Structure of initial, ultimate and inner chain units of polybutadiene obtained with a rare-earth catalyst as revealed by ^{13}C nuclear magnetic resonance spectroscopy

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The structure of initial, ultimate and inner chain units in polybutadiene produced with $NdCl_3.3(i\text{-}PrOH)\text{-}HAl(i\text{-}Bu)_2$ was studied by means of ^{13}C nuclear magnetic resonance spectroscopy. Initial units are shown to be predominantly of *trans*-$CH_3CH{=}CHCH_2$– structure. Conversely, 90% of inner units have *cis* configuration. Ultimate units obtained by quenching with H_2O (D_2O) are predominantly of 1,2 structure. On the basis of the data obtained, the polymerization mechanism was discussed.

(Keywords: structure; chain units; polybutadiene; rare-earth catalysis; ^{13}C nuclear magnetic resonance spectroscopy)

INTRODUCTION

The structure of the initial (IU) and ultimate chain units (UU) of polymers can provide valuable information on the mechanism of ionic polymerization of dienes[1].

In the present work the structure of UU after quenching by H_2O (D_2O) and also that of IU of polybutadiene obtained with $NdCl_3 \cdot 3(i\text{-}PrOH)\text{-}HAl(i\text{-}Bu)_2$ was investigated by ^{13}C n.m.r. spectroscopy. The conditions of polymerization were significantly different from those used to obtain *cis*-1,4-polybutadiene of high molecular mass with a lanthanide catalyst. In this study polymerization was carried out at low monomer concentration with a large content of diisobutylaluminium hydride (DIBAL-H) in the catalyst.

EXPERIMENTAL

Polymerization was carried out in hexane under purified argon. Butadiene (99.5% purity) and hexane (99% purity) were dried over alumina and then freshly distilled from $LiAlH_4$ before use. The catalyst was prepared by reaction of $NdCl_3 \cdot 3(i\text{-}PrOH)$ in toluene suspension with DIBAL-H at −20°C. The molar ratio Al/Nd amounted to 10. The suspension obtained was heated to room temperature. After precipitation of the solid phase, 90% of the liquid was decanted.

The solid residue was mixed with hexane solution of butadiene and kept at 20°C for 60 min. The neodymium concentration was 0.02 $mol\,l^{-1}$ and butadiene concentration was 0.1 $mol\,l^{-1}$. The polymer solution obtained was divided into two parts. In the first part, polymerization was quenched by H_2O (sample A); in the second one by D_2O (sample B). After thorough stirring, toluene solution of diphenyl-*p*-phenylenediamine was added to prevent oxidation. The solvent was removed *in vacuo* at room temperature. The residue was extracted with toluene and centrifuged, and the solvent was again removed. Polymers were dried for 30 h *in vacuo* at ambient temperature.

The ^{13}C n.m.r. spectra were recorded in 10 mm diameter tubes with a Bruker AM-500 spectrometer operating at 125.72 MHz. Polymer concentration on $CDCl_3$ was 15% (wt/wt). Spectra were obtained at 25°C using a pulse width of 12 μs, corresponding to the tip angle of 83° and a pulse delay of 8 s; 7500 scans were accumulated. The spectral width was 20 000 Hz, and the data size 32 000. Deuterochloroform (δ 77.04) was used as internal reference. The ^2H n.m.r. spectra were recorded according to ref. 1.

RESULTS AND DISCUSSION

The assignments of the peaks in the aliphatic and olefinic regions of the specimen of polymer B (*Figures 1* and *2*) are presented in *Tables 1* and *2*. Besides the resonances shown in the tables, there are some weak peaks. Some of them (δ 31.62, δ 29.73, δ 22.69 and δ 14.13) are attributed to impurities contained in the solvent. The symbols *C*, *T* and *V* are used for *cis*-1,4, *trans*-1,4 and 1,2 units respectively. For assignment of peaks of IU and UU, the chemical shifts of butadiene dimers obtained with organolithium compounds[2] as well as chemical shifts of *trans*-2-hexene[3] were utilized. In addition, to attribute resonance lines and to check the assignments, the relative intensities of peaks, differences in spectra of polymers A and B, and data on the subspectrum of CH groups obtained using the distortionless enhancement by polarization transfer (d.e.p.t.) technique were applied.

