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# Observation of immobile regions in natural rubber at ambient temperature by solid-state $^{13}$C CP/MAS NMR spectroscopy

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## Abstract

Employing $^{13}$C CP/MAS NMR spectroscopy, the existence of immobile regions in natural rubber (*cis*-1,4-polyisoprene) corresponding to a few percent of the monomer units has been detected at ambient temperature. For synthetic rubbers no immobile regions have been detected at all. Applying different physical and chemical treatments to natural rubber it is shown that mastication, γ-irradiation, and increasing the temperature, slightly above the ambient, reduce the amount of immobile regions. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords*: Natural rubber; Immobile regions; Solid-state $^{13}$C CP/MAS NMR

## 1. Introduction

Since the first $^{13}$C nuclear magnetic resonance (NMR) investigation of natural rubber (*cis*-1,4-polyisoprene) in solution and as a bulk matter [1], this polymer has been thoroughly examined by liquid-state $^{13}$C NMR spectroscopy in order to gain information on the structure/conformation of the polymeric chains with respect to the low content of the monomeric *trans*-1,4-isoprene units, linkages (head, tail), and structure of the end-groups [2–8]. Other properties, for example regarding crystallinity or immobility, require analysis in the solid state. Both solid-state $^{13}$C magic-angle spinning (MAS) and cross-polarization (CP)/MAS NMR experiments have been widely used in the studies of natural rubber in relation to vulcanization [9–15] or in mixtures with other polymers [16,17]. The different kinds of information that can be obtained from these experiments may be illustrated by for example the investigation of gutta percha (*trans*-1,4-polyisoprene) by Patterson and Koenig [18]. From single-pulse $^{13}$C MAS NMR of gutta percha five mobile carbons have been detected, while no resonances originating from immobile carbons were observed by this experiment. However, $^{13}$C CP/MAS NMR is a favourable technique for the detection of immobile carbon atoms at the expense of the mobile ones because it accentuates carbons experiencing non-vanishing heteronuclear $^{13}$C–$^{1}$H dipolar couplings. Employing $^{13}$C CP/MAS experiments at ambient temperature Patterson and Koenig observed two crystalline conformers in high quantities for gutta percha [18]. Like gutta percha it has been claimed that natural rubber is partly crystalline at room temperature, just on a much smaller scale [19], but no experimental evidence has been reported. Employing $^{13}$C CP/MAS NMR methods this study presents what we believe is the first experimental observation of different immobile regions in low concentration at ambient temperature for non-vulcanized natural rubber. Further, synthetic polyisoprenes and the effect of different chemical and physical treatments of natural rubber have been explored with special attention to the effect on these regions.

## 2. Experimental

### 2.1. Samples

Four different rubbers of commercial origin have been investigated. These are named Neorub (Sri Lanka), SMR CV60 (Malaysia), Natsyn 2200 (Goodyear), and Cariflex IR (Shell) by their manufacturers. The polyisoprene content in Neorub and SMR CV60 is approximately 92% while it is 95% for Natsyn 2200 and 98–100% for Cariflex IR. Neorub and SMR CV60 are both natural rubbers with the only difference that SMR CV60 is a Neorub sample which has

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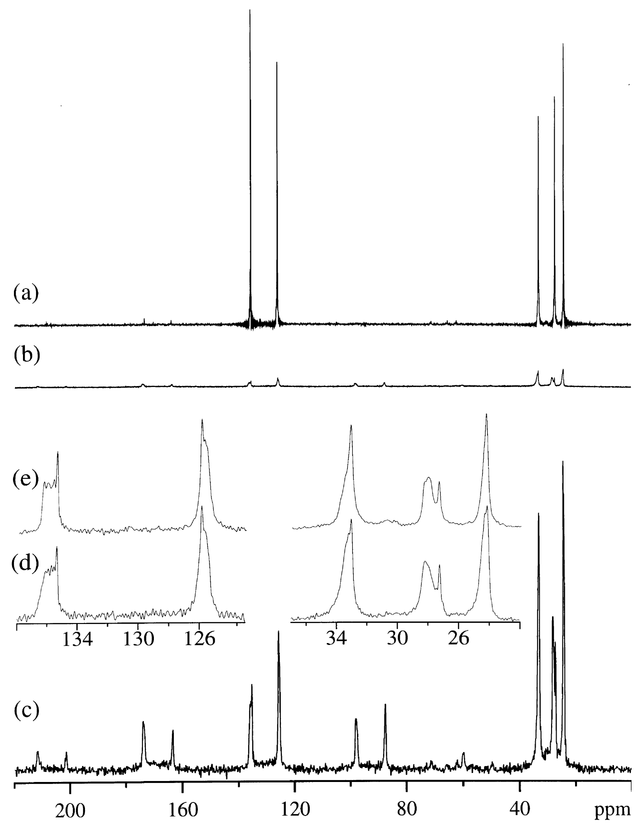


