Structure of initial and ultimate chain units of polydienes obtained with rare-earth catalysts as revealed by ^2H nuclear magnetic resonance spectroscopy

K. D. Skuratov, M. I. Lobach*, A. N. Shibaeva, L. A. Churlyaeva, T. V. Erokhina, L. V. Osetrova and V. A. Kormer
S.V. Lebedev All-Union Synthetic Rubber Research Institute (VNIISK), 198035 St Petersburg, Russia

(Received 12 August 1991; revised 16 December 1991; accepted 23 January 1992)

The structure of initial and ultimate chain units in polybutadiene and polyisoprene was studied by means of ^2H nuclear magnetic resonance spectroscopy. Polydienes were prepared with a neodymium catalyst; quenching was performed with deuteromethanol. The enrichment of quenched ultimate units by *trans*-1,4 structures at the expense of *cis*-1,4 structures at high polymer yields was observed. When using diisobutylaluminium deuteride DAl(i-Bu)$_2$, as chain transfer agent, it was shown that the principal site of chain transfer reaction was the Al–D bond. The initial unit of polybutadiene was predominantly of *trans*-1,4 structure.

(Keywords: structure; chain units; polybutadiene; polyisoprene; rare-earth catalysis; ^2H nuclear magnetic resonance spectroscopy)

INTRODUCTION

Study of the structure of initial units (IU) and ultimate units (UU) of polymer chains provides information on the mechanism of ionic polymerization of dienes. Recently, high-resolution Fourier-transform ^1H (refs 1, 2) and ^{13}C (refs 3–6) n.m.r. spectroscopy was used to investigate IU and UU of both 'living'[1–3] and quenched[4–6] oligomers and polymers.

In the case of polymers prepared with lanthanide catalysts, the application of n.m.r. spectroscopy for the investigation of 'living' chains is usually restricted by the heterogeneity of the systems, as well as the paramagnetism of lanthanides in most active catalysts.

This paper deals with the ^2H n.m.r. investigation of the structure of IU and quenched UU of polybutadiene and polyisoprene, obtained on rare-earth catalysts. Quenching with deuteromethanol was used for incorporation of a deuterium label in UU. Diisobutylaluminium deuteride, DAl(i-Bu)$_2$, was utilized for labelling of IU produced by chain transfer reaction.

A narrower range of chemical shifts is inherent to ^2H n.m.r. compared to ^{13}C n.m.r. spectra. In addition, the chemical shifts are less sensitive to the structure of adjacent atoms. The advantage of ^2H n.m.r. for IU or UU investigation is low natural abundance of deuterium (0.0156%). Therefore, the intensities of the resonances of inner units are less than those of IU or UU in polymers with molecular weights up to 10^4.

EXPERIMENTAL

Polymerization was carried out in hexane under purified argon. Monomers and solvent were dried over alumina and used freshly distilled from $LiAlH_4$. The catalyst was prepared by reaction of $NdCl_3 \cdot$(i-PrOH) with triisobutylaluminium (TIBAL) in the presence of a small amount of diene hydrocarbon. The molar ratio TIBAL/Nd amounted to 10.

In order to suppress the chain transfer reaction to TIBAL, about 90% of the liquid phase was replaced with fresh toluene after precipitation of the solid phase. The Al/Nd molar ratio in the catalyst was found to be 2 (analysis by complexonometry and oxalatometry). Polymerization was quenched by CH_3OD, and a small amount of diphenyl-*p*-phenylenediamine was also added. A greater amount of quenching agent or increased time of its contact with the reaction medium did not result in greater deuterium content in the polymer. The quenched polymerization system was thoroughly stirred with a little water to wash out the catalyst residues and the decomposed organoaluminium compounds. The solvent was removed *in vacuo* at room temperature. The residue was extracted with toluene and centrifuged. Polymer yield was determined by weighing the sample or by chromatographic measurements of unreacted monomer.