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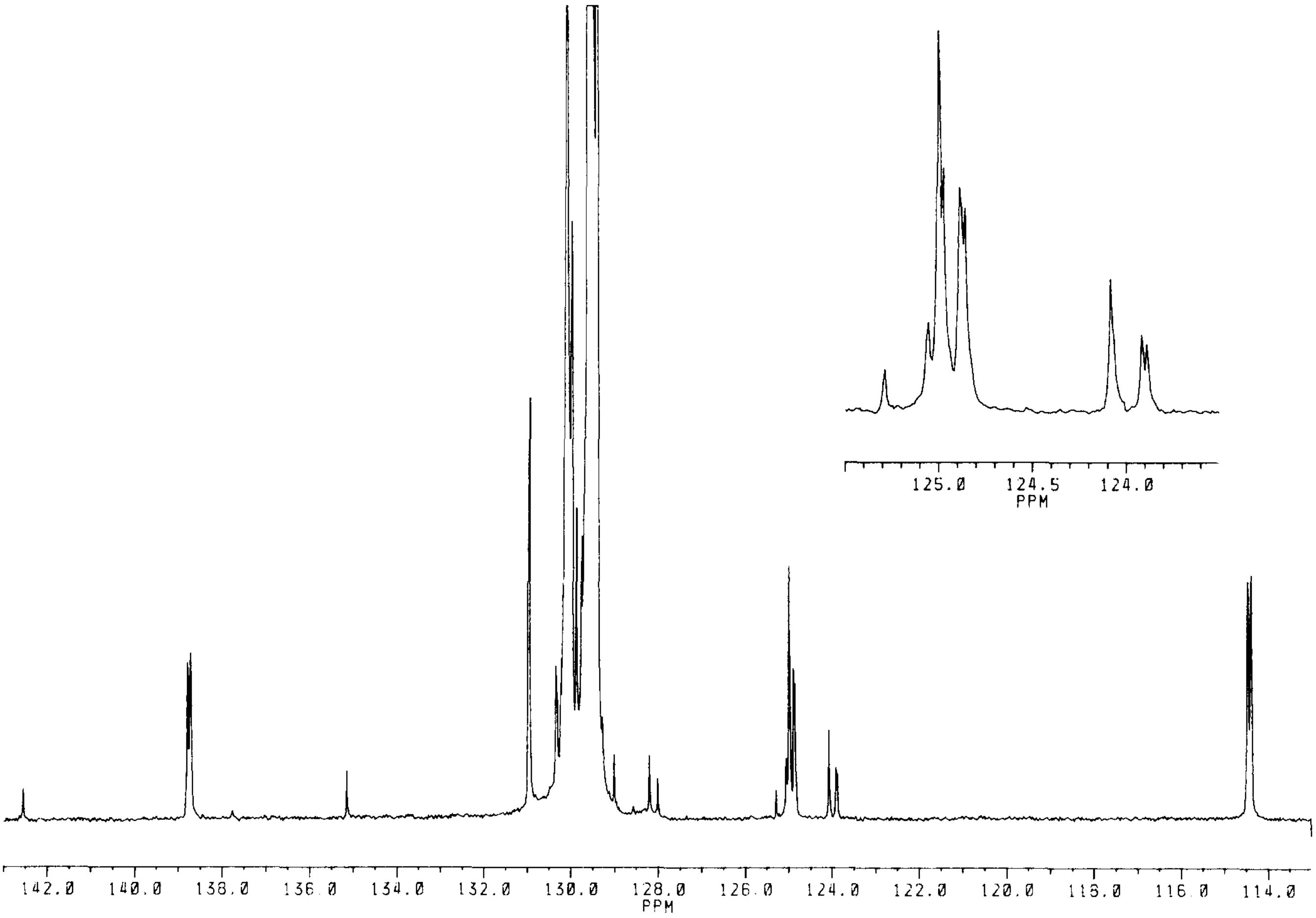


Figure 1 Olefinic region of ^{13}C n.m.r. spectrum of polybutadiene obtained with neodymium catalyst and quenched by D_2O (polymer B)