Fig. 1. $^{13}$C MAS NMR (75.43 MHz, $\nu_r = 2.9$ kHz) spectra of Neorub at 313 K obtained using (a) single-pulse excitation (4 s recycle period, 514 scans) and (b) CP (8 s recycle period, a contact time of 1.0 ms, and 9577 scans). Spectrum (c) is a vertical expansion of spectrum (b) scaled by a factor of 20. Inserts display magnifications of the regions 20 to 40 and 120 to 140 ppm for (d) Neorub and (e) a SMR CV60-type natural rubber.

been stabilized using hydroxylamine. Natsyn 2200 and Cariflex IR are both synthetic rubbers which differ by their content of *cis*-1,4-monomer units (97% and 90%, respectively) relative to the total content of isoprene monomer units. Further, three additional samples of Neorub were investigated. These samples were processed in different ways, i.e. one has been masticated and the two others were exposed to irradiation by γ-rays at a level of 100 and 300 kGy, respectively.

### 2.2. NMR measurements

High-resolution natural-abundance $^{13}$C NMR experiments were performed on a Varian XL-300 (7.05 T) spectrometer operating at 75.43 MHz for $^{13}$C. The experiments were carried out at various temperatures ranging from 295 to 353 K using a home built high-speed spinning CP/MAS variable temperature probe and 7 mm o.d. PSZ rotors (220 μl sample volume). Spinning speeds in the range $\nu_r = 2.8$–$3.7$ kHz were employed. High-power $^{1}$H decoupling was applied during acquisition. In the CP/MAS experiments a contact time of 1.0 ms and a recycle delay of 8.0 s have been employed. $^{13}$C chemical shifts are in ppm relative to an external sample of tetramethylsilane (TMS). All spectra were processed without line broadening.

## 3. Results and discussion

The presence of immobile regions in natural rubber at ambient temperature is recognized from Fig. 1 which shows the spectra of Neorub employing $^{13}$C single-pulse MAS (Fig. 1(a)) and $^{13}$C CP/MAS (Fig. 1(b) and (c)) experiments. The corresponding isotropic $^{13}$C chemical shifts are summarized in Table 1. A conspicuous difference between the two spectra lies in the absolute intensities for the two experiments. While the intensities for the resonances in the single-pulse MAS spectrum are high and an excellent signal-to-noise (S/N) ratio can be obtained in a few minutes for the highly mobile phase of natural rubber, the intensities in the CP/MAS spectrum are much lower and several hours are required to achieve an adequate S/N ratio. This is illustrated by a comparison of the spectra for the two

Table 1
Isotropic ($\delta_{\mathrm{iso}}$) and anisotropic ($\delta_\sigma$, $\eta_\sigma$) $^{13}$C chemical shielding parameters for the mobile and immobile carbons in isoprene rubbers from $^{13}$C MAS and CP/MAS NMR[a]

| Carbon | $\delta_{\mathrm{iso}}$ (ppm) | | | | $\delta_\sigma$ (ppm)[b] | $\eta_\sigma$[b] |
|---|---|---|---|---|---|---|
| | Mobile[b] *cis*-1,4 | Mobile[c] *trans*-1,4 | Mobile[c] 3,4 | Immobile[b] *cis*-1,4 | | |
| C1 | 33.0 | 40.8 | 111.9 | 33 | — | — |
| C2 | 135.4 | 135.1[d] | 147.9 | 136 | −91 | 0.86 |
| C3 | 125.9 | 125.1 | 48.4 | 126 | −79 | 0.38 |
| C4 | 27.3 | 27.5[d] | 32.0[d] | 28 | — | — |
| C5 | 24.1 | 16.6 | 19.3 | 24 | — | — |