Diisobutylaluminium deuteride was obtained by reaction of diisobutylaluminium chloride with lithium deuteride in ether according to ref. 7. After being twice distilled *in vacuo* the product contained 0.25 mol of ether per mole of DAl(i-Bu)$_2$ (by ^1H and ^2H n.m.r.). The product was free of chlorine as demonstrated by $AgNO_3$ test after alcoholysis. Samples of the polymer solutions obtained were placed into 10 mm diameter tubes. Toluene was substituted for the benzene/benzene-d$_1$ mixture in the required ratio ($\sim$1000:1). The resulting solutions contained 6–13% (wt/wt) of polymer.

The ^2H n.m.r. spectra were recorded at room temperature with a Bruker AM-500 spectrometer

---

*To whom correspondence should be addressed

0032-3861/92/245197-05

operating at 76.77 MHz (^2H) with external deuterium lock, using a pulse width of 12 μs corresponding to the tip angle 60°, and a pulse delay 6 s, accumulating 500–1000 scans. The spectral width was 730 Hz and the data size 8000. Benzene-d_1 (δ 7.15) was used as internal reference.

The deuterium content in *i*-type UU or IU was calculated using the equation:

$$N(i) = \frac{XbM}{78a}\frac{I(i)}{I(p)} \quad \begin{array}{l}\text{(moles of } ^2\text{H per mole}\\ \text{of monomer units)}\end{array} \qquad (1)$$

where a is weight of polymer sample (g); M is molecular weight of monomer (g); b is weight of solvent (g); X is molar fraction of benzene-d_1 in solvent, including also the natural abundance of deuterium; and $I(i)/I(p)$ is the ratio of integral intensities for the resonance under study and the resonance of the solvent.

Number-average degree of polymerization ($\bar{P}_n$) was calculated using the equation:

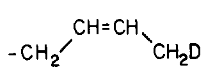
$$\bar{P}_n = 1\Big/\sum_i N(i) \qquad (2)$$

In the case of runs No. 21 and No. 22, the denominator of equation (2) represents the difference between total content of deuterium in IU and UU (runs b) and in IU (runs a).

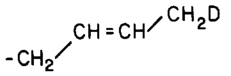
RESULTS AND DISCUSSION

From ^2H n.m.r. spectra of butadiene and isoprene oligomers obtained with ethyllithium in hexane, the following assignments were made for UU of polydienes:

Polybutadiene



(1) *cis*-1,4 UU
δ 1.49

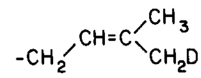


(2) *trans*-1,4 UU
δ 1.54

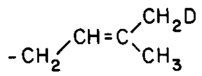
$-CH_2CHDCH{=}CH_2$

(3) 1,2 UU
δ 1.94

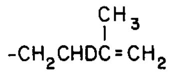
Polyisoprene



(4) *cis*-1,4 UU
δ 1.54



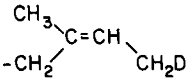
(5) *trans*-1,4 UU
δ 1.64



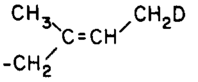
$-CH_2CHDC(CH_3){=}CH_2$

(6) 3,4 UU
δ 1.93

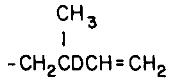
Since both head-to-head and tail-to-tail sequences and 1,2 units are completely absent in lanthanide polyisoprene[8], inverse structures **7**, **8** and **9** were not taken into consideration:



(7)



(8)



$-CH_2CD(CH_3)CH{=}CH_2$

(9)

The polymerization of butadiene with a catalyst based on neodymium chloride is known to proceed as 'living'