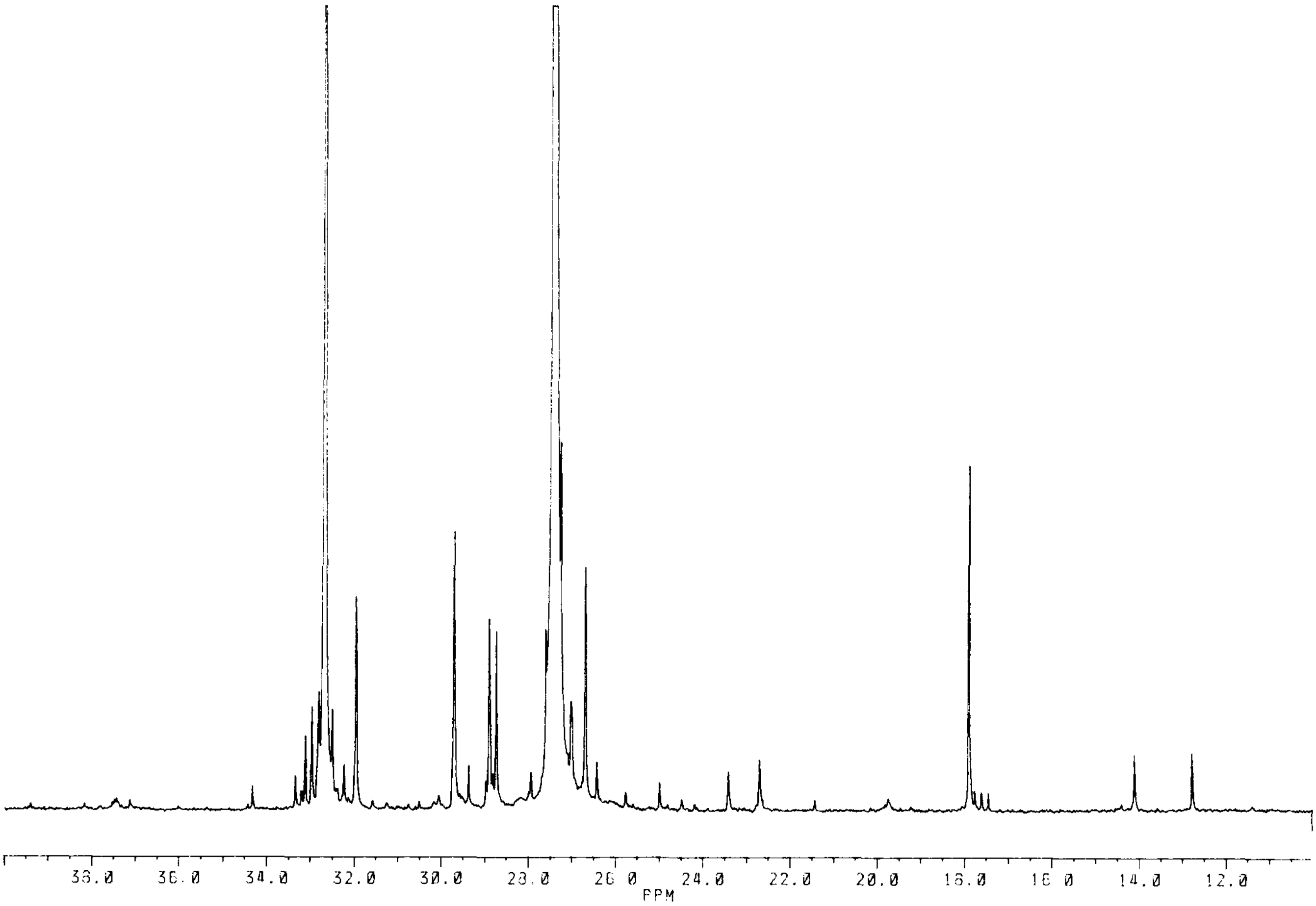


Figure 2 Aliphatic region of ^{13}C n.m.r. spectrum of polybutadiene obtained with neodymium catalyst and quenched by D_2O (polymer B)

Table 1 Peak assignments in the olefinic region of the ^{13}C n.m.r. spectrum of polybutadiene obtained with a neodymium catalyst and quenched by D_2O (polymer B)