[a] The chemical shielding parameters are related to the principal elements of the anisotropic shielding tensor ($\delta_{xx}$, $\delta_{yy}$, $\delta_{zz}$) according to $\delta_{\mathrm{iso}} = (\delta_{xx} + \delta_{yy} + \delta_{zz})/3$, $\delta_\sigma = \delta_{\mathrm{iso}} - \delta_{zz}$, $\eta_\sigma = (\delta_{xx} - \delta_{yy})/\delta_\sigma$ using the ordering $|\delta_{zz} - \delta_{\mathrm{iso}}| \geq |\delta_{xx} - \delta_{\mathrm{iso}}| \geq |\delta_{yy} - \delta_{\mathrm{iso}}|$. $\delta_{\mathrm{iso}}$ is referenced with respect to external TMS.

[b] Neorub. Anisotropic chemical shielding parameters are determined from ambient temperature spectra.

[c] Cariflex IR.

[d] Isotropic chemical shifts for C2 and C4 in the *trans*-1,4 monomer unit and the C4 in the 3,4 monomer unit taken from earlier studies [4,27].

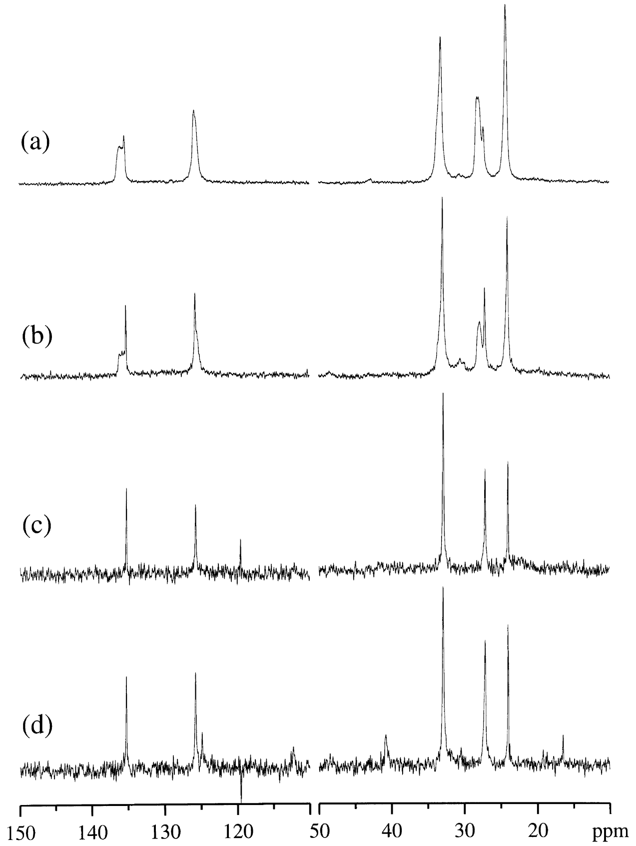
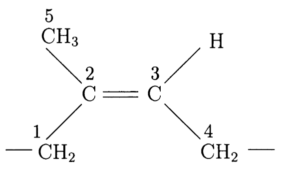


Fig. 2. $^{13}C$ CP/MAS NMR (75.43 MHz) spectra of (a) Neorub ($\nu_r = 3.1$ kHz, 9639 scans), (b) SMR CV60 ($\nu_r = 3.3$ kHz, 9799 scans), (c) Natsyn 2200 ($\nu_r = 3.6$ kHz, 5120 scans), and (d) Cariflex IR ($\nu_r = 3.6$ kHz, 8704 scans) all employing recycle periods of 8.0 s, contact times 1.0 ms, and temperature 295 K. In the spectra of Natsyn and Cariflex an artifact is present at ~120 ppm.

experiments in Fig.1(a), (b) and (c). Another striking difference between the MAS and CP/MAS spectra in Fig. 1 is the presence of two intense spinning sideband patterns in the CP/MAS spectrum (vertical expansion in Fig. 1(c)). These patterns originate from the $^{13}C$ resonances at approximately 126 and 136 ppm and must be caused by non-vanishing chemical shielding anisotropy (CSA) for the two ethylenic carbons (C3 and C2).

