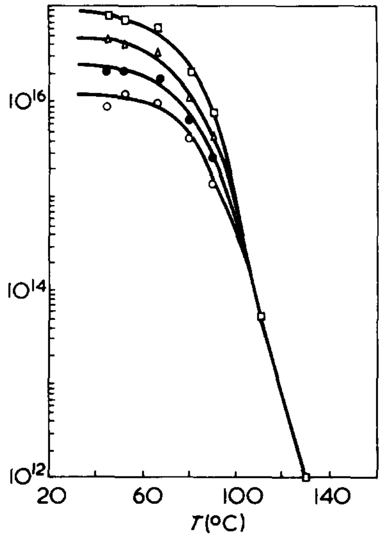

Figure 3 **Resistivity, ρ, (Ω cm) *versus T* for SAN at different electrification times, t. □, t = 900 sec; △, t = 300 sec; ●, t = 90 sec; ○, t = 30 sec**

compared with the mechanical data shown in *Figure 2*. In this Figure the shear moduli measured after different times, t, of application of the torque, are reported, using a Clash–Berg torsional stiffness tester. The isochronal curve obtained for $t = 10$ sec is generally used for T_g determination[13] and leads to $T_g = 106°C$ for SAN. The curve obtained for $t = 300$ sec shows a strong dependence of T_g on the time of the experiment. Mercier and Aklonis[14] discuss the existence of a 'true' transition (for $t = \infty$) for this type of measurement, and correlate these data with those obtained using the dilatometric technique.

To compare electrical and mechanical data more satisfactorily the results shown in *Figure 1* are replotted as resistivity, ρ, vs. temperature in *Figure 3*. While the mechanical data are time dependent in the viscoelastic region, the electrical results are affected by the time of the experiment only in the glassy region. In fact the glassy state is a quasi-equilibrium zone for the mechanical response while the viscoelastic region is a transition between a solid and liquid behaviour of the amorphous polymer. With respect to the electrical response, however, the glassy region is affected by the polarization process (i.e. is time dependent) while in the viscoelastic zone only the temperature effect on the stationary current is present.

CONCLUSIONS

In conclusion, it seems that one should be careful in correlating the discontinuity in the conductivity–temperature curve with the glass transition of the polymer, due to the complexity of the conduction phenomenon. The inflection in these curves can sometimes be an artefact because the data are taken after electrification times not long enough to achieve the steady state condition. In fact, while for poly(vinyl acetate)[1], the $\log\sigma$ vs. $1/T$ curve obtained at steadily increasing temperature shows a break point at T_g, it does not appear in the $\log\sigma_s$ vs. $1/T$ plot.

This fact seems to indicate that, if the polarization process is removed, the $\log\sigma_s$ vs. $1/T$ curve presents a break point only if the conduction mechanism is changed during the vitrification process. The situation is similar to the case of diffusivities of gases in glassy polymers[15], for which a break in the curve of log (diffusivity) vs. $1/T$ is not always observed at T_g, depending on the nature of the gas and the polymer.

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Structure of 3,4-(*cis*-1,4-)*trans*-1,4-polyisoprene by ^{13}C n.m.r.

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INTRODUCTION

For years ^1H n.m.r. and infra-red spectroscopic studies have given microstructure information only on content but not on arrangement of the isomeric units of polyisoprene. Little work has been done on polyisoprene using ^{13}C n.m.r. since the work of Duch and Grant[1]. A recent study on the *cis/trans* isomerized 1,4-polyisoprene[2] showed that the distribution of *cis–cis*, *cis–trans* and *trans–trans* linkages can be determined by ^{13}C n.m.r. Also a detailed account on the sequence structure of a binary polyisoprene with 3,4 and *cis*-1,4 structural units has recently been published[3]. The purpose of this communication is to report that ^{13}C n.m.r. spectroscopy gives detailed information on the sequence structure of a ternary polyisoprene with 3,4 and *cis/trans*-1,4 structural units.

EXPERIMENTAL

The sample was prepared using a sec-butyllithium catalyst in cyclohexane.