No. of peak or of resp. group	Assignment		Model		
	Structure	Chem. shift (ppm)	Structure	Chem. shift (ppm)	Ref.
1	$-[C]-\mathrm{CH_2CHD\underline{C}H{=}CH_2}$ + $-[C]-\mathrm{CH_2CH_2\underline{C}H{=}CH_2}$	138.78	$\mathrm{Et}-[C]-\mathrm{CH_2CH_2\underline{C}H{=}CH_2}$	138.58	2
2	$-[T]-\mathrm{CH_2CHD\underline{C}H{=}CH_2}$ + $-[T]-\mathrm{CH_2CH_2\underline{C}H{=}CH_2}$	138.71	$\mathrm{Et}-[C]-\mathrm{CH_2CH_2\underline{C}H{=}CH_2}$	138.55	2
3	*trans*-$\mathrm{CH_3CH{=}\underline{C}HCH_2}-$ + $-$*trans*-$\mathrm{CH_2CH{=}\underline{C}HCH_2D}$	130.95	*trans*-$\mathrm{CH_3CH{=}\underline{C}HCH_2CH_2CH_3}$	131.51	3
4	$-$(*trans* + *cis*)-$\mathrm{CH_2CH{=}\underline{C}HCH_2CH_2CH_2}$- $\mathrm{CH{=}CH_2}$ + $-$(*trans*+*cis*)-$\mathrm{CH_2CH{=}\underline{C}H}$- $\mathrm{CH_2CH_2CHDCH{=}CH_2}$	130.15–130.40			
5	$-[C]-$*trans*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	130.10	$-[C]-$*trans*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	130.24	4
6	$-[T]-$*trans*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	129.99	$-[T]-$*trans*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	130.08	4
7	$-[C]-$*cis*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	129.58	$-[C]-$*cis*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	129.67	4
8	$-[T]-$*cis*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	129.42	$-[T]-$*cis*-$\mathrm{CH_2\underline{C}H{=}CHCH_2}-$	129.48	4
9	*trans*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[C]-[C]-$ + $-[C]-[C]-$*trans*-$\mathrm{CH_2CH{=}\underline{C}HCH_2D}$	125.00	*trans*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[C]-\mathrm{Et}$	124.91	2
10	*trans*-$\mathrm{CH_3C\underline{H}{=}CHCH_2}-[C]-[T]-$ + $-[T]-[C]-$*trans*-$\mathrm{CH_2CH{=}\underline{C}HCH_2D}$	124.98			
11	*trans*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-[C]-$ + $-[C]-[T]-$*trans*-$\mathrm{CH_2CH{=}\underline{C}HCH_2D}$	124.89	*trans*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-\mathrm{Et}$	124.82	2
12	*trans*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-[T]-$ + $-[T]-[T]-$*trans*-$\mathrm{CH_2CH{=}\underline{C}HCH_2D}$	124.86			
13	*cis*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[C]-$	124.08	*cis*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[C]-\mathrm{Et}$	123.91	2
14	*cis*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-[C]-$	123.92	*cis*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-\mathrm{Et}$	123.77	2
15	*cis*-$\mathrm{CH_3\underline{C}H{=}CHCH_2}-[T]-[T]-$	123.89			
16	$-[C]-\mathrm{CH_2CHDCH{=}\underline{C}H_2}$ + $-[C]-\mathrm{CH_2CH_2CH{=}\underline{C}H_2}$	114.48	$\mathrm{Et}-[C]-\mathrm{CH_2CH_2CH{=}\underline{C}H_2}$	114.60	2
17	$-[T]-\mathrm{CH_2CHDCH{=}\underline{C}H_2}$ + $-[T]-\mathrm{CH_2CH_2CH{=}\underline{C}H_2}$	114.40	$\mathrm{Et}-[T]-\mathrm{CH_2CH_2CH{=}\underline{C}H_2}$	114.55	2

Thus, the resonance of CH_2D carbon of *trans*-1,4 UU appeared as a triplet ($J_{^{13}C-D}$ 19.3 Hz) shifted 0.28 ppm upfield with respect to the analogous methyl group position.

In the subspectrum of CH groups four resonances of CHD carbons at δ 33.11, δ 32.96, δ 33.81 and δ 32.66 with intensity ratio 1:2:2:1 were observed. These peaks represent two overlapping triplets of $-\mathrm{CH_2{-}\underline{C}HD{-}CH{=}CH_2}$ groups adjacent to *cis* and *trans* penultimate units respectively (isotopic shift to high field 0.38 ppm). Since, in the aliphatic region of polymer B, peaks No. 1, 2, 7 and 9 appear, a small amount ($<5\%$ of total 1,2 UU) of $-\mathrm{CH_2CH_2CH{=}CH_2}$ units is present. These units are formed due to admixture of HOD or H_2O contained in the deuterium oxide (the isotopic purity is 98–99%). These resonances coincide with those of polymer A. The resonances of the group $-$(*cis* + *trans*)-$\mathrm{CH_2CH{=}\underline{C}H{-}CH_2CH_2CHDCH{=}CH_2}$ are likely to appear near δ 130 ppm since, as noted[4,5], the peak of the $-\mathrm{CH{=}}$ carbon of a 1,4 inner unit shifts downfield by 0.5–0.6 ppm when the adjacent *cis*-1,4 unit is substituted by a 1,2 unit.

