Distribution of monomer units in butadiene–isoprene copolymers

In recent years ^{13}C n.m.r. spectroscopy has become the most powerful tool for the characterization of polymer and copolymer microstructure and distribution of their monomer units. In the present paper this technique was used to study butadiene–isoprene copolymers with macromolecules consisting mainly of *cis*-1,4- or *trans*-1,4-units both in butadiene and isoprene moieties.

^{13}C n.m.r. spectra of polymer samples were obtained with a Bruker HX-270 Spectrometer operating at 67.88 MHz by using the Fourier transform pulse technique. The spectra were ^{13}C–^{1}H decoupled and registered in the computer memory of 8K. The concentration of polymer solutions in $CDCl_3$ was 10–20% (w/v). As an internal standard tetramethylsilane was used. *Cis*-1,4-copolymers were prepared using the catalyst system containing cerium octoate reported by Trockmorton[1] and *trans*-1,4-copolymers were synthesized in the presence of $(C_4D_7NiI)_2$.

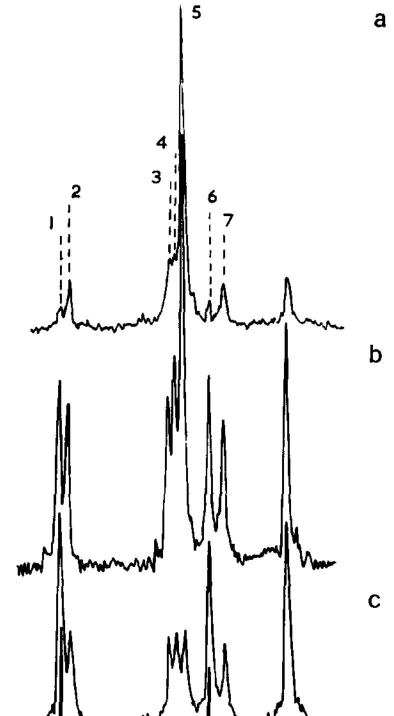


Figure 1 ^{13}C n.m.r. spectra of *cis*-1,4-copolymers of butadiene and isoprene: (a) 30 mol% isoprene; (b) 50 mol% isoprene; (c) 70 mol% isoprene; (d) 90 mol% isoprene

Figure 1 shows the alipahtic region of ^{13}C n.m.r. spectra of *cis*-1,4-butadiene–isoprene copolymers differing in composition. Discrete positions of signals, varying from sample to sample only in intensity, indicates that there is no marked 'far' screening. The line observed at 23.40 ppm relates to the carbon of the methyl groups of isoprene units in the copolymers. All other signals numbered in *Figure 1* are assigned to the carbon atoms C_1 and C_4 in butadiene and isoprene units of the copolymers. Three of them refer clearly to the blocks of monomers: the line at 27.45 ppm (signal 5) to the butadiene and the lines at 32.30 ppm and 26.45 ppm (signals 1 and 6, respectively) to the isoprene blocks. The other four signals (2, 3, 4 and 7) represent the carbon atoms of methylene groups at alternating monomer units distribution.

In the spectra of *trans*-1,4-copolymers of various compositions (*Figures 2a–2c*) the signals of monomer blocks are observed at 32.80 ppm (signal 2)–butadiene units; 39.80 ppm (signal 1)–carbon atom C_1; 26.75 ppm (signal 5)–carbon atom C_4 and at 16.05 ppm (CH_3 group)–isoprene units.

To make further discussion more convenient let us denote the methylene carbons whose spectral lines are discussed with the letters B (butadiene) and I (isoprene). Then, add to the right or to the left side of these capital letters lower case letters denoting the neighbouring monomer unit which perturbs the chemical shift of carbon atoms under discussion. The subscripts 1 and 4 refer to carbon atom C_1 and C_4 of the isoprene units. So the blocks of isoprene and butadiene will take the forms i_4I_1, I_4i_1, and bB, Bb while the mixed sequences will be designated as i_4B, Bi_1, bI_1 and I_4b.