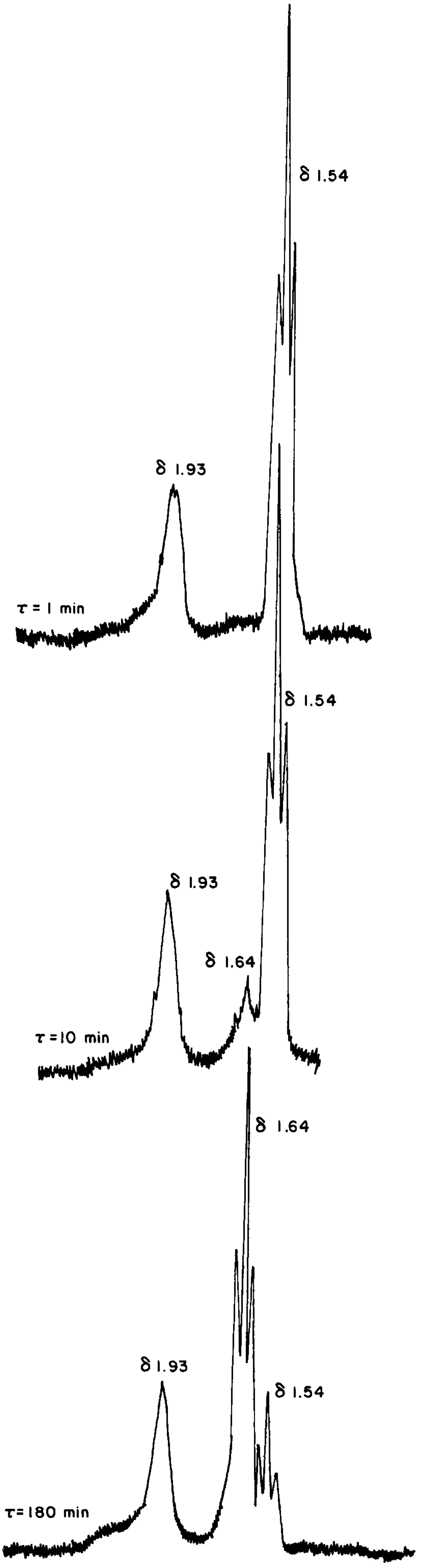


Figure 1 ^2H n.m.r. spectra of polyisoprenes obtained with a neodymium catalyst and quenched by CH_3OD (hexane; 20°C; $C_M = 0.03\ mol\ l^{-1}$; $C_{Nd} = 0.003\ mol\ l^{-1}$)

Table 1 Structure of quenched UU of polydienes obtained with a neodymium catalyst (hexane; 20°C; quenching agent CH_3OD; $C_M = 0.03$ mol l^{-1}; $C_{Nd} = 0.003$ mol l^{-1})

Run No.	Polymerization time (min) [Polymerization temperature (°C)]	Polymer yield (%)	Structure of UU[a]		$\bar{P}_n$
			1,4 / 1,2(3,4)+1,4	*trans* / *trans*+*cis*	
		Polybutadiene			
1	1[20]	45	0.72	mainly *cis*	66
2	2[20]	63	0.73	mainly *trans*	78
3	10[20]	96	0.70	mainly *trans*	102
4	20[20]	99.2	0.69	mainly *trans*	98
5	120[20]	>99.5	0.61	mainly *trans*	113
6	120[20] + 40[60] + 60[20]	>99.5	0.43	mainly *trans*	112
7	40[60]	>99.5	0.53	mainly *trans*	100
		Polyisoprene			
8	1[20]	39	0.67	0	46
9	5[20]	85	0.69	0.14	60
10	10[20]	95.5	0.69	0.19	73
11	20[20]	99.3	0.67	0.43	70
12	30[20]	>99.5	0.67	0.63	78
13	180[20]	>99.5	0.64	0.80	79
14	180[20] + 60[60] + 60[20]	>99.5	0.55	0.84	89
15	60[60]	>99.5	0.55	0.74	84