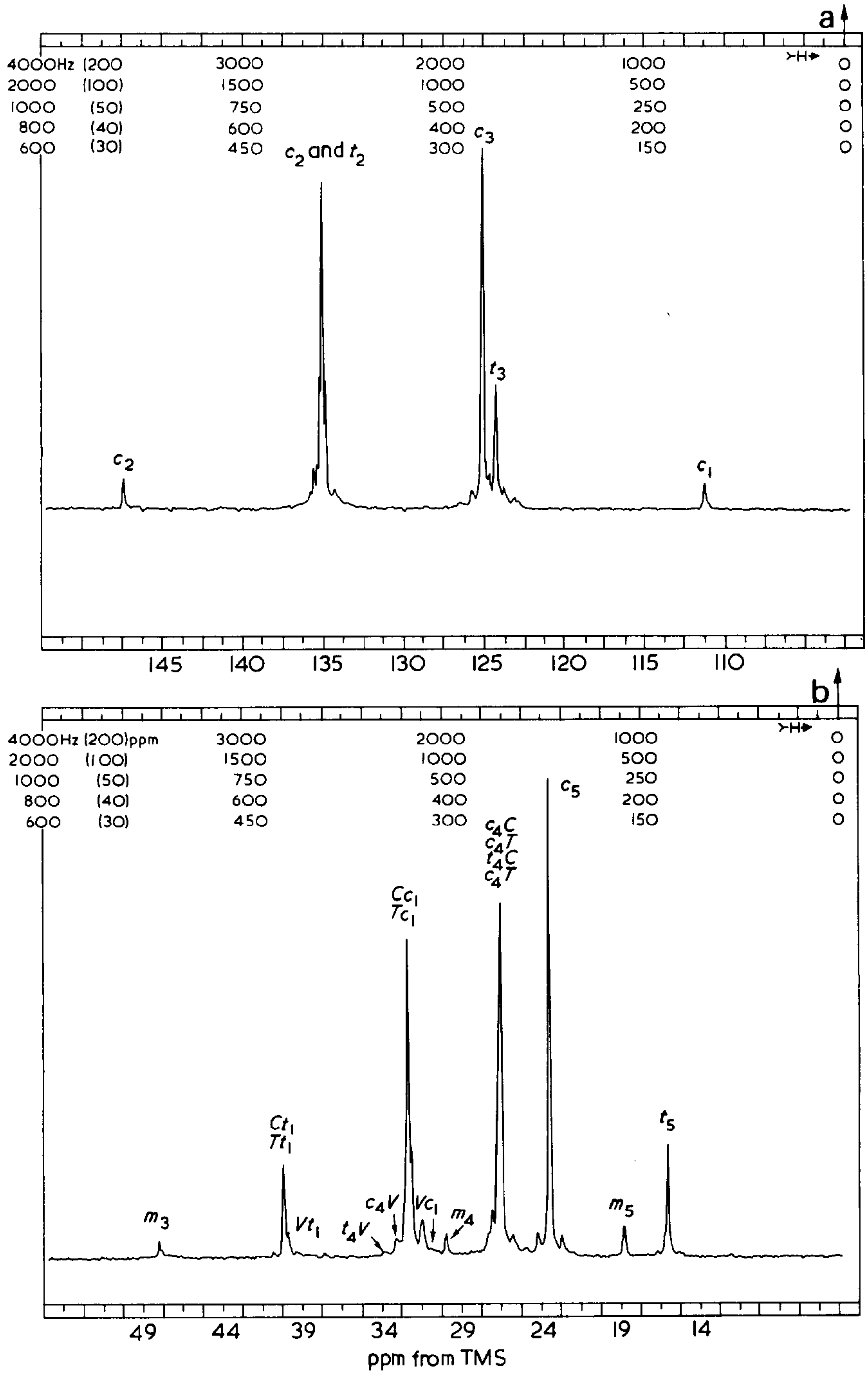


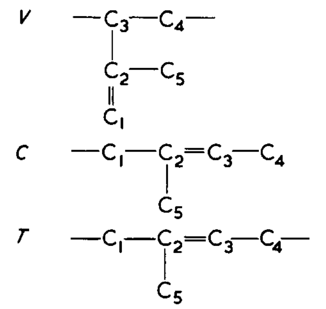
Figure 1 ^{13}C n.m.r. spectrum (20 MHz) of 3,4-(*cis*-1,4-)-*trans*-1,4-polyisoprene: (a) olefinic region and (b) aliphatic region

The *DSV* was 0.75.

The ^{13}C n.m.r. proton decoupled spectrum was obtained on a Varian CFT–20 Spectrometer using a 90° pulse with an acquisition time of 1.023 sec and a pulse delay of 14 sec. A proton n.m.r. spectrum was obtained on a Varian HR–300 NMR Spectrometer. The sample contained 4.4% 3,4-polyisoprene, 17.1% *trans*-1,4-polyisoprene and 78.6% *cis*-1,4-polyisoprene. No 1,2-polyisoprene peaks were detected in either the ^1H or ^{13}C n.m.r. spectra.

RESULTS AND DISCUSSION

In order to label the position of a particular carbon atom in a given sequence the *i*th C atom of 3,4 units (*V*), *trans*-1,4 units (*T*) and *cis*-1,4 units (*C*) is marked by v_i, t_i and c_i, respectively. The carbon atoms are numbered according to the following scheme:



The assumption is made throughout that the enchainment of the structural units is always head to tail. In a sequence of symbols the enchainment of the corresponding units is head-to-tail from right-to-left. Thus, the notation Iv_3C means the tertiary C-atom, C*, of the central *V*-unit in the following chain segment:

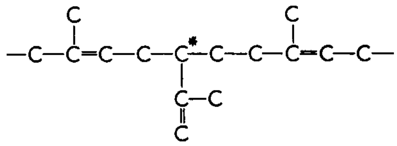


Figure 1 shows the ^{13}C n.m.r. spectrum of 3,4-(*cis*-1,4-)*trans*-1,4-polyisoprene. In the olefinic region (a) very little fine structure due to the different isomeric structure of neighbouring units is noted. However, the β C-atoms, c_3 and t_3, on the 1,4-units are observed as two separate peaks with the signal for c_3 at 125.1 ppm and for t_3 at 124.3 ppm. In the aliphatic region (b) again little fine structure is evident in the spectrum.