The assignment of the lines characterizing the latter four types of monomer sequences can be effected using the spectral parameters of methylation (Δ) found empirically for saturated α, β and α′ carbon atoms in alkenes by comparing the corresponding low molecular

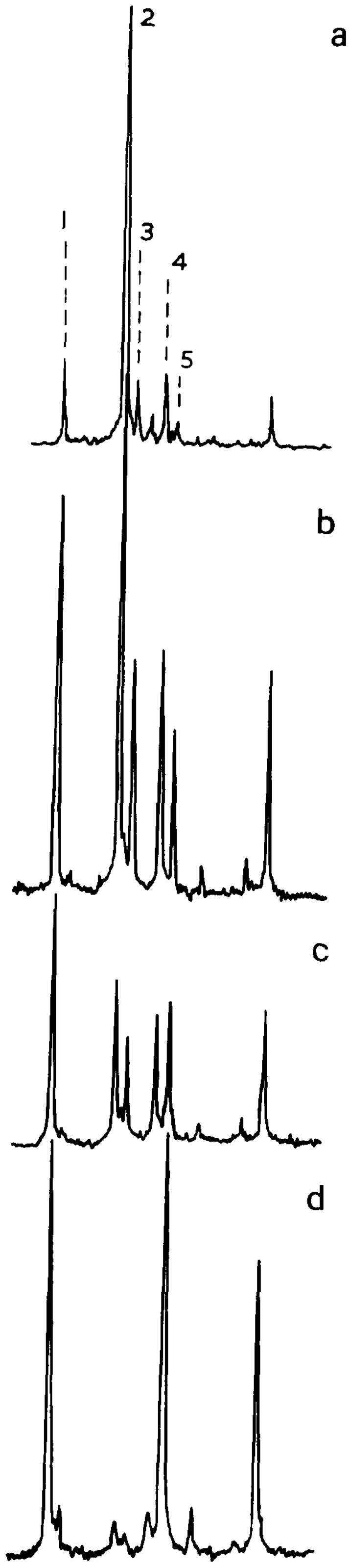
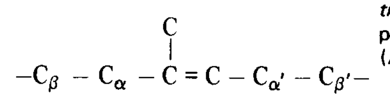


Figure 2 ^{13}C n.m.r. spectra of *trans*-1,4-copolymers of butadiene and isoprene: (a) 35 mol% isoprene; (b) 50 mol% isoprene; (c) 75 mol% isoprene and (d) polyisoprene synthesized in the presence of $(C_4D_7NiI)_2$

models of *cis*-1,4- and *trans*-1,4-configurations[2]:



$$-C_\beta - C_\alpha - \overset{\overset{\displaystyle C}{|}}{C} = C - C_{\alpha'} - C_{\beta'}-$$

Δ *cis:* -1.2 $+ 4.5$ $+ 0.7$

Δ *trans:* -1.6 $+ 7.1$ -5.1

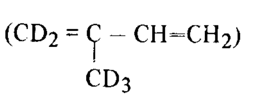
Let these be the parameters for calculation of the chemical shifts of methylene carbon atoms in the alternating triad BIB. As a starting point for this calculation the chemical shifts for the methylene carbon atoms in *cis*-1,4 (δ = 27.45 ppm) and *trans*-1,4 (δ = 32.80 ppm) polybutadienes should be taken. Substitution of an isoprene unit for a central monomer unit in the triad BBB gives the following chemical shifts of the saturated carbon atoms C_α and $C_{\alpha'}$ in an isoprene unit: $\delta(bI_1) = 31.95$ ppm and $\delta(I_4b) = 28.15$ ppm for a *cis*-1,4-unit, and $\delta(bI_1) = 39.90$ ppm and $\delta(I_4b) = 27.70$ ppm for a *trans*-1,4-unit. Taking into account the parameters of methylation for a carbon atom C_β, the signal of carbon in the sequence Bi_1 may appear at δ = 26.25 ppm and 31.20 ppm for *cis*-1,4- and *trans*-1,4-units, respectively.

