide (DMSO), according to the synthesis reported by Frauenrath et al.[7] The overall yield of the two-step monomer synthesis starting from a secondary amine, allyl alcohol, and formaldehyde is on the order of 20–30% after purification.

Characterization of Monomers 1a–g. The following listings summarize the ^{1}H-NMR and ^{13}C-NMR spectroscopic data of the monomers prepared in the course of this study. Some of these monomers (**1a, 1d, 1g**) have been reported by Frauenrath.[7]

5-(*N*,*N*-Diisopropylamino)isoprene (1a): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.40 (dd, J = 11, 18 Hz, 1H; H_2C=C*H*), 5.36

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(d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.35, 5.10 (each br s, 2H; H_2C=CCH_2), 5.00 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.20 (br s, 2H; H_2CN), 3.02 (sept, J = 7 Hz, 2H; $N(CH(CH_3)_2)_2$), 0.98 (d, J = 7 Hz, 12H; $N(CH(CH_3)_2)_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 145.9 (C-2), 138.2 (C-3), 116.2 (C-4), 112.6 (C-1), 46.5 (C-5), 48.1 ($N(CH(CH_3)_2)_2$), 20.6 ($N(CH(CH_3)_2)_2$).

5-(*N,N*-Diisobutylamino)isoprene (1b): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.37 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.43 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.24, 5.12 (each br s, 2H; H_2C=C-CH_2), 5.05 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.07 (br s, 2H; H_2CN), 2.02 (d, J = 7 Hz, 4H; $N(CH_2$-isopropyl$)_2$), 1.71 (m, J = 7 Hz, 2H; $N(CH_2CH(CH_3)_2)_2$), 0.95 (d, J = 7 Hz, 12H; $N(CH_2CH(CH_3)_2)_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 144.2 (C-2), 138.1 (C-3), 117.1 (C-4), 113.8 (C-1), 58.2 (C-5), 64.0 ($N(CH_2CH(CH_3)_2)_2$), 26.4 ($N(CH_2CH(CH_3)_2)_2$), 21.0 ($N(CH_2CH(CH_3)_2)_2$).

5-(*cis*-2,6-Dimethyl-*N*-piperidyl)isoprene (1c): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.41 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.17 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.60, 5.09 (each br s, 2H; H_2C=CCH_2), 5.07 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.18 (br s, 2H; H_2CN), 2.41 (m br, J = 7 Hz, 2H; *cis*-2,6-dimethylpiperidyl-CH), 1.57 (m br, 4H; *cis*-2,6-dimethylpiperidyl-CH_2), 1.29 (m br, 2H; *cis*-2,6-dimethylpiperidyl-CH_2), 0.94 (m br, J = 7 Hz, 6H; cis-2,6-dimethylpiperidyl-CH_3); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 146.1 (C-2), 138.2 (C-3), 117.1 (C-4), 111.5 (C-1), 52.1 (C-5), 58.7 (*cis*-2,6-dimethylpiperidyl-CH), 34.8 (*cis*-2,6-dimethylpiperidyl-CH_2), 24.3 (*cis*-2,6-dimethylpiperidyl-CH_2), 21.8 (*cis*-2,6-dimethylpiperidyl-CH_3).

5-(*N,N*-Diethylamino)isoprene (1d): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.34 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.40 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.15, 5.08 (each br s, 2H; H_2C=CCH_2), 5.02 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.01 (br s, 2H; H_2C-N), 2.51 (q, J = 7 Hz, 4H; $N(CH_2CH_3)_2$), 0.95 (t, J = 7 Hz, 6H; $N(CH_2CH_3)_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 144.0 (C-2), 137.1 (C-3), 117.0 (C-4), 114.0 (C-1), 55.2 (C-5), 45.0 ($N(CH_2CH_3)_2$), 11.8 ($N(CH_2CH_3)_2$).

5-(*N,N*-Dipropylamino)isoprene (1e): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.38 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.42 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.19, 5.10 (each br s, 2H; H_2C=CCH_2), 5.04 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.11 (br s, 2H; H_2CN), 2.36 (t, J = 7 Hz, 4H; $N(CH_2CH_2CH_3)_2$), 1.35 (m, J = 7 Hz, 8H; $N(CH_2CH_2CH_3)_2$), 0.88 (t, J = 7 Hz, 6H; $N(CH_2CH_2CH_3)_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 144.1 (C-2), 137.9 (C-3), 116.9 (C-4), 113.8 (C-1), 56.6 (C-5), 53.9 ($N(CH_2CH_2CH_3)_2$), 20.7 ($N(CH_2CH_2CH_3)_2$), 11.8 ($N(CH_2CH_2CH_3)_2$).

5-(*N,N*-Dibutylamino)isoprene (1f): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.38 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.42 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.19, 5.10 (each br s, 2H; H_2C=CCH_2), 5.04 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.11 (br s, 2H; H_2CN), 2.36 (t, J = 7 Hz, 4H; $N(CH_2CH_2CH_2CH_3)_2$), 1.35 (m, J = 7 Hz, 8H; $N(CH_2CH_2CH_2CH_3)_2$), 0.88 (t, J = 7 Hz, 6H; $N(CH_2CH_2CH_2CH_3)_2$); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 144.2 (C-2), 137.9 (C-3), 117.0 (C-4), 113.9 (C-1), 56.6 (C-5), 53.9 ($N(CH_2CH_2CH_2CH_3)_2$), 29.2 ($N(CH_2CH_2CH_2CH_3)_2$), 20.7 ($N(CH_2CH_2CH_2CH_3)_2$), 14.1 ($N(CH_2CH_2CH_2CH_3)_2$).

