Solid-state ^{13}C nuclear magnetic resonance spectra of the α and β conformers of *trans*-1,4-polyisoprene

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(Received 6 May 1986; revised 20 July 1987; accepted 31 July 1987)

Solid-state ^{13}C nuclear magnetic resonance (n.m.r.) was used to study the two different conformers of *trans* natural rubber (NR). The α and β conformers of *trans* NR were observed to give different ^{13}C chemical shifts. The relative magnitude and direction of the chemical shift for the methyl carbon on the β conformer are predicted by a steric perturbation model. The α conformer gave longer relaxation times than the β conformer. For this highly mobile semicrystalline polymer, spin diffusion was not a major contributer to the relaxation process.

(Keywords: n.m.r.; 1,4-polyisoprene; conformers)

INTRODUCTION

Gutta percha, *trans*-1,4-polyisoprene (TPI), can adopt at least two different crystal modifications, orthorhombic β (ref. 1) and monoclinic α (ref. 2). The α conformer is produced naturally and is the thermodynamically stable form of TPI. Upon heating the α phase to above 65°C and then rapidly quenching the amorphous rubber, the β phase crystallizes. The transformation of TPI between the two crystal forms has been studied extensively[3-7]. Recently the Fourier transform infra-red (*FT*i.r.) spectra and the normal-coordinate analysis of the two polymorphic forms of TPI were obtained[8]. The spectra of the amorphous phases of the two conformers were found to be identical. The spectra of the crystalline phases were quite different.

We became interested in the *trans* form of natural rubber (NR), because of our previous solid-state ^{13}C nuclear magnetic resonance (n.m.r.) studies on the structure changes produced by peroxide cure[9] of *cis* natural rubber. In that study, it was found that *cis–trans* rearrangement occurred in addition to crosslinking. It has been shown that solid-state ^{13}C n.m.r. is very sensitive in detecting changes in the carbon spectra due to differences in conformation and crystal packing[10-12]. In this study we will use the techniques of high-resolution solid-state ^{13}C n.m.r.[13] to characterize the α and β conformers of TPI.

EXPERIMENTAL

Sample preparation

The *trans*-1,4-polyisoprene (TPI) has the classification of gutta percha. The β conformer was prepared by heating the TPI to 80°C in a platten press to get an amorphous material. The sample was removed from the press and quenched in an ice/water bath. The α conformer was prepared by dissolving the TPI in CS_2 and letting the solvent evaporate at room temperature. Both samples were annealed at 55°C in order to increase their crystallinity and crystal perfection. The two polymorphic forms (α and β) were verified by *FT*i.r. and X-ray diffraction.

Fourier transform ^{13}C nuclear magnetic resonance

The ^{13}C solid-state spectra were acquired on a Nicolet Technology NT-150 spectrometer operating at 38 MHz and equipped with a cross-polarization accessory. Radiofrequency amplifiers were adjusted to satisfy the Hartmann–Hahn[14] condition between 62 and 67 kHz. The high-power proton decoupling fields were the same strength as the spin-lock fields. Spectra obtained by the cross-polarization[15], magic-angle sample spinning[16], and dipolar decoupling[17] (CP/MAS/DD) techniques used a 1 ms contact time and a 2 s delay between pulses. The solid samples were packed into hollow Beams–Andrews rotors[16,18] machined out of polyoxymethylene or polychlorotrifluoroethylene or a hybrid spinner consisting of both materials. The 'magic angle' was set by maximizing the intensity of the carbonyl resonance of glycine. All free induction decays (FID) were zero-filled to 8000 data points. A normal Bloch decay experiment (MAS/SD) with 12 W decoupling power and a Bloch decay experiment using high-power proton decoupling (MAS/DD) were used to probe the amorphous (highly mobile) phases. The relaxation measurements (T_{1C}, T_{1H} and $T_{1\rho}^{H}$) were obtained by the pulse sequences used by Schaefer and Sullivan[11,20,21]. The delay between pulses in T_{1C}, T_{1H} and $T_{1\rho}^{H}$ was 20, 5 and 2 s respectively. the chemical shifts are reported relative to tetramethylsilane (TMS).