It should be noted that the real spectra of *cis*-copolymers (*Figure 1*) actually show two clearly separated lines at 32.30 ppm and 31.95 ppm which correspond to the carbon atoms C_1 of the isoprene units in the sequences i_4I_1 and bI_1, respectively. In this way the effect of methylation (nearly +0.35 ppm) for the carbon atoms of $C_{\beta'}$ type manifests itself. The correctness of our assignment is confirmed by the fact that the variation of the intensity of this line depends on a copolymer composition.

The same effect should give rise to the splitting of a line assigned to the sequence i_4B (nearly 27.80 ppm) from the signal of a butadiene block bBb (27.45 ppm) which is observed in the real spectrum.

Based upon the estimated chemical shifts and the above considerations, all the aliphatic carbon signals of *cis*-1,4-copolymers have been assigned (*Table 1*).

Correctness of these assignments has been confirmed by examining the spectra of 1:1 copolymers of perdeuteriobutadiene and isoprene (*Figure 3a*) and also butadiene and isoprene-d_5 (*Figure 3b*)



$$(CD_2 = \underset{\underset{\displaystyle CD_3}{|}}{C} - CH{=}CH_2)$$

Table 1 ^{13}C n.m.r. chemical shifts of the methylene carbon atoms in *cis*-1,4 and *trans*-1,4-copolymers of butadiene and isoprene and refined parameters of methylation (Δ) of alkenes

Signal no	Units sequence	Chemical shift (ppm)	Δ (ppm)
Cis-1,4-copolymers			
1	i_4I_1	32.30	–
2	bI_1	31.95	+4.50 (C_α)
3	I_4b	28.05	+0.60 ($C_{\alpha'}$)
4	i_4B	27.80	+0.35 ($C_{\beta'}$)
5	bBb	27.45	–
6	I_4i_1	26.45	–
7	Bi_1	25.90	−1.55 (C_β)
Trans-1,4-copolymers			
1	i_4I_1	39.80	–
	bI_1	39.80	+7.00 (C_α)
2	i_4B	32.80	0.00 ($C_{\beta'}$)
	bBb	32.80	–
3	Bi_1	31.30	−1.50 (C_β)
4	I_4b	28.20	−4.60 ($C_{\alpha'}$)
5	I_4i_1	26.75	–

In the first case the ^{13}C n.m.r. spectrum showed the absence of intensive singlet signals 4, 5 and 7 of butadiene units and in the second case the disappearance of the signals 1, 2 and the signal of the methyl group. Instead, the spectra showed the corresponding multiplets ^{13}C–D of low intensity.

It should be pointed out that the chemical shifts of lines assigned to the protonated and deuterated copolymers do not coincide throughout. Deviations occur for the protonated carbon atoms neighbouring the deuterated ones. In the spectrum of the butadiene–isoprene-d_5 copolymer (*Figure 3b*) the signals 6 and 7 are seen to deviate upfield by nearly 0.20 ppm as compared with the similar signals in the spectra of non-deuterated *cis*-copolymers. The spectrum of the isoprene–butadiene-d_6 copolymer (*Figure 3a*) shows the signals 2 and 3 also shifted upfield by 0.10–0.15 ppm. The character of these deviations suggests that they may be accounted for by no other reason than the isotope effect of neighbouring deuterosubstituted carbon atom.

The ^{13}C n.m.r. spectra of *trans*-1,4-copolymers of butadiene and isoprene (*Figures 2a–2c, Table 1*) are interpreted in the similar way: signal 4(δ = 28.20 ppm) corresponds to the sequence I_4b and the signal 3(δ = 31.30 ppm) to the sequence Bi_1. Estimated value of the chemical shift of the sequence bI_1(δ = 39.90 ppm) as well as the absence of splitting of the signal 1 are indicative of this signal being the sum of two lines related to the sequences i_4I_1 and bI_1. Parameters of methylation of the carbon atom $C_{\beta'}$ for a *trans*-1,4-unit seems to approach zero. Thus it is reasonable to assume that the sequence i_4B should have a signal close to the line of the methylene carbon atoms in the blocks of *trans*-1,4-polybutadiene (δ = 32.80 ppm). The coincidence of chemical shifts of the signals assigned to the blocks bI_1 and i_4I_1 as well as i_4B and bBb is evidenced also by higher intensities of spectral lines 1 and 2 as compared with those expected for the blocks of isoprene and butadiene units.