5-(*N*-Piperidyl)isoprene (1g): ^{1}H-NMR (200 MHz, $CDCl_3$) δ = 6.37 (dd, J = 11, 18 Hz, 1H; H_2C=CH), 5.42 (d, J = 18 Hz, 1H; HCH=CH, *trans*), 5.12 (br s, 2H; H_2C=CCH_2), 5.05 (d, J = 11 Hz, 1H; HCH=CH, *cis*), 3.03 (br s, 2H; H_2C-N), 2.34 (br s, J = 6.5 Hz, 4H; piperidyl-H), 1.55 (m br, J = 6.5 Hz, 4H; piperidyl-H), 1.43 (m br, J = 6.5 Hz, 2H; piperidyl-H); ^{13}C-NMR (50 MHz, $CDCl_3$) δ = 142.8 (C-2), 138.0 (C-3), 117.2 (C-4), 114.0 (C-1), 54.6 (C-5), 51.8 (piperidyl-C), 26.0 (piperidyl-C), 24.1 (piperidyl-C).

Polymerization. Monomers and solvents (benzene, hexane, THF, triethylamine, and dioxane) were purified as described earlier.[5] The room temperature polymerizations summarized in Table 1 were performed under nitrogen atmosphere (>99.9993 vol %). Before polymerization, the reaction vessel was heated for 24 h to 120 °C under high vacuum and purged with nitrogen. After monomer and solvent condensation, the initiator—*sec*-butyllithium (s-BuLi, 1.3 M solution in cyclohexane/hexane 98/2 by vol, purchased from Merck)—was added into the reaction vessel. In general the reaction was terminated after 48 h by addition of methanol. The polymer was precipitated in methanol and dried under reduced pressure.

In bulk polymerizations (monomers **1a,c**) *sec*-butyllithium was directly added via a syringe to the monomer kept at −50 °C.

The complex initiator system—s-BuLi/TMEDA (ratio 1:2)—was also used to start the anionic polymerization of **1a** in benzene at room temperature.[6]

Structural Characterization. ^{1}H-NMR (200 and 400 MHz) and ^{13}C-NMR spectra (50 and 100 MHz) were recorded on Bruker 200- and 400-MHz spectrometers in deuterated chloroform at room temperature. To elucidate the polymer microstructure conventional NOE and rotating-frame NOE experiments, also known as CAMELSPIN (crossrelaxation *a*ppropriate for *mini*-molecules *emu*lated by *spin*-locking) or ROESY were performed.[8]

Size exclusion chromatography (SEC) was performed in THF as eluent on a LPK GPC. A differential refractometer and a UV spectrometer set at 254 nm were used as detectors connected in series. Four cross-linked polystyrene columns of gel pore sizes 50, 10^3, 10^4, and 10^5 Å were used. The molecular weights were determined via a calibration with respect to polystyrene standards.

The ^{1}H- and ^{13}C-NMR spectroscopic data of the homopolymers are as follows.

Poly[5-(*N,N*-diisopropylamino)isoprene] (2a): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.28 (s br, 1H, HC=C), 3.00, 2.94 (s br, 4H, $N(CH(CH_3)_2)_2$, CH_2N), 2.08 (s br, 4H, CH_2-allyl), 0.94 (d, J = 7 Hz, 12H, $N(CH(CH_3)_2)_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 138.4 (C-2), 127.0 (C-3), 50.8 (C-5), 46.3 ($N(CH(CH_3)_2)_2$), 28.5 (C-1), 26.9 (C-4), 20.5 ($N(CH(CH_3)_2)_2$).

Poly[5-(*N,N*-diisobutylamino)isoprene] (2b): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.21 (s br, 1H, HC=C), 2.74 (s br, 2H, CH_2N), 2.11 (s br, 4H, CH_2-allyl), 1.95 (d, J = 6.5 Hz, 4H, $N(CH_2CH(CH_3)_2)_2$), 1.69 (m br, J = 6.5 Hz, 2H, $N(CH_2CH(CH_3)_2)_2$), 0.83 (d, J = 6.5 Hz, 12H, $N(CH_2CH(CH_3)_2)_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 137.6 (C-2), 128.3 (C-3), 63.6 ($N(CH_2CH(CH_3)_2)_2$), 62.5 (C-5), 28.5 (C-1), 26.5 (C-4), 26.5 ($N(CH_2CH(CH_3)_2)_2$), 21.1 ($N(CH_2CH(CH_3)_2)_2$).

Poly[5-(*cis*-2,6-dimethyl-*N*-piperidyl)isoprene] (2c): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.59 (s br, 1H, HC=C), 2.96 (s br, 2H, CH_2N), 2.39 (s br, 2H, *cis*-2,6-dimethylpiperidyl-CH), 2.04 (s br, 4H, CH_2-allyl), 1.49, 1.25 (m br, 6H, *cis*-2,6-dimethylpiperidyl-CH_2), 0.94 (d, J = 7 Hz, 6H, *cis*-2,6-dimethylpiperidyl-CH_3); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 138.9 (C-2), 124.8 (C-3), 58.1 (*cis*-2,6-dimethylpiperidyl-CH_2N), 56.6 (C-5), 30.4 (C-1), 27.0 (C-4), 34.4, 23.9 (*cis*-2,6-dimethylpiperidyl-CH_2), 21.8 (*cis*-2,6-dimethylpiperidyl-CH_3).