RESULTS

Chemical shifts

The spectra of *cis* and *trans* NR, obtained by MAS/SD, are shown in *Figure 1*. Narrow resonances are observed

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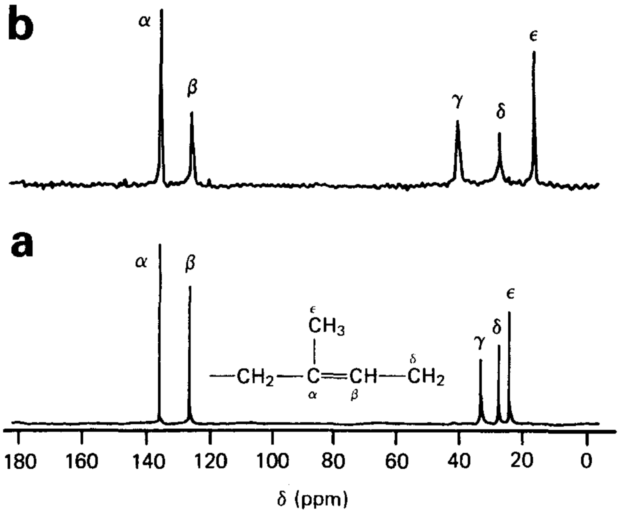


Figure 1 Spectra of (a) *cis*- and (b) *trans*-polysioprene obtained by one pulse experiment

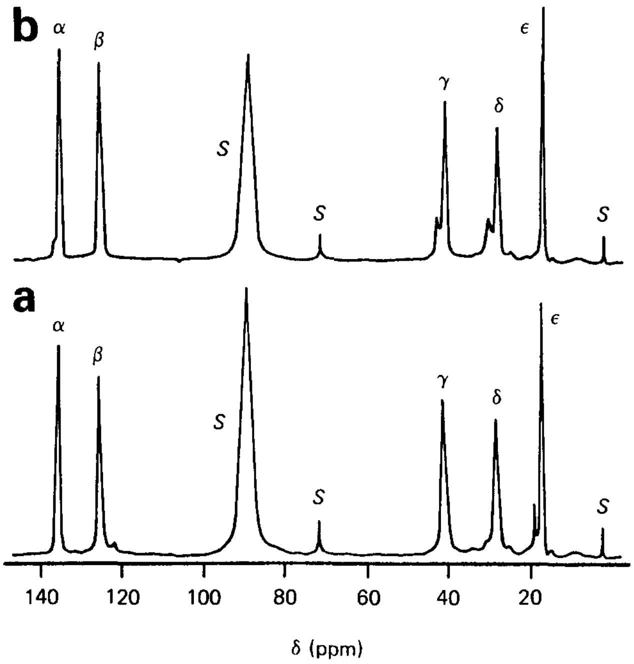


Figure 2 Spectra of *trans* natural rubber obtained by MAS/DD pulse sequence: (a) α conformer, (b) β conformer

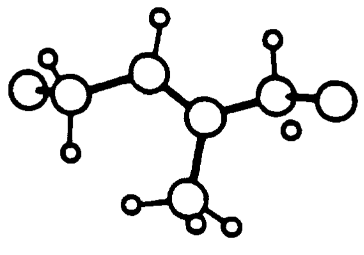
for these elastomeric solids because of rapid motion ($\tau \simeq 10^{-10}$ s) which averages nearly all the dipolar and chemical shift interactions[19]. It has been suggested that there exists a second quite slow motion in the case of polybutadiene[19]. Presumably similar effects occur for this NR system. The observed structure features are identical to those found by Duch and Grant[22]. They are the olefinic quaternary carbon, the methine carbon, the methylene carbon adjacent to the quaternary carbon, the other methylene attached to the methine carbon, and the methyl carbon. The observed widths of the resonances in the *trans* spectrum are broader than those found in the *cis* isomer. This is due to the presence of crystalline material. The spectra of the two crystalline conformers of TPI obtained by MAS/DD are shown in *Figure 2*. The centre resonances at 90 and 72 ppm are due to the rotor impurities. Spectrum (a) of the α phase shows six major resonances at 135.7, 125.7, 41.2, 28.0, 18.7 and 17.3 ppm and a weak signal at 122.0 ppm. Spectrum (b) of the β phase shows five major resonances at 135.7, 125.8, 41.3, 28.2 and 17.3 ppm, relative to TMS. In addition two weak resonances, one at 137 ppm and the other at 16.8 ppm, are observed. Because the MAS/DD experiment probes the highly mobile carbons, these weak resonances are assigned to carbons in the more rigid crystalline phase.

The conformation and the crystallographic data for the α and β conformers are listed in *Table 1*: *N* is the number of chains per unit cell; *C* = *cis* and *T* = *trans*, the configuration of the C–C double bond; and *S* and $\bar{S}$ depict the two types of skew conformations about the C–C single bond of the main chain. The two conformations of TPI are illustrated in *Figure 3*.