The assignment of peaks of inner units does not differ substantially from published data[4–6]. Using the above assignments the structure of IU, UU as well as inner units of polymers A and B may be considered.

For quantitative estimation based on ^{13}C n.m.r. spectra it is essential that nuclei under investigation should have similar nuclear Overhauser enhancement (NOE) values and also that the pulse delay should substantially exceed the spin–lattice relaxation times (T_1) of the nuclei studied. Practically, neither the increase in pulse delay from 5 s to 20 s nor the use of a broad-band decoupler only during the acquisition time to suppress the NOE changes the ratio of *C*, *T* and *V* units in polybutadiene as evaluated using the resonances of olefinic carbons[4].

Short spin–lattice relaxation times ($T_1 < 1$ s) and similar values of NOE (2.7–3.0) are inherent in aliphatic carbons of polybutadiene ($>$CH– and $-CH_2-$ groups)[7].

In the present work we assumed that peaks of olefinic and aliphatic ($>$CH– and $-CH_2-$ groups) carbons can be used for estimation of IU, UU as well as inner unit structures.

In the aliphatic regions of spectra of polybutadienes A and B, peaks of methyl carbons of *cis*-IU and *trans*-IU (δ 12.9 and δ 17.9, respectively) are observed. In the case of polymer A, the resonance at δ 17.9 belongs also to the methyl group of *trans*-UU. The resonance of the CH_2D- group of *trans*-UU in polymer B is shifted upfield compared to the resonance of the CH_3- group of *trans*-IU. *Cis*-1,4 structures are absent in UU. Ultimate

Table 2 Peak assignments in the aliphatic region of the ^{13}C n.m.r. spectrum of polybutadiene obtained with a neodymium catalyst and quenched by D_2O (polymer B)

No. of peak or of resp. group	Assignment		Model		
	Structure	Chem. shift (ppm)	Structure	Chem. shift (ppm)	Ref.
1	$-[C]-\mathrm{CH_2\underline{C}H_2CH{=}CH_2}$	33.33	$\mathrm{Et}-[C]-\mathrm{CH_2\underline{C}H_2CH{=}CH_2}$	33.74	2
2	$-[T]-\mathrm{CH_2\underline{C}H_2CH{=}CH_2}$	33.2	$\mathrm{Et}-[T]-\mathrm{CH_2\underline{C}H_2CH{=}CH_2}$	33.65	2
3	$-[C]-\mathrm{CH_2\underline{C}HDCH{=}CH_2}$	32.96^a			
4	$-[T]-\mathrm{CH_2\underline{C}HDCH{=}CH_2}$	32.81^a			
5	$[C]-$ -*trans*-$\mathrm{CH_2CH{=}CH\underline{C}H_2}$ $[T]-$	32.5– 32.8	$[C]-$ -*trans*-$\mathrm{CH_2CH{=}CH\underline{C}H_2}$ $[T]-$	32.65	6
6	-*trans*-$\mathrm{CH_2CH{=}CH\underline{C}H_2CH_2CHDCH{=}CH_2}$	31.96	Et-*trans*-$\mathrm{CH_2CH{=}CH\underline{C}H_2CH_2CH_2CH{=}CH_2}$	32.43	2
7	$-[C]-\mathrm{\underline{C}H_2CH_2CH{=}CH_2}$	28.97	$\mathrm{Et}-[T]-\mathrm{\underline{C}H_2CH_2CH{=}CH_2}$	29.45	2
8	$-[C]-\mathrm{\underline{C}H_2CHDCH{=}CH_2}$	28.89			
9	$-[T]-\mathrm{\underline{C}H_2CH_2CH{=}CH_2}$	28.81	$\mathrm{Et}-[T]-\mathrm{\underline{C}H_2CH_2CH{=}CH_2}$	29.33	2
10	$-[T]-\mathrm{\underline{C}H_2CHDCH{=}CH_2}$	28.73			
11	$[C]-$ -*cis*-$\mathrm{CH_2CH{=}CH\underline{C}H_2}$ $[T]-$	27.2– 27.6	$[C]-$ -*cis*-$\mathrm{CH_2CH{=}\underline{C}HCH_2}$ $[T]-$	27.35	6
12	-*cis*-$\mathrm{CH_2CH{=}CH\underline{C}H_2CH_2CHDCH{=}CH_2}$	26.68	Et-*cis*-$\mathrm{CH_2CH{=}CH\underline{C}H_2CH_2CH_2CH{=}CH_2}$	27.00	2
13	*trans*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-$	17.89	*trans*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-[C]-\mathrm{Et}$ *trans*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-[T]-\mathrm{Et}$	17.92 17.93	2 2
14	-*trans*-$\mathrm{CH_2CH{=}CH\underline{C}H_2D}$	17.61^b			
15	*cis*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-$	12.79	*cis*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-[C]-\mathrm{Et}$ *cis*-$\mathrm{\underline{C}H_3CH{=}CHCH_2}-[T]-\mathrm{Et}$	12.74 12.76	2 2