Poly[5-(*N,N*-diethylamino)isoprene] (2d): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.29, 5.27 (s br, 1H, HC=C), 2.93, 2.84 (s br, 2H, CH_2N), 2.40 (q br, 4H, J = 7 Hz, $N(CH_2CH_3)_2$), 2.10 (s br, 4H, CH_2-allyl), 0.96 (t, J = 7 Hz, 6H, $N(CH_2CH_3)_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 137.2 (C-2), 128.0 (C-3), 60.0, 51.9 (C-5), 46.5 ($N(CH_2CH_3)_2$), 36.0, 29.1 (C-1), 26.7 (C-4), 11.8 ($N(CH_2CH_3)_2$).

Poly[5-(*N,N*-dipropylamino)isoprene] (2e): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.29, 5.25 (s br, 1H, HC=C), 2.91, 2.82 (s br, 2H, CH_2N), 2.24 (t br, 4H, J = 7.5 Hz, $N(CH_2CH_2CH_3)_2$), 2.08 (s br, 4H, CH_2-allyl), 1.43 (m br, 4H, $N(CH_2CH_2CH_3)_2$), 0.84 (t, J = 7.5 Hz, 6H, $N(CH_2CH_2CH_3)_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 137.3 (C-2), 128.0 (C-3), 61.2, 53.0 (C-5), 55.8 ($N(CH_2CH_2CH_3)_2$), 36.0, 29.0 (C-1), 26.7 (C-4), 20.3 ($N(CH_2CH_2CH_3)_2$), 12.0 ($N(CH_2CH_2CH_3)_2$).

Poly[5-(*N,N*-dibutylamino)isoprene] (2f): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.28, 5.26 (s br, 1H, HC=C), 2.91, 2.82 (s br, 2H, CH_2N), 2.28 (m br, 4H, J = 7.5 Hz, $N(CH_2CH_2CH_2CH_3)_2$), 2.09 (s br, 4H, CH_2-allyl), 1.32 (m br, 8H, $N(CH_2CH_2CH_2CH_3)_2$), 0.88 (t, J = 7 Hz, 6H, $N(CH_2CH_2CH_2CH_3)_2$); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 137.4 (C-2), 128.0 (C-3), 61.3, 53.2 (C-5), 53.5 ($N(CH_2CH_2CH_2CH_3)_2$), 36.0, 29.2 (C-1), 29.4 ($N(CH_2CH_2CH_2CH_3)_2$), 26.7 (C-4), 20.6 ($N(CH_2CH_2CH_2CH_3)_2$), 14.1 ($N(CH_2CH_2CH_2CH_3)_2$).

Poly[5-(*N*-piperidyl)isoprene] (2g): ^{1}H-NMR ($CDCl_3$, 200 MHz) δ = 5.31, 5.28 (s br, 1H, HC=C), 2.85, 2.74 (s br, 2H, CH_2N), 2.27 (s br, 4H, piperidyl-CH_2-N), 2.08 (s br, 4H, CH_2-allyl), 1.52, 1.40 (m br, 6H, piperidyl-CH_2); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ = 136.3 (C-2), 128.3 (C-3), 66.3, 58.0 (C-5), 54.6 (piperidyl-CH_2N), 36.3, 29.5 (C-1), 26.8 (C-4), 26.2 (piperidyl-CH_2), 24.5 (piperidyl-CH_2).

Table 1. Reaction Conditions and SEC Analysis of the Polymerization of 5-(*N,N*-Dialkylamino)isoprenes 1a-g Carried Out in Benzene at Room Temperature Using *sec*-Butyllithium as Initiator

	10^3·[I],[a] mol·L^{-1}	[M$_0$][b] mol·L^{-1}	yield, %	M_n theor[c]	expl[d]	M_w/M_n[d]
1a	2.4	0.26	20	18 500	5000	1.5
1b	6.5	0.18	55	5 400	4700	1.5
1c	5.2	0.18	30	6 200	2500	1.3
1d	2.6	0.28	40	15 000	8000	1.2
1e	2.8	0.12	18	7 300	3500	1.2
1f	3.2	0.16	15	10 500	6300	1.5
1g	2.6	0.32	13	18 600	5200	1.8

[a] Initiator concentration. [b] Initial monomer concentration. [c] Number average molecular weight calculated from ratio of monomer and initiator concentrations. [d] From size exclusion chromatography calibrated with polystyrene standards.

Results

Polymerization Behavior. Anionic polymerizations have been performed under a nitrogen atmosphere. After monomer and solvent condensation, the initiator was added into the reaction vessel. The reaction mixture became lightly yellow (living carbanion). In general, the reaction was terminated after 48 h by addition of methanol. The polymer was precipitated in methanol and dried under reduced pressure. Table 1 summarizes the experimental conditions and SEC results of the materials used in this study.