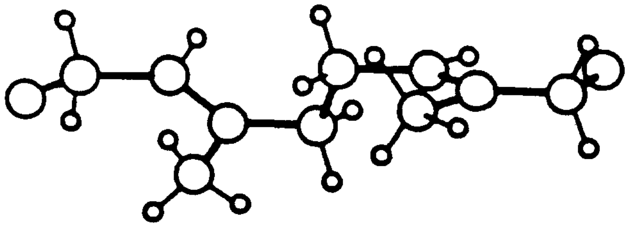
The spectra obtained by the CP/MAS/DD pulse sequence are plotted in *Figure 4*. Spectrum (a) is of the α conformer. All the resonances observed by the MAS/DD pulse sequence are observed in the CP/MAS/DD spectra, though the relative intensities are different. The resonances of the two methylene and the quaternary carbons are not resolved. One set of the spinning sidebands of the olefinic crystalline material are observed at 56 and 42 ppm. The ^{13}C chemical shifts of the carbons in the crystalline phase obtained by the CP/MAS/DD and MAS/DD experiment are listed in *Table 2*. The

Table 1 Computation and crystallographic data for α and β conformers of *trans*-1,4-polyisoprene

trans-1,4-polyisoprene	$\{\underset{\gamma}{CH_2}-\underset{\alpha}{C}(\underset{\varepsilon}{CH_3})=\underset{\beta}{CH}-\underset{\delta}{CH_2}\}_n$
α form	Monoclinic, $P2_1/c$, $-C^5_{2h}$ $a = 7.98$ Å, $b = 6.29$ Å, $c = 8.77$ Å, $\beta = 102.0°$, $N = 4$ (2/0) *trans CTS–trans CT*$\bar{S}$
β form	Orthorhombic, $P2_12_12_1$ $a = 7.78$ Å, $b = 11.78$ Å, $c = 4.72$ Å, $N = 4$ *trans ST*$\bar{S}$, $\rho = 1.05$ g cm^{-3}



β conformer



α conformer

Figure 3 Conformational structures of the two forms of *trans* natural rubber

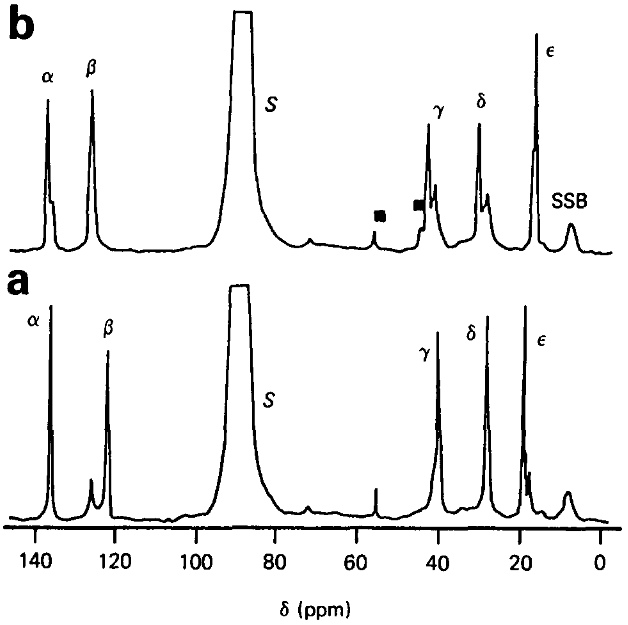


Figure 4 Spectra of *trans* natural rubber obtained by CP/MAS/DD: (a) α conformer, (b) β conformer

Table 2 Chemical shifts (ppm) of crystalline resonances

	Cross-polarization		Dipolar decoupling	
	β-trans NR	*α-trans* NR	*β-trans* NR	*α-trans* NR
C_α	137.0	136.0	137.1	136.2
C_β	125.7	121.8	–	122.0
C_γ	42.8	39.8	43.0	40.0
C_δ	30.2	27.7	30.4	–
C_ε	16.5	18.6	16.8	18.7

chemical shifts obtained by the two different experiments agree within 0.3 ppm.