The signals of low intensity observed in the spectra of *trans*-1,4-copolymers may be attributed to the presence of small amounts of *cis*-1,4-isoprene units and also to isoprene units with head-to-head and tail-to-tail types of addition. The spectrum of the polyisoprene homopolymer synthesized in the presence of $(C_4D_7NiI)_2$ (*Figure 2d*) shows clearly the signals assigned to the following structures: δ = 38.60

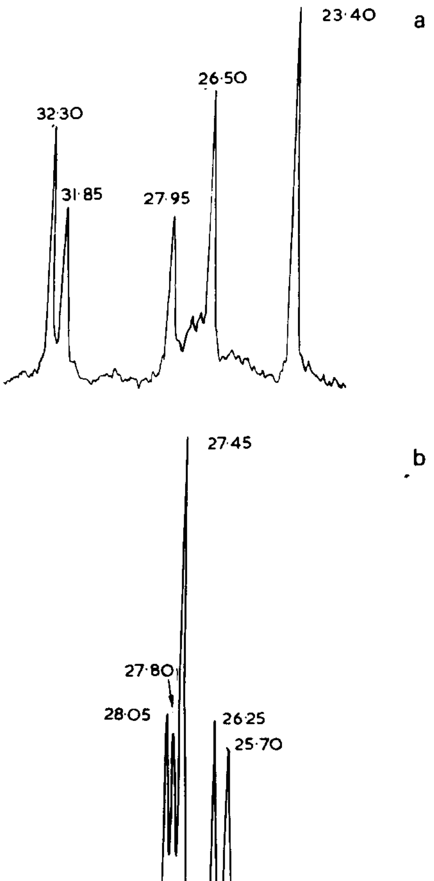


Figure 3 ^{13}C n.m.r. spectra of *cis*-1,4-copolymers of (a) butadiene-d_6 and isoprene; (b) butadiene and isoprene-d_5

ppm (head-to-head), δ = 28.40 ppm (tail-to-tail)[3] and δ = 32.10 ppm and 23.45 ppm (*cis*-1,4-units). Tentative analysis of this polyisoprene microstructure revealed it to contain 5–6% *cis*-1,4-units and 94–95% *trans*-1,4-units of which nearly 10% have 'head-to-head' and 'tail-to-tail' types of addition.

Investigation of the ^{13}C n.m.r. spectra of *cis*-1,4 and *trans*-1,4-copolymers of butadiene and isoprene has shown that the polymer molecule of either configuration has random monomer sequence distribution. Equal probability of any type of monomer sequence distribution is supported, e.g. by the fact that the ratio of intensities of lines 1–7 in an equibinar *cis*-1,4-copolymer approaches the theoretical values, that is 2:2:2:2:4:2:2. With an increasing content of one comonomer (*Figures 1a, 1c, 2a, 2c*) the monomer minorities are distributed both between its own and between the 'strange' units. Even at 10-fold excess of one comonomer, the copolymer does contain the microblocks of minor monomer.

Detailed sequence analysis of *cis*-1,4- and *trans*-1,4-copolymers of butadiene and isoprene has enabled us to refine the parameters of methylation of a 1,4-polydiene macromolecule. This was possible because the isoprene unit surrounded by butadiene units is a far better model than hexenes and heptanes used in ref 2. Refined values of parameters of methylation (Δ) and assignments of resonance signals of the methylene carbon atoms in *cis*-1,4 and *trans*-1,4-copolymers of butadiene and isoprene are listed in *Table 1*.

M. I. Lobach, I. A. Poletayeva, A. S. Khatchaturov, N. N. Druz and V. A. Kormer

S. V. Lebedev Synthetic Rubber Research Institute, Leningrad, 198035, USSR

(Received 13 July 1977)

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