The polymerizations of monomers **1a-g** were carried out in benzene at room temperature. No complete consumption of monomer was observed. For monomers **1a** and **1d**, it has been shown that higher monomer conversion (about 60%) can be obtained at lower temperatures (−15 °C) using mixed solvents (benzene/hexane 1:1), as well as in the bulk polymerization of **1a** at −50 °C. Additional experiments varying the polymerization conditions were performed using the diisopropyl derivative **1a**.[5] No polymer was formed using the complex initiator obtained by the addition of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) to s-BuLi (room temperature, benzene). Polymerizations of **1a** were also attempted in polar solvents. When THF (−50 °C) or dioxane (room temperature) was used as solvent, no polymer is obtained; however, in triethylamine (−50 °C), a small quantity of polymer could be isolated.

In accordance with the low yield, the theoretical molecular weights are not reached. The polymers **2a-g** have lower molecular weight than calculated for 100% conversion (number average molecular weights given in Table 1 were determined by SEC. The polar polymer backbone may have a different elution behavior. A preliminary light-scattering study of one sample of poly(**1a**) indicates a lower value of the molecular weight ($M_{w(LS)}/M_{w(SEC)}$ = 0.75) than obtained via SEC. The polymers show relatively broad molecular weight distributions (M_w/M_n > 1.3). The polymers obtained by polymerization at lower temperature have higher number average molecular weights and narrower molecular weight distributions (**2a**, M_n = 9200, M_w/M_n = 1.2; **2d** M_n = 8800, M_w/M_n = 1.2). The bulk polymerization of **1a** and **1d** also resulted in polymers with higher number average molecular weights, respectively M_n = 8400 and 9800; however, these polymers had a broad molecular weight distribution ($M_w/M_n \approx 1.6$).

Polymer Microstructure. In our preliminary work, the microstructure of poly[5-(*N,N*-diisopropylamino)-isoprene] (**2a**) was assigned from NMR spectroscopy in analogy to polyisoprene.[5] The anionic polymerization resulted in a highly stereoregular cis-4,1-polymer (>95%). In Figure 1a,b sections of the ^{1}H-NMR spectra of the polymers **2a-g** are shown. The signals at 5.3 ppm are

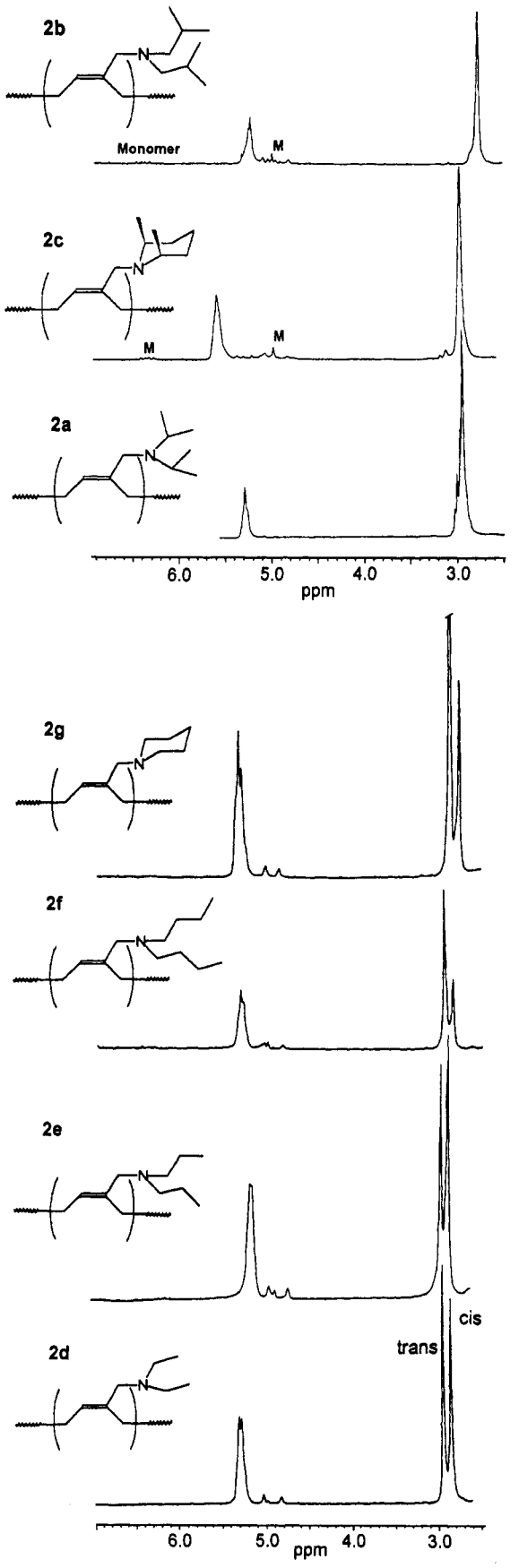
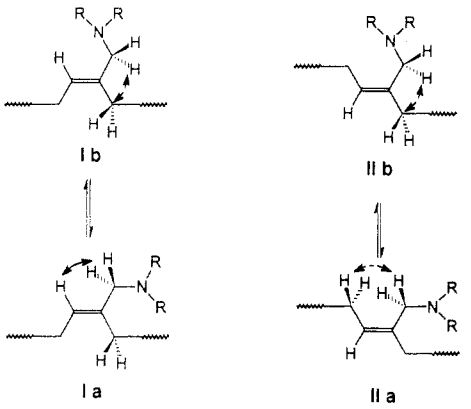


Figure 1. Sections of the ^{1}H-NMR spectra of poly[5-(*N,N*-dialkylamino)isoprenes]: (a) polymers with branched alkyl side chains, **2a-c** (M indicates traces of monomer), (b) polymers without methyl branches in alkyl substituent, **2d-g**.