Since some of the resonances of carbons in the amorphous and crystalline phases are not resolved, we used the T_1 CP pulse sequence reported by Sullivan[20] to differentiate these carbons based on their different T_1 values. *Figure 5* is a plot of the spectra obtained with a τ delay of 5 s. The negative peaks (indicated by dots) are due to carbons in the crystalline phase which have longer T_1 relaxation times than those in the amorphous phase. It can be inferred that the crystalline phase of the β conformer has shorter T_1 than the α conformer. Because of the differences in the T_1 relaxation times, we are able to resolve the isotropic chemical shifts of the carbons in the amorphous and crystalline phases. *Table 3* lists the chemical shift differences of the crystalline and amorphous phases. The chemical shift differences of the α conformer and the amorphous phase were found to range between 0.5 and 4.0 ppm. The observed solid-state chemical shift difference of the β conformer and its amorphous phase was between 0.6 and 2.3 ppm. The CP/MAS/DD spectrum of the β conformer shows the low-field component of the three doublets to be due to the carbons in the crystalline phase (C_α 137 ppm, C_γ 43 ppm and C_δ 30.5 ppm. The other two resonances are not resolved into doublets. The difference in the crystalline chemical shifts of the two crystal forms are listed in *Table 4*. The crystalline chemical shift values of the α phase are found to occur at lower fields than the β phase for all carbons except for the methyl group, which occurs at higher field. The difference in the chemical shifts ranges from 1.0 ppm for the quaternary carbon to 4.0 ppm for the methine carbon. The difference in the direction of the methyl carbon may be due to steric perturbations as proposed by Grant and Cheney[23].

Relaxation measurements

The observed ^1H T_{1H} values are lised in *Table 5*. Both the α and β conformers gave two distinct values. The times observed for the α conformer were 230 ms (crystalline) and 151 ms (amorphous). The observed T_{1H} for the β conformer were 190 ms (crystalline) and 130 ms

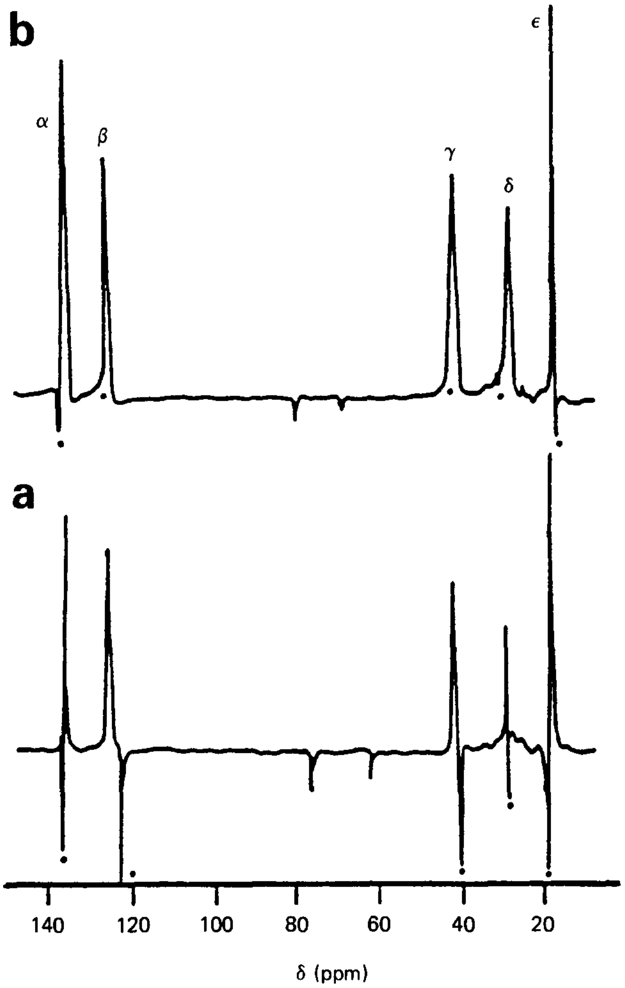


Figure 5 Comparison of the spectra obtained by the T_1 inverse recovery pulse sequence: (a) α conformer, (b) β conformer. The τ delay is of 5 s

Table 3 Chemical shift differences of crystalline and amorphous resonances

	α phase,[a] Δ (ppm)	β phase, Δ (ppm)
C_α	0.6	1.5
C_β	−3.8	0.6
C_γ	−1.2	1.9
C_δ	−0.5	2.3
C_ε	1.5	−0.6

[a] Negative sign indicates upfield direction or increased shielding

Table 4 Difference in chemical shifts of the two crystalline phases

	Carbon types	$\Delta(\beta-\alpha)$[a] (ppm)
C_α	$>CH=$	+1.0
C_β	$-CH=$	+3.9
C_γ	$-CH_2-$	+3.0
C_δ	$-CH_2-$	+2.5
C_ε	$-CH_3$	−2.1[b]

[a] Negative sign indicates upfield direction or increased shielding
[b] The resonances of the amorphous phase were within ±0.2 ppm

Table 5 Observed piston spin–lattice relaxation times T_{1H} (ms) obtained through CP

	α conformer	β conformer
Crystalline	230	190
Amorphous	151	130

Uncertainty = ±10%

(amorphous). These results indicate that spin diffusion is the dominant relaxation process, with the more mobile amorphous phase being the diffusion sink.