[a] Average error for 1,4/(1,2 + 1,4) for polybutadiene and 1,4/(3,4 + 1,4) and *trans*/(*trans* + *cis*) for polyisoprene listed in *Tables 1–3* is about ±0.05 and for $\bar{P}_n$ is ±10%

polymerization[9]. In the case of isoprene, 'living' polymerization is accompanied by slight chain transfer to monomer[10]. Triisobutylaluminium (TIBAL) and especially diisobutylaluminium hydride (DIBAL-H) are effective chain transfer agents[10]. The structures of butadiene UU obtained on quenching of metal–polymer bonds with CH_3OD are shown in *Table 1*. Polymerization was carried out using a catalyst with a small content of TIBAL (Al/Nd molar ratio = 2) at low monomer/neodymium molar ratio (M/Nd = 10). In runs No. 1–5, some 0.6–0.7 of the ultimate units had 1,4 structures. The signals involved were overlapping, thus preventing estimation of *cis*/*trans* ratio in the 1,4 UU. The position of the peak maximum enables us to suppose, however, that at a relatively small polymer yield (run No. 1) *cis*-1,4 UU are predominant. Conversely, in runs No. 2–5 *trans*-1,4 units prevail. In the case of polyisoprene (runs No. 8–13) the fraction of *trans*-1,4 UU depends strongly on polymer yield. At a monomer conversion of 85%, *trans*-1,4 UU appear and this structure becomes predominant at higher conversions (*Figure 1*)*.

This result corroborates well known data concerning kinetic anti-stereocontrol in polymerization of dienes[11,12], in particular when lanthanide catalysts are used[13,14]. The enrichment by *trans*-1,4 UU at high polymer yields is due to monomer consumption and respective decrease in propagation rate; consequently the *anti*–*syn* isomerization of the initial UU structure occurs more often towards the end of the polymerization run.

In a special experiment, the reaction mixture was held additionally for an hour at 60°C and then an hour at 20°C. Since we have not observed an appreciable decrease in deuterium content in the polymer after keeping the reaction mixture at 60°C, thermal decomposition of the metal–polymer bonds under the conditions of the experiment is negligible. The *cis*/*trans* ratio did not change substantially; 1,4 UU content, however, decreased slightly. This can be explained by the fact that the chain transfer reaction to TIBAL occurs more often at higher temperature. (We shall show later that in macromolecules after transfer the molar fraction of 1,4 UU amounts to 0.2.) The decrease of 1,4 content is also observed when the polymerization is carried out at 60°C (run No. 15). Similar effects were also recorded for polybutadiene (runs No. 6 and 7).

Table 2 Structure of quenched UU of polydienes obtained with a neodymium catalyst in the presence of $HAl(i\text{-}Bu)_2$ (hexane; 20°C; quenching agent CH_3OD; $C_M = 0.3$ mol l^{-1}; $C_{Nd} = 0.0003$ mol l^{-1}; $C_{HAl(i\text{-}Bu)_2} = 0.021$ mol l^{-1})[a]

Run No.	Polymerization time (min)	Polymer yield (%)	1,4 / 1,2(3,4)+1,4	$\bar{P}_n$
		Polybutadiene		
16	10	30	0.17	130
		Polyisoprene		
17	25	37	0.19	210
18	40	53	0.24	150
19	150	95	0.22	140
20	5000	>99.5	0.22	86

[a] Content of *cis*-1,4 units in polydienes (runs No. 16–22) exceeded 90%

In ^2H n.m.r. spectra of polybutadiene obtained at high concentration of chain transfer agent (DIBAL-H), the signals corresponding to structure **1** (δ 1.49) and structure **3** (δ 1.94) were detected. In the case of polyisoprene, the peaks from structures **4** and **6** appear at δ 1.54 and δ 1.93 respectively. The content of 1,4 units in UU is approximately 0.2 in both polybutadiene and polyisoprene (*Table 2*). It should be noted as well that,

---

*Splitting of the CH_2D– signal is due to spin–spin interaction D–C–H ($J_{D\text{–}H} = 2.1$–2.2 Hz)