Scheme 3



characteristic of the vinyl proton of 4,1-units, whereas the signals of the 4,3-units appear at about 4.8 ppm.[9] Additional small signals around 4.8 ppm and at about 6.0 ppm arise from traces of unreacted monomer. No signals characteristic of 1,2-units were detected. The resonance signals around 2.0 ppm are overlapping signals of the allylic protons of the polymer backbone and at 3.0 ppm the resonance of the methylene protons attached to carbon C-5 is observed. At higher field (1–2 ppm), the polymers show different resonance signals characteristic of the alkyl substituents linked to the nitrogen (see Experimental Section).

The polymers derived from monomers with linear alkyl substituents (ethyl, **2d**; propyl, **2e**; butyl, **2f**) and the aliphatic six-ring membered piperidine heterocycle **2g** show higher fractions of 4,3-units (6–12 mol %) than polymers **2a-c**. However this fraction is still considerably lower than in the anionic polymerization of isoprene in the presence of triethylamine, where polymers with 20–40% 4,3-vinyl content are obtained at different initiator/triethylamine ratios.[10] Polymerization of **1a** in triethylamine also resulted in a polymer with predominant 4,1-units (>90%), like in the polymerizations in nonpolar solvents.

The resonance peak at 5.3 ppm, which practically is a single peak for poly[5-(*N*,*N*-diisopropylamino)isoprene] (**2a**)[5] and **2b,c**, appears as two signals for the polymers **2d–g**, which could be related to a variation of the polymer microstructure.

The most characteristic proton signals which give access to the assignment of the polymer microstructure are the resonance signals at about 3.0 ppm, which arise from the methylene protons attached to carbon C-5, as in the case of the methyl protons for polyisoprene, where the signals of cis- and trans-4,1-units arise at 1.74 and 1.65 ppm, respectively.[9,11] While polymers **2a-c** only show one signal in this region, two signals (2.8 and 2.9 ppm) appear in polymers **2d-g**. These two signals may be assigned to the presence of cis- and trans-4,1 units.

To distinguish between cis- and trans-4,1-isomers (Scheme 3), conventional NOE and two-dimensional nuclear Overhauser effect measurements (ROESY), where spin diffusion is less significant,[7] were performed in the case of poly[5-(*N*,*N*-diethylamino)isoprene] (**2d**). In the cis-4,1-isomer **I**, a short through-space contact between the vinylic proton and the methylene protons at C-5 should occur, which would be absent in the case of the trans-4,1-isomer **II**, where the longer spatial distance between the protons would prohibit a signal enhancement. Thus an enhancement of the vinylic proton resonances upon irradiation of the CH_2N should be detected for isomer **I** in the conventional NOE experiment. In Figure 2a,b, the