From previous ^{13}C n.m.r. work[1,3,4] on both pure isomeric polyisoprene and binary polymers of different isomeric units of polyisoprene, assignments can be made for all the lines in the aliphatic region of the spectrum (b). These assignments appear in *Table 1* along with the corresponding sequences. To arrive at the calculated chemical shift values shown in *Table 1* the equation suggested by Grant and Paul[5] for linear saturated hydrocarbons was used with modifications for branching[6] and double bond position. The basic equation states that the chemical shift δ_i of the *i*th C-atom can be expressed by the following relationship:

$$\delta_i = B + \sum_{j=1}^{S} A_j n_{ij} + C + D_x(d) \qquad (1)$$

where A_j is an additive shift parameter for the *j*th position; n_{ij} is the number of atoms in the *j*th position relative to carbon *i* and *B* is a constant whose value is close to that of the chemical

Table 1 Chemical shift data and relative intensities in 3,4-(*cis*-1,4-)*trans*-1,4-polyisoprene

Signal	Carbon atom and sequence[a]	Chemical shift (ppm)		Relative intensities	
		Calculated	Experimental	Calculated[b]	Experimental
1	It_5I[c]	15.9	15.9	0.052	
	It_5V	16.0		0.002	0.058
	Vt_5I	16.0		0.002	
2	Iv_5I	18.8	18.7	0.013	0.015
3	Ic_5I	23.4	23.4	0.240	
	Ic_5V	23.5		0.011	0.232
	Vc_5I	23.5		0.011	
4	Ic_4I	26.4	26.4	0.240	
	Vc_4I	26.4		0.011	0.333
	It_4I	26.8		0.052	
	Vt_4I	26.8		0.002	
5	Iv_4I	29.9	29.9	0.013	0.016
6	IVc_1I	30.1	30.3	0.011	0.008
7	Ic_1I	32.2	31.3	0.240	
	Ic_1V	32.3	32.0 32.2	0.011	0.245
8	Ic_4VI	33.7	33.2	0.011	0.012
9	It_4VI	34.1	33.8	0.002	0.006
10	IVt_1I	37.6	37.6	0.002	0.003
11	It_1I	39.8	39.8	0.052	0.062
	It_1V	39.9	40.0	0.002	
12	Iv_3I	48.0	47.9	0.013	0.013

[a] Symbols as explained in text; [b] calculated for a Bernoullian distribution; [c] I is either a *cis* or *trans*-1,4-unit

shift of methane. *C* is an additive constant which takes into account the shieldings of carbon nuclei at either the position of branching or alpha thereto. For example, factors for methyl carbons bonded to tertiary and quarternary carbons are denoted 1°(3°) and 1°(4°), respectively, and secondary carbons bonded to tertiary and quaternary carbons are denoted 2°(3°) and 2°(4°). $D_{x(x)}$ is an additive constant taken from pure *cis*-1,4- and *trans*-1,4-polyisoprene[4] for carbon atoms attached to a double bond. $D_{v3(\alpha)}$ and $D_{v5(\alpha)}$, methine carbons bonded to a double bond and a methyl bonded to a double bond, respectively, were determined from this work by taking the difference between the experimentally observed line and the results of the calculated line position using equation (1) without the $D_{x(\alpha)}$ term.

Table 2 Chemical shift parameters

Shielding effect	Factor (ppm)
α ($n = 1$)	+9.1
β ($n = 2$)	+9.4
γ ($n = 3$)	−2.5
δ ($n = 4$)	+0.3
ϵ ($n = 5$)	+0.1
1°(3°)	−1.1
1°(4°)	−3.4
2°(3°)	−2.5
2°(4°)	−7.2
3°(2°)	−3.7
3°(3°)	−9.5
4°(1°)	−1.5
4°(2°)	−8.4
$D_{c1}(\alpha)$	−5.2
$D_{c4}(\alpha)$	+1.2
$D_{c5}(\alpha)$	+3.4
$D_{t1}(\alpha)$	+2.4
$D_{t4}(\alpha)$	+1.6
$D_{t5}(\alpha)$	−4.1
$D_{v3}(\alpha)$	+6.1
$D_{v5}(\alpha)$	−1.3
B	−2.6

Using equation (1) and the chemical shift parameter in *Table 2*, the line positions in *Table 1* were calculated. Excellent agreement between the calculated and experimental line positions was noted with the maximum deviation between an experimental and calculated line being 0.5 ppm.

The relative experimental intensities listed in *Table 1* were tested against Bernoullian statistics and excellent agreement was obtained (See *Table 1*). Only lines having relative intensity equal to or greater than 0.2% of the total spectrum integral were included in the calculation.

Further work is underway to investigate the microstructure of polyisoprene containing all four structurally different units (i.e. 1,2-, 3,4, *cis*-1,4 and *trans*-1,4-polyisoprene).

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