Table 3 Contents of IU and UU in polydienes obtained with a neodymium catalyst in the presence of DAl(i-Bu)$_2$ (hexane; 20°; $C_M = 0.2$ mol l^{-1}; $C_{Nd} = 0.0003$ mol l^{-1}; $C_{DAl(i\text{-}Bu)_2} = 0.030$ mol l^{-1})

Run No.	Polymerization time (min)	Polymer yield (%)	Quenching agent	$N(i) \times 10^3$			
				1,4 IU	1,4 IU + 1,4 UU	1,2 UU	$\bar{P}_n$
			Polybutadiene				
21a	30	70	CH_3OH	4.4			
21b	30	70	CH_3OD		5.1	4.9	180
			Polyisoprene				
22a	90	86	CH_3OH	3.7			
22b	90	86	CH_3OD		4.6	4.2	200

unlike polymers from runs No. 8–13, UU are not enriched with *trans*-1,4 structures when polymerization time increased (run No. 20). Substantially different ratios of 3,4 and 1,4 UU in polyisoprenes obtained in the absence (runs No. 8–13) and in the presence of DIBAL-H (runs No. 17–20) are indicative of essentially different types of metal–polymer bonds. In the absence of DIBAL-H the alcohol reacted predominantly with 'living' chains. The ratio of 'living' to 'transferred' chains in runs No. 17–20 can be approximately estimated using data of ref. 10. As the molecular weight of polyisoprene is influenced primarily by chain transfer to DIBAL-H, other termination reactions being negligible, the number of macromolecules equals the number of metal–polymer bonds. Under the polymerization conditions used (runs No. 17–20), each active site produces at least 10 macromolecules even at monomer conversions as low as 20%. Hence at least 90% of metal–polymer bonds represent Al–C linkages. The predominance of structures **3** and **6** in the products of decomposition of metal-polydienyls formed in the presence of DIBAL-H is in accordance with data on the formation of but-1-ene during alcoholysis of *cis*-crotyldiethylaluminium etherate[15].

In order to elucidate which of the bonds, Al–C or Al–H in DIBAL-H, participates in the chain transfer reaction, polybutadiene (runs No. 21a,b) and polyisoprene (runs No. 22a,b) were synthesized using diisobutylaluminium deuteride as chain transfer agent (*Table 3*). The reaction medium was divided into two parts in both runs. The first one was quenched by methanol, the second one by methanol-d$_1$. When methanol was used, the peak at δ 1.54, corresponding to *trans*-1,4 UU† (structure **2**), was observed.

In the case of polyisoprene, the signal at δ 1.54 was detected. These data do not permit us, however, to establish the structure of polyisoprene IU.

The ratio of the number of polybutadiene chains, formed due to a reinitiation reaction of this type, to the total number of metal–polymer bonds can be calculated according to the following equation:

$$\begin{aligned} X &= N(\text{run No. 21a})/[N(\text{run No. 21b}) \\ &\quad - N(\text{run No. 21a})] \\ &= 0.8 \pm 0.1 \end{aligned} \tag{3}$$

In the case of polyisoprene, a similar value, 0.7 ± 0.1, was obtained. Thus the Al–D bond of the DAl(i-Bu)$_2$ is the main site of the chain transfer reaction. When using HAl(i-Bu)$_2$ as chain transfer agent, the ratio X should be even greater owing to the kinetic isotope effect (k_H/k_D).

The IU in polybutadiene (run No. 21) have predominantly *trans*-1,4 structure. It should be noted that the IU of polybutadiene obtained with catalysts based on DAl(i-Bu)$_2$ without the addition of chain transfer agents are also of *trans*-1,4 structure.

The total content of *cis*-1,4 units in polybutadiene (run No. 21) exceeds 90%. Therefore, the stereoselectivity of the reinitiation stage that follows chain transfer to DAl(i-Bu)$_2$ differs essentially from that of the propagation stage. This difference seems to be due to a change in the ratio of rates of propagation and *anti–syn* isomerization reactions when passing from the crotyl complex to UU, arising from addition of the next monomer molecules.