The carbon T_{1C} values are listed in *Table 6*. The T_{1C} for the amorphous carbons are reported but they should be considered as highly suspect results because of the extreme difficulty of accurate measurement. The resonances of the α, β and δ carbons were still negative after a τ delay of 50 s, and therefore their values are estimates based on peak intensity. The T_{1C} values for all the crystalline carbons were longer than for the amorphous carbon. Again the α phase T_{1C} relaxation times are longer than those observed for the β phase. Because of peak overlap we used peak intensities and the null point method to calculate the T_{1C} values.

The relative relaxation time differences between the carbons follow the trend observed by Schaefer[24] for *cis*-polyisoprene. The quaternary and methyl carbons had the longest relaxation times and the methylene carbon the shortest.

T_{1C} relaxation times are listed in *Table 7*. The values reported are the average of both phases (crystalline and amorphous). The α phase was once again observed to have the longer T_{1C} relaxation times except for CH_3.

DISCUSSION

Chemical shifts

We employed the model of Grant and Cheney[23] to predict the effect of steric crowding on the chemical shift in the solid state. In the steric hindrance model, a CH bond is compressed or expanded by the mutual repulsion of a bonded and nearby non-bonded hydrogen. The shift depends on the angle θ between the CH bond and the interhydrogen separation vector and the CH bond and the hydrogen–hydrogen distance *r*. We used the empirical expression developed by Grant and later modified by Garroway[25]:

$$\delta_c = -1680 \cos\theta \exp(-26.71r) \qquad (1)$$

Here *r* is in nanometres and δ_c is the chemical shift difference on the δ scale. The net shift of the carbons in the α and β conformations of TPI was calculated by summing the contributions of equation (1) for hydrogen–hydrogen separations out to 0.27 nm; the separations were calculated from the X-ray data of Bunn[1] (α conformation) and Takahashi[2] (β conformation). Bunn reported in his study that the methyl in the β conformer is tilted out of the C=C double-bond plane because of steric hindrance by the methylene group three bonds away. For this repulsion a value of −0.52 ppm was calculated. The observed difference between the amorphous and crystalline chemical shifts was −0.6 ppm. This is in very good agreement with the steric hindrance model. All other values calculated were less than the observed chemical shift differences. The α conformer has no reported steric hindrance and no calculated shift differences were of the right magnitude. It is interesting to note that the methyl (ε) and quaternary (α) carbons shift in the same direction. More studies are needed in order to understand the effect of the chain conformation of TPI on the observed chemical shift.

Relaxation measurements

Longer relaxation times (T_{1C}) were consistently measured for the α conformer. This would indicate that the α conformer has greater motional freedom than the β conformer[24] or that the β conformer has higher densities of motions that aid in its relaxation. This interpretation is based on a relaxation model in which the dipolar interactions are modulated by the segmental motions. The methine and methylene carbon relaxation times are expected to differ by a factor of 2. However, the difference may be due to a reduction in the effective dipolar coupling caused by segmental motion.

Table 6 Observed ^{13}C spin–lattice relaxation times T_{1C} (s) obtained through CP

Carbon	Phase	α phase	β phase
C_α	c	>60	20
	a	5	0.06
C_β	c	>60	5
	a	0.10	0.06
C_γ	c	>60	6
	a	0.09	0.03
C_δ	c	2.5[a]	7
	a		0.05
C_ε	c	17	11
	a	0.30	0.40

[a] Average of both phases
Uncertainty = ±15%

Table 7 Observed carbon $T_{1\rho}$ (ms) for the α and β phases

	α phase	β phase
C_α	154.4	85.3
C_β	23.5	21.3
C_γ	27.3	16.9
C_δ	29.0	15.8
C_ε	54.2	80.0

Uncertainty = ±15%
Average of both phases

SUMMARY

Different ^{13}C chemical shifts were observed for the α and β conformers of *trans* NR. The direction of the chemical shifts of the methyl carbon in the β conformation relative to the α conformation were predicted by the steric perturbation model. The α conformer consistently gave longer relaxation times than the β conformer, indicating greater segmental motion.

ACKNOWLEDGEMENTS

The authors would like to thank Dr William Ritchey for his most helpful discussions, the US Army Tank Automotive Command for making this work possible under Contract No. DAAE07-83-K-R010 and the Goodyear Tire and Rubber Company.

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