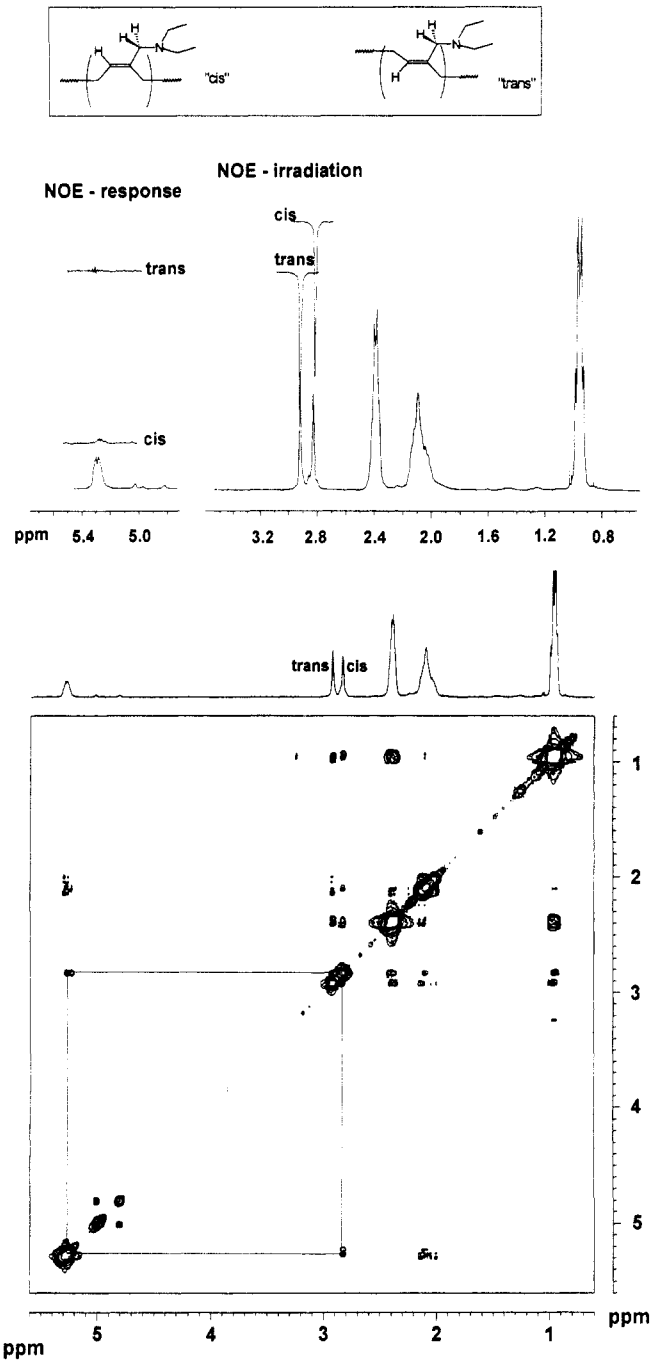


Figure 2. Microstructural analysis of poly[5-(*N*,*N*-diethylamino)isoprene] (**2d**) (400 MHz, $CDCl_3$); for detailed discussion see the text: (a, top) ^{1}H-NMR spectrum and one-dimensional NOE experiments, (b, bottom) two-dimensional ^{1}H-ROESY spectrum.

NOE and ROESY spectra of **2d** are shown. Only upon irradiation at the resonance frequency at 2.84 ppm is observed an enhancement of the vinyl proton resonance. No enhancement could be detected by irradiating at 2.93 ppm. This result is also supported by the two-dimensional ROESY experiment. Crosspeaks are only observed between the vinylic protons at 5.28 ppm and the methylene protons at 2.84 ppm (Figure 2b). The signal at 2.84 ppm thus can be unambiguously assigned to the cis-4,1-units and the resonance signal at 2.93 ppm to the trans-4,1-units. This assignment is valid also to the other polymers **2e-g**. Table 2 summarizes the effects of the different tertiary amino groups on the polymer microstructure. The fractions were calculated from the ^{1}H-NMR spectra. For polymers **2a-c**, only one signal around 3.0 ppm is observed. The vinyl proton also show up as a single resonance signal

Table 2. Microstructure of Poly[5-(*N,N*-dialkylamino)isoprenes] 2a–g[a]

polymer	cis-4,1	trans-4,1	4,3
2a–c	>95		<5
2d	45	43	12
2e	52	43	5
2f	24	68	8
2g	30	64	6

[a] Polymerization was carried out in benzene at room temperature.

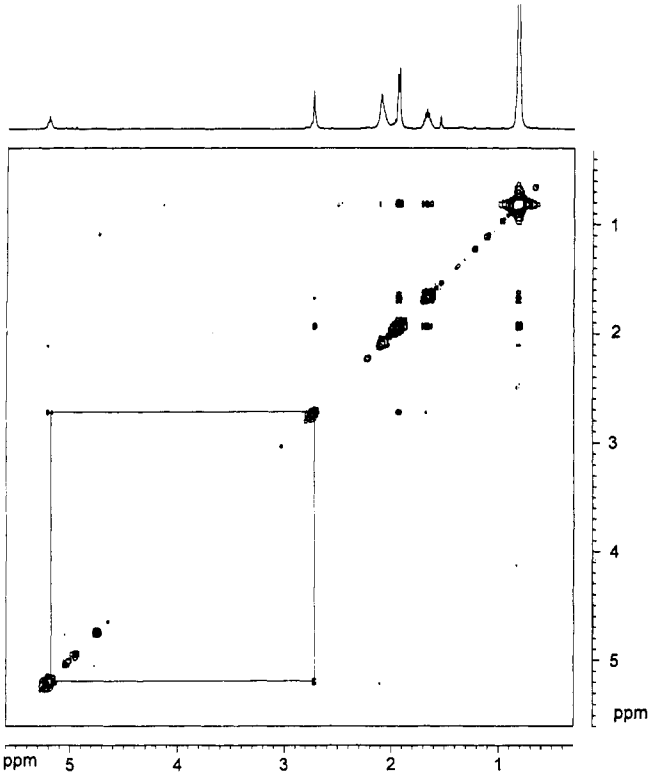


Figure 3. Microstructural analysis of poly[5-(*N,N*-diisobutylamino)isoprene] (**2b**): two-dimensional ^{1}H-ROESY spectrum (400 MHz, $CDCl_3$).

at 5.3 ppm. The additional signals at 3.0 ppm observed in the spectrum of poly(**1a**) results from the methine proton ($NCH(CH_3)_2$). While polymers **2a** and **2c** show singlet resonances at 2.9 ppm, the corresponding signal of **2b** is observed at higher field (2.8 ppm). Whereas the resonance signal of the vinylic proton of **2a** and **2b** appears at 5.3 ppm, the corresponding resonance signal of **2c** is shifted to the lower field (5.5 ppm). The NMR spectra indicate a stereoregular double bond configuration in these polymers. A direct conclusion from the chemical shifts of the C^5H_2 protons of polymers **2d-g** to the microstructure of polymers **2a-c** may be problematic. In our early study, a cis-4,1-structure was assigned to polymer **2a**. From the comparison of the chemical shift of the methylene protons a trans configuration could be possible too. To elucidate the microstructure of poly[5-(*N,N*-diisopropylamino)-isoprene] (**2a**) NOE experiments are performed. Upon irradiation at 3.0 ppm (CH_2N protons) a nuclear Overhauser enhancement was detected at the vinyl protons at 5.28 ppm. This confirms the cis-4,1-assignment of poly-[5-(*N,N*-diisopropylamino)isoprene] (**2a**). The ROESY spectrum of poly[5-(*N,N*-diisobutylamino)isoprene] (**2b**) (Figure 3) also shows the presence a short through-space contact between the methylene proton attached to carbon C-5 and the vinyl proton (see off-diagonal signals as indicated in Figure 3). Obviously we again deal with a cis-4,1-configuration of the double bond.

