Distribution of Cis-1,4 and Trans-1,4 Units in 1,4-Polyisoprene Prepared with Butyllithium in Nonpolar Solvent

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ABSTRACT: The dyad distribution of cis-1,4 and trans-1,4 units in 1,4-polyisoprene prepared with butyllithium in benzene has been investigated by means of ^{13}C NMR spectroscopy. The study has been made on the bulk at 350 K using low molecular weight material. The spectra show clearly the splitting of the C_1 methylene resonances due to the dyad effects. The fractions of the dyad sequences compare favorably with those expected for a random distribution of cis-1,4 and trans-1,4 units along the polymer chains.

Recently, Tanaka and Sato[1] have shown that ^{13}C NMR spectroscopy affords a valuable means of investigating the dyad distribution of cis-1,4 and trans-1,4 units in cis-trans isomerized 1,4-polyisoprenes. The success of their analysis was based on the fact that the methylene C_1 cis and C_1 trans resonances observed for the two stereoregular *cis-* and *trans-*1,4-polyisoprene are each split into two peaks in the spectra of cis-trans isomerized materials. The C_1 carbons defined by Tanaka and Sato correspond to Duch and Grant[2] assignments with the following nomenclature

$$\overset{1}{-CH_2}-\overset{2}{C}\,\overset{5}{(CH_3)}=\overset{3}{CH}-\overset{4}{CH_2}-$$

The chemical shift difference between the C_1 cis and the C_1 trans signals of the stereoregular polymers is close to 7.4 ppm. Fortunately, both signals do not overlap the other carbon resonances of the 1,4 units. Therefore, the splitting observed for the C_1 cis resonance was attributed to cis-cis and trans-cis linkages while that observed for the C_1 trans resonance was attributed to trans-trans and cis-trans linkages.

It is the purpose of the present work to apply a similar analysis to 1,4-polyisoprene prepared by butyllithium in nonpolar solvent such as benzene. The microstructure of this polyisoprene is 71% cis-1,4, 22% trans-1,4, 7% 3,4, and ~0% 1,2. As pointed out by Tanaka and Sato, polyisoprene samples containing 3,4 units in addition to 1,4 units exhibit more complicated ^{13}C NMR spectra due to 1,4–3,4 and 3,4–3,4 linkages. Fortunately, the present polyisoprene is characterized by a small amount of 3,4 units already known to be distributed at random along the polymer chains.[3] As we shall see shortly, this feature enables one to draw conclusions concerning the dyad distribution of the cis-1,4 and trans-1,4 units in the present polymer. Such a study would provide additional relevant information concerning the mechanism of butyllithium-initiated polymerization of butadiene derivatives. At the present moment, it is established that both 1,3-butadiene[4] and 2,3-dimethyl-1,3-butadiene[5] lead to a Bernoullian distribution of cis-1,4 and trans-1,4 units when polymerized with butyllithium in nonpolar solvents. It was thus interesting to investigate the generality of this behavior for the butyllithium-initiated polymerization of 1,3-butadiene derivatives.

The polyisoprene sample studied here was prepared in a sealed high vacuum system using *sec*-butyllithium as initiator and benzene as solvent. Its microstructure already mentioned was determined by 100 MHz ^1H NMR spectroscopy. Its number average molecular weight determined by vapor pressure osmometry is 8×10^3.

The ^{13}C NMR proton noise-decoupled spectra were measured in the bulk at 350 K and 22.6 MHz using a Bruker WH-90 spectrometer. At this temperature the low molecular weight material was a viscous liquid giving well resolved spectra which showed the C_1 resonance splitting due to the dyad effects. The neat samples were studied in 10-mm Wilmad NMR tubes with a 5-mm capillary containing D_2O inserted concentrically for external locking on deuterium. The instrumental conditions were as follows: pulse width, 4 μs (corresponding to a flip angle of 30°); spectral sweep width, 2000 Hz; acquisition time, 2 s; number of pulses, 2000. A pulse spacing of 2 s was considered suitable from a T_1 standpoint since, according to Schaefer,[6] the spin–lattice relaxation times of the sp^3 carbons in *cis-* and *trans-*polyisoprene are all shorter than 0.5 s. Schaefer's measurements were carried out on the bulk at 313 K.

Figure 1 shows the spectrum of the upfield aliphatic region investigated in the present study. The signals corresponding to the 1,4 units are assigned according to Duch and Grant[2] while those corresponding to the 3,4 units are assigned by assuming that the methine C_3 signal appears at higher field than the methylene C_4 signal. The values for both the chemical shifts and the intensities of the C_5 and C_1 signals are listed in Table I. Figure 2 shows the expanded spectrum of the C_1 trans and C_1 cis resonances with the curve decomposition lines used to establish the relative areas of the individual peaks corresponding to the identified dyad sequences.