^{a}Triplets, $J_{\mathrm{C-D}} \sim 19$ Hz
^{b}Triplet, $J_{\mathrm{C-D}} = 19.3$ Hz

Table 3 Structure of initial and ultimate units of polybutadiene obtained with a neodymium catalyst and quenched by D_2O (polymer B)

Unit type	Structure^a		
	cis-1,4	*trans*-1,4	1,2
IU	25	75	–
UU	–	12	88
UU	–	10^b	90^b

^{a}Average error ±1%
^{b}Calculated using ^{2}H n.m.r. data

units are predominantly of 1,2 structure (peaks at δ 138, δ 114, δ 32.8–33.3 and δ 28.7–29.0). Also, some *trans*-UU are present.

The structure of IU (*Table 3*) can be estimated from the peaks of olefinic carbons at δ 124 (*cis*) and δ 125 (*trans*) by equations (1) and (2):

$$(C)_{\mathrm{IU}}:(T)_{\mathrm{IU}} = I_{13-15}:(I_{9-12}X) \qquad (1)$$

$$(C)_{\mathrm{IU}} + (T)_{\mathrm{IU}} = 100\% \qquad (2)$$

The latter resonances correspond to *trans*-1,4 IU as well as *trans*-1,4 UU and the respective intensity fraction X of IU can be evaluated from the peaks of methyl groups according to equation (3):

$$X = I_{13}:(I_{13} + I_{14}) \qquad (3)$$

The structure of UU can be evaluated from the peaks of olefinic carbons by equations (4) and (5):

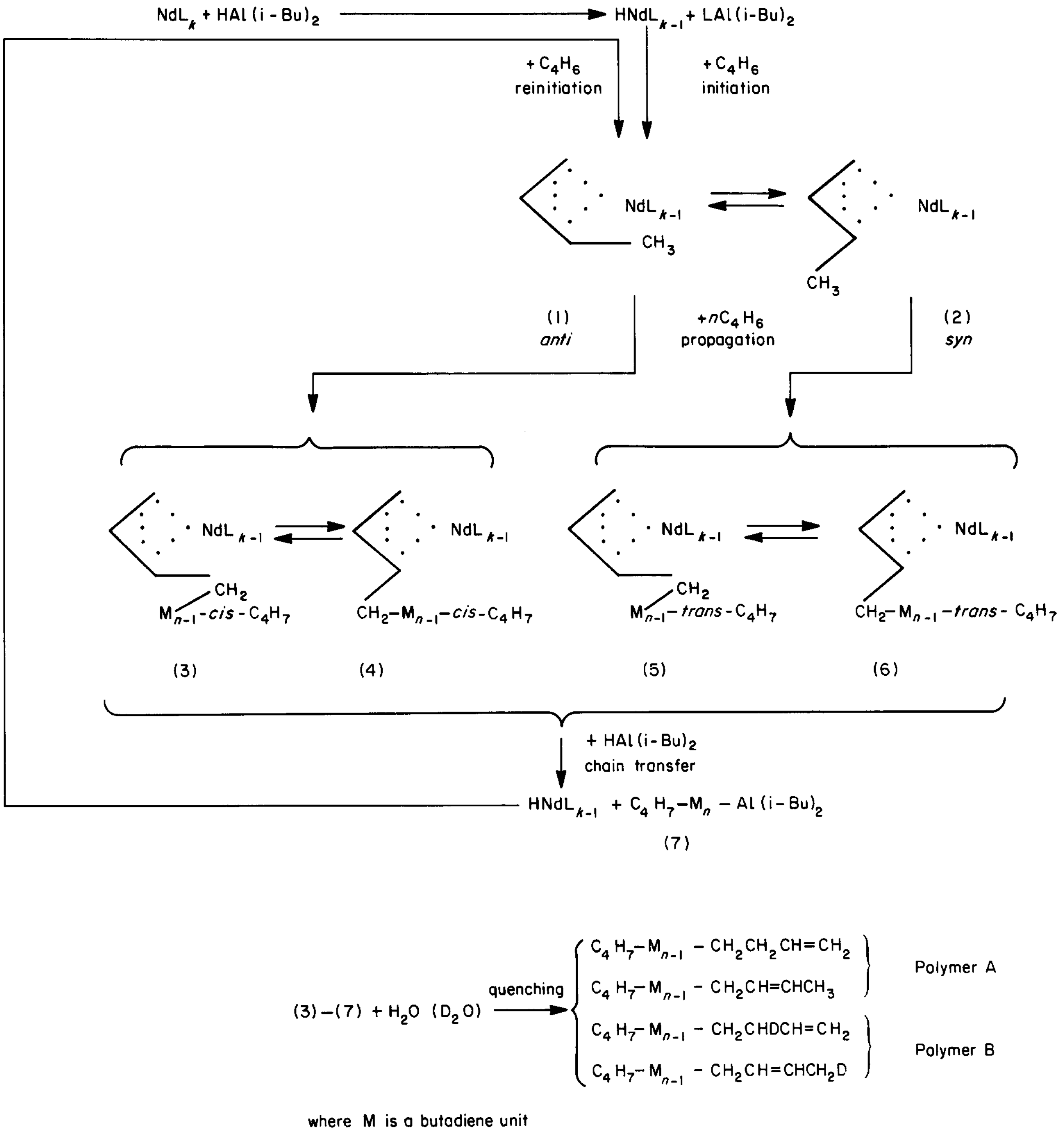
$$(V)_{\mathrm{UU}}:(T)_{\mathrm{UU}} = \tfrac{1}{2}(I_{1,2} + I_{16,17}):[I_{9-12}(1 - X)] \qquad (4)$$