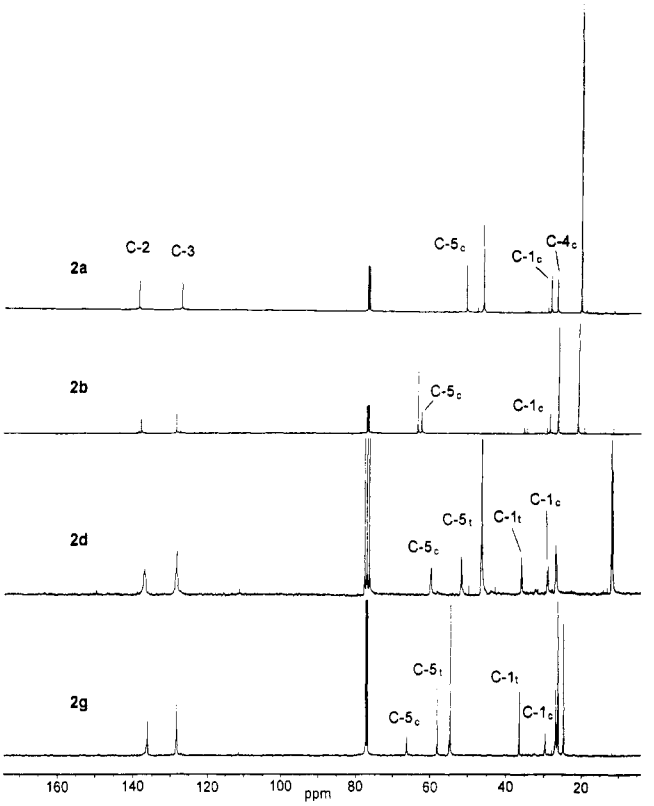


Figure 4. ^{13}C-NMR spectra of selected poly[5-(*N,N*-dialkylamino)isoprenes]: **2a**, poly[5-(*N,N*-diisopropylamino)isoprene]; **2b**, poly[5-(*N,N*-diisobutylamino)isoprene]; **2d**, poly[5-(*N,N*-diethylamino)isoprene]; **2g**, poly[5-(*N*-piperidyl)isoprene].

Table 3. Assignment of the ^{13}C-NMR Spectra of Poly[5-(*N,N*-dialkylamino)isoprenes] 2a–g[a]

polymer	$C\text{-}1_c$	$C\text{-}1_t$	C-2	C-3	C-4	$C\text{-}5_t$	$C\text{-}5_c$
2a	28.5		138.4	127.0	26.9		50.8
2b	28.5		137.6	128.3	26.5		62.5
2c	30.4		138.9	124.8	27.0		56.6
2d	29.5	36.3	136.3	128.3	26.8	66.3	58.0
2e	29.0	36.0	137.3	128.0	26.7	61.2	53.0
2f	29.2	36.0	137.4	128.0	26.7	61.3	53.2
2g	29.1	36.0	137.2	128.0	26.7	60.0	51.9
polyisoprene	32.3	40.1	135.1	125.1	26.5	16.0	23.4

[a] For comparison the assignments of the polyisoprene are listed. The chemical shifts of the alkyl substituents are given in the Experimental Section.

In the 2D-ROESY spectrum of poly(**1d**) (Figure 2b), through-space contacts between C^5H_2 (around 3.0 ppm) and allylic protons (2.0 ppm) of the cis–trans isomers are observed (as shown in Scheme 3, dotted line). In poly(**1b**) (Figure 3), no crosspeak between these protons is detected. It could indicate that the bulky isobutyl side groups hinder the rotation of the N–C bond and the cis-4,1-double bond conformation **Ia** is dominant. In this case, the through-space interaction between the methylene protons and the allylic protons (C^1H_2) is unfavored.

The microstructural assignment based on the proton spectra is further supported by ^{13}C-NMR spectra (Figure 4). Table 3 summarizes the ^{13}C-NMR assignments for the polymers **2a-g** and polyisoprene.[12] The olefinic carbons C-2 and C-3 and the allylic carbon C-4 have similar chemical shifts for all polymers. The carbon resonances of C-5 and of the allylic carbon C-1 are sensitive to the stereochemistry at the double bond. While the ^{13}C-NMR spectra of polymers **2a-c** (Figure 4) show only one resonance signal for each of these carbons, two signals corresponding to cis- and trans-4,1-isomers can be distinguished in polymers **2d-g**. The trans-4,1-units show

signals around 40 ppm for C-1 and 60 ppm for C-5, while the cis-4,1-resonances are observed at higher field, about 30 ppm (C-1) and 55 ppm (C-5). The relative position of the resonances related to cis and trans structural units are the same as for polyisoprene in the case of C-1; i.e., the signal corresponding to the cis-4,1-structure occurs at higher field and that of trans-4,1-units at lower field with a chemical shift difference ($\Delta\delta$) of about 7 ppm, similar to polyisoprene ($\Delta\delta$ = 8 ppm). A different behavior is observed for C-5, probably owing to the influence of the tertiary amino substituent. From the NOE experiments we have assigned a cis-4,1-microstructure for the polymers **2a** and **2b**. Both polymers show the same chemical shift for C-1 (28.5 ppm), but completely different chemical shifts for C-5 (50.8 and 62.5 ppm, respectively). Poly(**1c**) shows the resonance for C-5 at 56.6 ppm, intermediate between the corresponding resonances of **2a** and **2b**; however, the resonance signal of C-1 is observed at 30.4 ppm, similar to **2a,b**. Thus we also can assign the microstructure of polymer **2c** as cis-4,1.