*cis*-1,4



Average values for the CSA parameters, determined by numerical fitting (using the STARS program [20]) of the spinning sideband intensities [21] observed at different spinning frequencies for these carbons, are included in Table 1. These values are slightly smaller than those for the alkene carbons in ethene and *cis*/*trans* 2-butene determined at 30 K ($\delta_\sigma \sim -105$ ppm and $\eta_\sigma = 0.7$–0.9) [22,23]. This indicates that the immobile regions do not constitute fully rigid systems but that they exhibit some dynamic behavior at ambient temperature. Close inspection of the resonances in the CP/MAS spectrum (see expansions in Fig. 1(d)) reveals that in addition to five distinct and narrow resonances at positions identical to those for the MAS spectrum (Fig. 1(a)), a number of broad and partly resolved/overlapping resonances appear in the regions for the five carbons of the mobile phase. Obviously, these new and additional resonances observed using CP arise from carbon atoms within immobile regions of the polymer chains (e.g. at the bends). From the expansions in Fig. 1(d) we note that the resonances for the immobile carbons are particularly well-resolved in the regions around 28 ppm (C4) and 136 ppm (C2) while for C1, C3, and C5 the broad resonances for the immobile carbons overlap with the narrow resonances from the mobile regions. Inspection of the reasonably well-resolved $^{13}C$ CP resonances at 28 and 136 ppm shows that at least four different resonances (as observed for C2 at 136 ppm), corresponding to different *cis*-1,4-monomer segments, are observed from the immobile regions. The appearance of the intensities and number of different resonances from the carbons in the immobile regions may vary slightly from one rubber to another. This is illustrated by the expansions for the spectrum of a SMR CV60-type rubber shown in Fig. 1(e). From the expansions we observe for example three distinct resonances for the C2 carbons (~136 ppm) and intensity changes for C4 carbons (~28 ppm).

To explore whether the presence of immobile carbons/regions are related to the origin of the polyisoprenes, the four different rubbers (vide supra) have been examined by $^{13}C$ CP/MAS at 295 K. According to the spectra shown in Fig. 2 only the natural rubbers, Neorub (Fig. 2(a)) and SMR CV60 (Fig. 2(b)), exhibit resonances which originate from immobile regions while the synthetic rubbers (Fig. 2(c) and (d)) show low-intensity resonances only at the isotropic shifts originating from the mobile carbons. Further, from comparison of the spectra in Fig. 2(a) and (b) we conclude that Neorub has a larger content of the immobile regions than the SMR CV60 rubber. This shows that hydroxylamine treatment decreases the amount of immobile regions. The spectra of the synthetic rubbers are characterized by a lower S/N ratio than for the natural rubbers. The reason is that the CP efficiency is reduced because the heteronuclear dipolar couplings are averaged by chain mobility. The lack of immobile carbons regions for the synthetic rubbers may be an effect of the reduced number of adjacent *cis*-1,4-monomer units in the polymer chain [24] such that the probability of observing immobile carbons is proportional to this number. In Fig. 2(a), (b) and (c) the very narrow resonances all arise from the mobile *cis*-1,4-monomer carbons whereas in the spectrum of Cariflex IR (Fig. 2(d)) additional mobile carbons originating from the *trans*-1,4- and 3,4-monomer units are observed.