The microstructure determined from the relative areas of the methyl C_5 signals is 72% cis-1,4, 21% trans-1,4, and 7% 3,4. This compares favorably with the ^1H NMR results. On the other hand, a cis-trans molar ratio of 3.5 is obtained from the relative areas of the methylene C_1 cis and C_1 trans resonances. Since the C_4 signal corresponding to 3,4 units overlaps slightly the C_1 cis resonances, the later analysis was made by assuming the C_4 signal area as intense as that of the C_5 signal observed at 19.0 ppm. The above cis-trans molar ratio also compares favorably with the value of 3.2 obtained from the ^1H NMR analysis. Thus, under the experimental conditions used for the present ^{13}C NMR study, quantitative measurements are feasible among both the various methyl and sp^3 methylene resonances.

The fractions of the 1,4 unit dyad sequences determined from the above C_1 signal intensities are listed in Table II together with predicted fractions based on Bernoullian distribution of cis-1,4, trans-1,4, and 3,4 units. A fairly close agreement is found between the measured and the predicted distributions.

Also listed in Table II are the predicted fractions for the various 3,4–1,4 dyads. They suggest that the (3,4)–(cis-1,4) dyad C_1 resonance would contribute 7% to the total C_1 cis signal intensity. Unfortunately, this resonance is not distinguishable in the spectrum of Figure 2. However, since the largest positive departure from the predicted Bernoullian fractions occurs for the (cis-1,4)–(cis-1,4) dyad, it seems likely that the C_1 resonances of the two dyads would coincide in the present spectrum.

Table I
Chemical Shifts and Relative Intensities of the C_5 and C_1 Signals Observed in the Spectrum of Figure 1

Carbon	Chemical shift,[a] ppm	Rel int,[b] arbitrary units
C_5 cis	23.25	11.6
trans	15.89	3.4
3,4	19.05	1.2
C_1 cis-cis	32.34	9.1
trans-cis	32.01	2.7
trans-trans	39.74	1.0
cis-trans	40.05	2.3

[a] Chemical shifts are given in ppm downfield from TMS using as reference the C_5 cis chemical shift reported by Tanaka and Sato.[1] [b] Intensities obtained from the relative areas measured on the expanded scale spectra.

Table II
Bernoullian Model Fitting for the Dyad Distribution in the Present Polyisoprene

Dyad[a]	Obsd fraction	Predicted fraction[b,c]
cc	0.60	0.54
tc	0.18	0.17
dc		0.05
tt	0.07	0.05
ct	0.15	0.17
dt		0.02

[a] The nomenclature c, t, and d is used here for cis-1,4, trans-1,4, and 3,4 units, respectively. [b] Predicted assuming $P_c = 0.71$, $P_t = 0.22$, and $P_d = 0.07$. [c] Since the dd, cd, and td dyad fractions are not measured in the present study, the fractions given above have been normalized in such a way that $[(cc) + (tc) + (dc) + (tt) + (ct) + (dt)] = 1$.

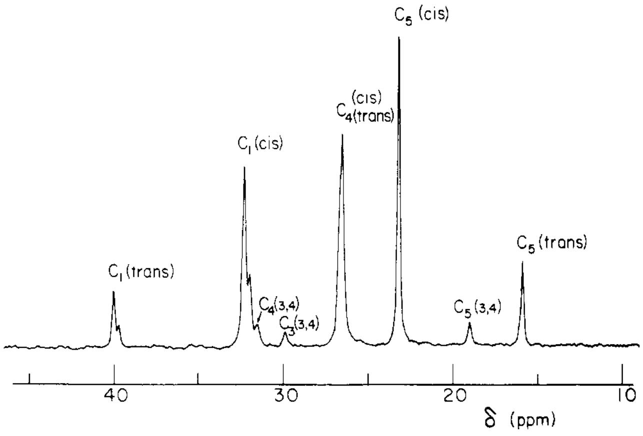

Figure 1. Aliphatic region of the ^{13}C NMR spectrum (22.6 MHz) of butyllithium-initiated polyisoprene. Chemical shifts are in ppm from TMS.

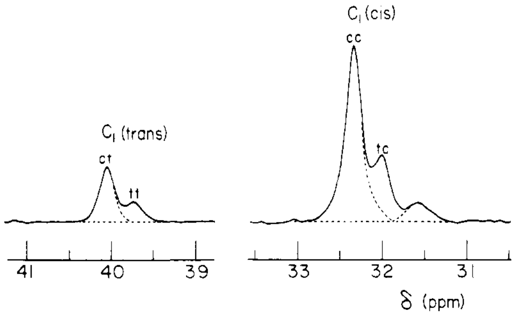

Figure 2. Expanded ^{13}C NMR spectrum of the C_1 cis and C_1 trans methylene resonances. Broken lines indicate the curve decomposition used in the present analysis.

Since the present polyisoprene contains only 7% of randomly distributed 3,4 units, the bias resulting from the undiscernible (3,4)–(cis-1,4) dyad C_1 resonance should not lead in principle to important interpretative errors. Therefore, according to the present study, one may conclude that the cis-1,4 and trans-1,4 unit distribution in the highly 1,4-polyisoprene prepared with butyllithium in nonpolar solvents is nearly random. This behavior seems to be a general feature of butyllithium-initiated polymerization of the 1,3-butadiene derivatives.

References and Notes

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