$$(V)_{\mathrm{UU}} + (T)_{\mathrm{UU}} = 100\% \qquad (5)$$

The content of various structures in UU is close to the values obtained using ^{2}H n.m.r. data (*Table 3*). Thus, the intensity ratio for CH_2D– and CH_3– resonances of *trans*-1,4 units can be used for quantitative analysis. It should be noted that good agreement is observed between IU and UU content, as calculated by equations (1)–(5).

Care should be taken when calculating the structure of IU from the methyl carbon resonances since values of T_1 and NOE for the nuclei involved are unknown. This can be seen from the difference between the *cis*-IU/*trans*-IU ratio for polymer **B** evaluated by methyl carbons (0.18), and that calculated from areas in the olefinic region (0.33).

The resonances at δ 125 and δ 124 are split owing to various structures (*cis* or *trans*) of the second unit from the beginning of the macromolecule. The splitting is about 0.1–0.2 ppm. The fraction of *cis* structures in the second units (0.5–0.6) is much larger than in IU (0.25)



Scheme 1 Proposal for polydiene synthesis

and does not depend on the *cis* or *trans* structure of IU. Additional splitting owing to various (*cis* or *trans*) structures of the third units is also observed.

The downfield components of the olefinic carbons of IU (δ 125.00, δ 124.89 and δ 123.92) apparently correspond to triads, where the third unit from the beginning of the macromolecule is of *cis* structure.

Because of poor resolution, the *cis*/*trans* ratio in the third units is only roughly estimated as 1.5–2 for units adjacent to *trans*-IU (δ 125).

The average microstructure of inner units can be estimated by equations (6)–(9) using the olefinic region:

$$(C) = (CC) + \tfrac{1}{2}[(CT) + (TC)] \qquad (6)$$

$$(T) = (TT) + \tfrac{1}{2}[(CT) + (TC)] \qquad (7)$$

$$[(TC) + (CT)]:(TT):(CC) = (I_5 + I_8):I_6:I_7 \qquad (8)$$

$$(CC) + (TT) + (TC) + (CT) = 100\% \qquad (9)$$

as well as by equations (10) and (11) using the aliphatic region:

$$(C)/(T) = I_{11,12}:I_{5,6} \qquad (10)$$

$$(C) + (T) = 100\% \qquad (11)$$

The content of *trans*-1,4 inner units in polymers A and B amounts to 13 ± 2% (equations (6)–(9)). Evaluation using olefinic carbon intensities provides a value of 11 ± 2%.