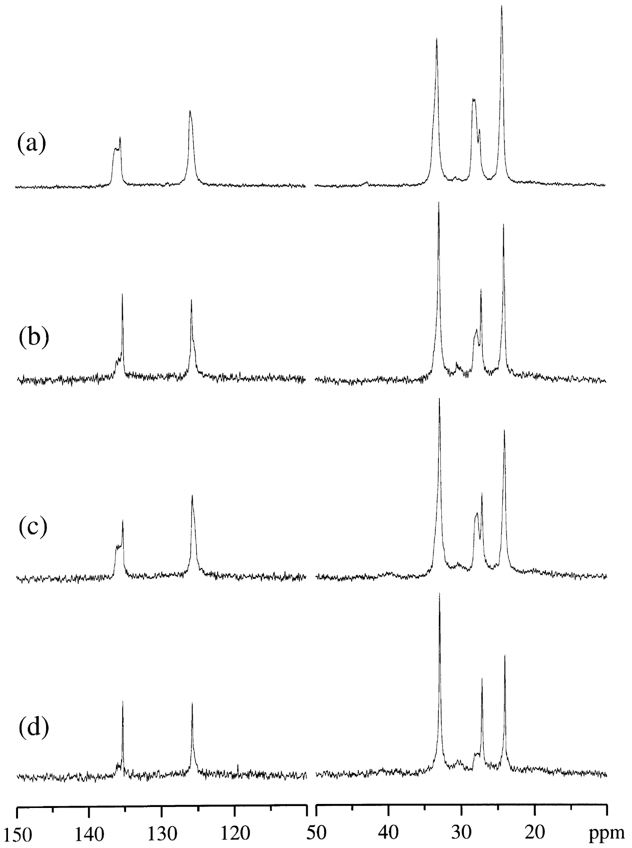
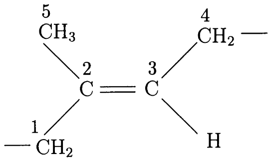
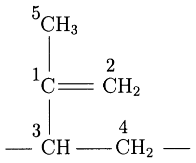


Fig. 3. $^{13}$C CP/MAS NMR (75.43 MHz) spectra of the four versions of Neorub (a) basic ($\nu_r$ = 3.1 kHz, 9639 scans), (b) masticated ($\nu_r$ = 2.9 kHz, 5116 scans), and γ-irradiated by (c) 100 kGy ($\nu_r$ = 3.6 kHz, 8364 scans) and (d) 300 kGy ($\nu_r$ = 3.7 kHz, 7846 scans). All experiments employ a recycle period of 8.0 s, contact time 1.0 ms, and temperature 295 K.

*trans*-1,4



3,4



As can be seen from Table 1, the characteristic *trans*-1,4 resonances are located at 16.6 and 40.8 ppm, while the characteristic 3,4 resonances are located at 19.3, 48.4, 111.9, and 147.9 ppm. Additional resonances from these two monomer units are superimposed on the *cis*-1,4 resonances.

To investigate if other physical or chemical treatment of the natural rubber affects the amount of immobile regions, a masticated and two γ-irradiated samples of Neorub have been examined by $^{13}$C CP/MAS at 295 K (Fig. 3). γ-Irradiation has been shown to increase the *trans*-1,4-monomer content and the degree of cross linking [25]. As can be seen by comparing the spectra of the basic Neorub materials (Fig. 3(a)) with those of the masticated (Fig. 3(b)) and the two irradiated samples (Fig. 3(c) and (d)), the content of immobile carbons decrease as a result of both treatments. The decrease is more pronounced when the irradiation dose is raised. Comparing the spectra of the γ-irradiated samples and the synthetic rubbers we observe that in both cases the presence of even small amounts of *trans*-1,4 units (0.4% and 3.0%) lowers the content of immobile regions. For the synthetic Natsyn 2200 rubber with a *trans*-1,4-monomer content around 3%, these regions are not present at all. Combined with the information about the number of adjacent *cis*-1,4-monomer units in the various rubbers [24], it is tempting to conclude that immobile regions are present at ambient temperature only if this number is sufficiently high. The presence of even a small amount of *trans*-1,4-monomer units lowers this number and therefore reduces the content of immobile regions.