SUMMARY

The structure of the initial units and that of the ultimate units quenched by CH_3OD in *cis*-1,4-polybutadiene and *cis*-1,4-polyisoprene was studied by means of ^{2}H n.m.r. spectroscopy (76.8 MHz). Polydienes were prepared with $NdCl_3 \cdot 3$(i-PrOH)–Al(i-Bu)$_3$ catalyst (Al/Nd = 2 (mol/mol)) in hexane at 20°C ($C_M = 0.03$ mol l^{-1}; $C_{Nd} = 0.003$ mol l^{-1}). The fraction of 1,4 structures in UU amounts to 60–70%. The enrichment of UU by *trans*-1,4 structures at the expense of *cis*-1,4 structures at high polymer yields was observed. When using DAl(i-Bu)$_2$ as chain transfer agent, it was shown that the principal site of chain transfer reaction was the Al–D bond. The initial unit of polybutadiene was of *trans*-1,4 structure.

ACKNOWLEDGEMENTS

We are grateful to Dr L. S. Bresler and Dr G. B. Erussalimsky for useful suggestions. We thank Dr A. V. Lubnin, who supplied us with butadiene and isoprene oligomers, and Dr N. A. Kartsivadze for the chromatographic analyses.

REFERENCES

1 Dolinskaya, E. R., Maretina, E. Yu., Erussalimsky, G. B. and Kormer, V. A. *Vysokomol. Soed* (*A*) 1987, **29**, 1877

2 Dolinskaya, E. R., Maretina, E. Yu., Erussalimsky, G. B. and Kormer, V. A. *Vysokomol. Soed.* (*A*) 1987, **29**, 2521

3 Bywater, S. and Worsfold, D. *J. Organomet. Chem.* 1978, **159**, 229

4 Khachaturov, A. S., Ivanova, V. P., Estrin, A. S., Abramenko,

---

†Formation of some *cis*-butadiene IU is not ruled out since the resonances of *cis*- and *trans*-butadiene IU (or UU) are poorly resolved

E. L. and Valuev, V. I. *Vysokomol. Soed.* (*A*) 1990, **32**, 637

5 Lubnin, A. V., Osetrova, L. V. and Podkorytov, I. S. *Zh. Obshch. Khim.* 1989, **59**, 1159

6 Khachaturov, A. S., Ivanova, V. P., Abramenko, E. L., Estrin, A. S. and Valuev, V. I. *Dokl. Akad. Nauk SSSR* 1989, **30**, 390

7 Eisch, J. J. and Rhee, S. G. *J. Am. Chem. Soc.* 1974, **96**, 7276

8 Kormer, V. A., Vasilyev, V. A., Bubnova, S. V. and Dolinskaya, E. R. *Kauchuki Rezina* 1986, 5

9 Bodrova, V. S., Piskareva, E. P. and Kormer, V. A. *Dokl. Akad. Nauk SSSR* 1987, **293**, 645

10 Bodrova, V. S., Piskareva, E. P., Bubnova, S. V. and Kormer, V. A. *Vysokomol. Soed.* (*A*) 1988, **30**, 2301

11 Kormer, V. A., Lobach, M. I., Klepikova, V. I. and Babitskii, B. D. *J. Polym. Sci., Polym. Lett. Edn* 1976, **14**, 317

12 Kormer, V. A. and Lobach, M. I. *Macromolecules* 1977, **10**, 572

13 Bolognesi, A., Destri, S., Zhou-Zi-nan and Porri, L. *Makromol. Chem., Rapid Commun.* 1984, **5**, 679

14 Monakov, Yu. B., Marina, N. G., Savelyeva, I. G., Zhiber, L. E., Duvakina, N. V. and Rafikov, S. R. *Dokl. Akad. Nauk SSSR* 1984, **278**, 1182

15 'Metoden der organischen Chemie. Houben-Weil', Georg Thieme Verlag, Stuttgart, 1970, Vol. 13/4, 4th Edn, p. 145