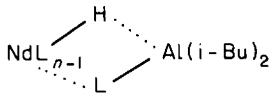
We did not take into account the inner units of 1,2 structure since the corresponding signal at δ 143 of the $-\mathrm{CH}(\underline{\mathrm{C}}\mathrm{H}{=}\mathrm{CH}_2)\mathrm{CH}_2-$ group is less intense than resonances of 1,4 inner units by a factor of 10^3. It should be borne in mind that the peaks of *cis*-$\mathrm{CH}_3\mathrm{CH}{=}\underline{\mathrm{C}}\mathrm{HCH}_2-$ units are obscured by large resonances of inner units (δ 129–130.5), reducing the accuracy of evaluation of IU structure.

The number-average degree of polymerization estimated from the olefinic region by equation (12) (*Table 3*) amounts to 30 ± 3 for polymers A and B:

$$\bar{P}_n = I_{1-17} : [\tfrac{1}{2}(I_{1,2} + I_{16,17}) + I_{9-15}] \qquad (12)$$

Scheme 1 can be proposed for polydiene synthesis on the basis of results obtained and published data[1,8–10]. The scheme covers the principal stages of polybutadiene synthesis with a lanthanide catalyst, namely, active site formation, initiation, propagation, chain transfer and metal–polymer bond quenching.

Active sites are produced by interaction of DIBAL-H with $\mathrm{NdCl_3 \cdot 3(ROH)}$. The following bimetallic complex is likely to form[11]:



The polymerization process was carried out at high concentration of chain transfer agent (DIBAL-H). Therefore, in view of earlier data[8], each active site is supposed to produce several macromolecules, i.e. each initiation act is followed by several reinitiations. Since isobutyl groups adjacent to IU are shown to be practically absent, the metal–hydrogen bond is the principal site of the chain transfer reaction. Initial formation of *anti*-π-allyl UU by monomer insertion in the propagation reaction and its capability to isomerize into *syn*-π-allyl structure has been demonstrated[1,9,10].

Presuming kinetic anti-stereocontrol also for the initiation (reinitiation) reaction, the great fraction of *trans* structures in IU, significantly exceeding that in the second and particularly the next inner units, should be indicative of a greater ratio k_{is}/k_p for the crotyl complex than for the products of insertion of the next monomer molecules.

One possible cause for this difference may be the ability of the double bond adjacent to a crotyl substituent to coordinate on the metal atom in complexes **3** and **5**. Such a possibility is lacking in the case of complexes **1** and **2**. These effects can play a significant role in stereoregulation, as was previously mentioned for allylic derivatives of nickel[12,13].

It should be noted that, at low monomer/neodymium ratio, the initiation reaction proceeds up to high conversion. Our unpublished results show that the induction period of polymerization increases as the initial monomer concentration decreases.

In preparation of polymers A and B, complete dissolution of catalyst particles did not occur, in contrast to the case when monomer/neodymium molar ratio was 10^3–10^4. It should be noted that, in the polymers described, relatively high content of *trans*-1,4 structures in inner units was observed. The fraction of these structures in polybutadiene obtained with monomer/neodymium ratio of 20 000 does not exceed 1%.

As monomer is consumed, the role of chain transfer to DIBAL-H[1,9] and *anti–syn* isomerization of UU[1] increases. The content of *trans* structures in penultimate units is greater than the average content of *trans* structures in inner units. This is accounted for by the significant contribution of the UU of short chains formed at high monomer conversion to the total number of UU.

SUMMARY

The structure of initial, second, penultimate and ultimate units in polybutadiene ($\bar{P}_n \sim 30$) produced with $\mathrm{NdCl_3 \cdot 3(i\text{-}PrOH)\text{–}HAl(i\text{-}Bu)_2}$ in hexane at 20°C was studied by means of ^{13}C n.m.r. spectroscopy (125.7 MHz); C_M/C_{Nd} = 5:1 (mol). It is the Al–H bond that participates in the reinitiation reaction after chain transfer to diisobutylaluminium hydride. Initial units are shown to be predominantly of *trans*-$\mathrm{CH_3CH{=}CHCH_2}-$ structure (*trans*/*cis* = 3:1), while the fraction of *cis* structures in second units amounts to 0.5–0.6 and on average to 0.9 in inner units. Ultimate units obtained by quenching with H_2O (D_2O) are predominantly of 1,2 structure. On the basis of the data obtained, the polymerization mechanism was discussed.

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