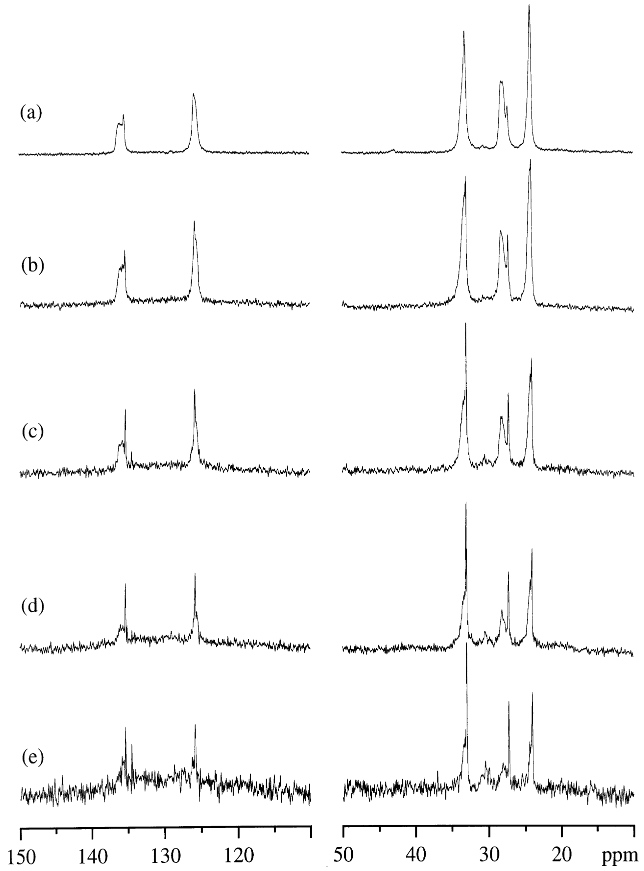


Fig. 4. $^{13}$C CP/MAS NMR (75.43 MHz) spectra of Neorub recorded at (a) 295 K ($\nu_r$ = 3.1 kHz, 9639 scans), (b) 313 K ($\nu_r$ = 2.8 kHz, 7938 scans), (c) 323 K ($\nu_r$ = 2.9 kHz, 9577 scans), (d) 328 K ($\nu_r$ = 2.8 kHz, 16 000 scans), and (e) 333 K ($\nu_r$ = 2.9 kHz, 9181 scans) all employing a recycle period of 8.0 s and contact time 1.0 ms.

Being aware that the experiments are performed well above the glass transition temperature ($T_g$ = 206 K) [26], we further studied Neorub at five different temperatures in the interval 295–333 K to examine whether the immobile regions are affected by a temperature increase slightly above ambient (Fig. 4). From comparison of these spectra the effect of heating is most clearly illustrated by following the intensity of the broad resonances around 28 and 136 ppm. As the temperature increases the intensities for the immobile resonances decrease because of the increased chain mobility which tends to average the heteronuclear dipolar couplings. Increasing the temperature from 295 K (Fig. 4(a)) to 323 K (Fig. 4(c)) results in a decrease of the intensities for the broad band of resonances around 126 and 136 ppm and at 333 K (Fig. 4(e)) the resonances for the immobile carbons can barely be observed. The decreasing content of immobile regions and increasing mobility for the polymer chain are the reasons for the reduction in S/N ratio because of the loss in CP efficiency by increasing the temperature.

## 4. Conclusions

In this work, it has been demonstrated that immobile regions in natural rubber can be observed at ambient temperature by $^{13}C$ CP/MAS NMR. Evidence has been obtained that the content of immobile regions increases with the number of adjacent *cis*-1,4-monomer units in the polymer chain. This number, i.e. the amount of immobile regions, decreases as a result of treatment with hydroxylamine, γ-irradiation, and mastication. At higher temperatures the anisotropic interactions are averaged because of molecular dynamics whereas the content of the *trans*-1,4-monomer units in the polymer chain increases by the other methods. Synthetic polyisoprenes have also been examined by $^{13}C$ CP/MAS NMR but no indication of the presence of immobile regions for these samples are observed.

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