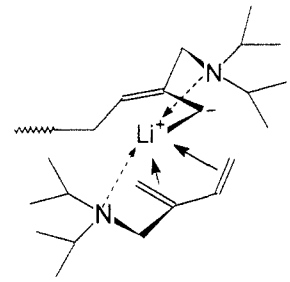
Different alkyl substituents at the amino groups of polymers **2d-g** cause different chemical shift of the C-5 resonances of the cis- and trans-4,1-units. Based on ^{1}H-NMR spectra, we can attribute the high-field resonance signals (52–58 ppm) to C-5 in a cis configuration and the low-field signals (60–66 ppm) to the C-5 resonance of the trans units.

Discussion

As has been documented by the experiments presented above, the stereochemistry of the anionic polymerization of (dialkylamino)isoprenes strongly depends on the type of dialkyl substituent attached to the amino group. While polymers **2a-c** have a stereoregular cis-4,1-microstructure, polymers **2d-g** have a mixed cis/trans-4,1-microstructure (Table 2). (Diethyl- and (dipropylamino)isoprenes are formed in almost equal amounts of cis- and trans-4,1-units, while for the dibutyl or piperidyl side chains the fraction of trans-4,1-structures is higher. In the following we attempt to give an explanation for these experimental findings.

The bulky side groups like the isopropyl, isobutyl and cis-2,6-dimethylpiperidyl favor an "s-cis" geometry of the monomer. In the case of the anionic polymerization of isoprene in nonpolar solvents, it is known that the addition of monomers in the s-cis configuration leads to a cis chain end which slowly isomerizes to trans, the thermodynamically stable form in nonpolar solvents.[3] If the propagation is faster than the cis–trans interconversion of the chain end, a mostly cis-4,1-structure is obtained. The anionic polymerization of isoprene in the presence of tertiary amines TMEDA and pentamethyldiethylenetriamine (PMDT) has been studied.[13,14] The complexation of the amine with the active site induces a complete isomerization of all living chain ends to the s-cis configuration, when the ratio (amine:living end) is equal to 0.5.[13] As known from other organolithium amine complexes, lithium prefers to be complexed by two to four amino groups.[15] In nonpolar solvents, the lithium counterion preferably may complex to the amino group located at the growing chain end. Such a complexation would be preferred for enthalpic and entropic reasons and would hinder the isomerization of the living chain end. The additional complexation of the lithium counterion by a second amino group of the incoming next monomer may additionally direct the reaction toward the observed stereoregular growth (Scheme 4). In the case of the monomers **1d-g** the steric requirement of the side groups would not be enough to induce a complete stereospecific addition of the monomer to the living chain end.

Scheme 4



Despite of the fact that the aminoisoprenes **1a-g** should have a polarity comparable to that of triethylamine, diethyl ether, or anisole—compounds which are well-known modifiers of polydiene microstructure during anionic polymerization, causing an increase in the fraction of 4,3-units—all polymers derived from aminoisoprenes show only small fractions of 4,3-units in the polymer backbone. The addition of the monomer to the carbanion occurs almost exclusively by 4,1-addition. The polymerization of **1a** in triethylamine as well as the bulk polymerizations (**1a,d**) also result in polymers with high 4,1-content (>90%). It has to be recognized that only a very low yield was obtained for the polymerization of **1a** in triethylamine.

One so far not fully understood experimental result are the limited yields despite the fact that the yellow color of the "living" anion does not disappear even after several days of reaction. The experiments show that the total yield strongly depends on the reaction temperature and reaction medium. So far no kinetic experiments were performed to follow the conversion and molecular weight as a function of reaction time.

The yields are higher at lower temperature. This could be due to the presence of some impurities in the monomer which react slowly with the growing chain end. However, the possibility to prepare high molecular weight copolymers in quantitative yield by anionic polymerization[17] makes it most likely that the purity of the monomer may not be the explanation of the limited yield during homopolymerizations.

Even more interesting is the observation that **1a** does not polymerize in polar solvents (THF and dioxane) as well in the presence of TMEDA, despite the fact that the initiator reacts with the monomer in THF under the formation of a carbanionic species.[16] These results lead us to the suggestion that the polar compounds strongly coordinate to the Li^+ counterion at the living chain end, hindering the addition of the monomer. Recent studies[18] demonstrate formation of stable complexes of lithium dialkylamides and related N-lithiated species with THF.

To elucidate the open problems related to the details of the surprising control of the polymer microstructure, NMR studies of the living chain end in polar and nonpolar solvents are in progress, as well the anionic polymerization of **1** in the presence of other counterions, e.g. potassium.[16]

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