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Segmental mobility in poly(isoprene) rubber studied by deuterium-carbon NMR correlation spectroscopy

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Summary

A HMQC based deuterium-carbon correlation method is used for the first time to study the segmental mobility in a fully deuterated poly(isoprene) (PI) rubber network. The isotropic J_{CD} couplings can be utilized for polarization transfer between ^{2}H and ^{13}C spins in a mobile solid polymer. This makes it possible to correlate the ^{2}H resonances with the ^{13}C chemical shifts of the attached carbon in a two-dimensional (2D) experiment, and thus allow the extraction of the individual ^{2}H signals. The experimental data obtained from the 2D correlation spectrum indicates differences in the segmental mobility of the C-D vectors in perdeuterated PI. The conclusions are fully consistent with ^{2}H and ^{13}C T_1 relaxation data. The results shown in this paper demonstrate the potential of ^{2}H-^{13}C NMR correlation spectroscopy in solid systems which produce overlapped 1D ^{2}H spectra.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a widely used method in elastomer research to study chemical composition, morphology and filler-matrix interactions (1). Technical elastomer products, even if manufactured carefully, are often inhomogeneous due to insufficient mixing of the components during compounding and to extrusion of thermal conductivity effects during vulcanisation. Two important factors determing the mechanical properties of a polymer are chain mobility and order. For example, it is known that molecular dynamics and order largely influence material properties like impact strength (2) and drawability (3). The precise characterization of molecular organization and mobility is thus essential to understanding the macroscopic behaviour of polymers.

Orientational or molecular order refers to the anisotropic distribution of chain segments that can be induced by the orienting effect of some external agent. For uniaxially stretched rubbery networks, segmental orientation results from the distortion of the configurations of the network chains when the network is macroscopically deformed. In the undistorted state, the orientations of the chain segments are random and hence the network is isotropic because the chain may occupy all possible orientations, without any bias. In the other hypothetically extreme case of an infinite degree of network stretching, the molecular segments align exclusively along the direction of the stretch.

Molecular order and dynamics in rubbery networks differ distinctly from that in crystalline or glassy polymers. Whereas the chains in crystalline or glassy solids are fully or partly frozen, those in an elastomeric network are extremely flexible and have freedom to move from one configuration to another, subject to the constraints imposed by the network connectivity. The chain orientation in glassy or crystalline networks is mostly induced by intermolecular couplings between closely packed neighbouring molecules, while in the rubbery network intramolecular conformational distributions predominantly determine the degree of segmental orientation. From the viewpoint of NMR, crosslinked elastomers exhibit both liquid-like and solid-like features. At temperatures well above the glass transition temperature, the time scales of molecular motion are liquid-like. In fact, models which describe the Brownian motion of a polymer chain in solution can be extended to describe adequately also the rubbery state (4). However, the presence of permanent crosslinks and topological constraints prevents the chain motion from being isotropic. Thus, anisotropic spin interactions such as dipolar and quadrupolar interactions are not always completely averaged out and give rise to solid-like NMR properties.

The deuterium quadrupolar interaction is an established tool for obtaining geometrical and dynamical information at the molecular level in polymers. For example, ^{2}H NMR has often been used in studies of the deformation behaviour in strained elastomers (5,6,7,8,9,10). For an undeformed rubber, a single resonance line in the deuterium NMR spectrum is observed because the quadrupolar interaction is averaged out by fast and essentially isotropic molecular motion of the network chains. Uniaxial mechanical deformation (stretching or compression) induces orientational order of the polymer chains and the motional averaging of quadrupolar interaction is incomplete (11,12,13). As a result, the deuterium line broadens or even splits into a resolved doublet. In the latter case, each C-D pair gives rise to one doublet, which yields directly the averaged quadrupolar coupling. For partially (methylene labelled) deuterated butadiene rubbers it has been shown that the lineshape of the ^{2}H NMR spectrum reveals the orientational distribution of network vectors due to the crosslinks, whereas the observed splitting gives information about the magnitude of ordering due to segmental interactions (14,15).

The two major problems encountered in ^{2}H NMR investigations of fully enriched materials are spectral assignment and overlap. These problems arise mainly from the small chemical shift differences between the deuterons. These obstacles are particularly severe for perdeuterated rubbery systems. Figure 1b shows the one-dimensional (1D) ^{2}H spectrum of fully deuterated poly(isoprene) (PI). It is clear that the high molecular mobility and low chemical shift dispersion results in a completely overlapped spectrum. Recently, some of us addressed the assignment problem in ^{2}H NMR by introducing novel two-dimensional (2D) ^{2}H-^{13}C experiments (16,17,18,19). These experiments correlate ^{2}H resonances with ^{13}C chemical shifts thereby enabling ^{2}H-^{13}C connectivities to be traced out, which yields the assignment of the ^{2}H signals on the basis of the ^{13}C spectrum and thus the measurement of the individual ^{2}H lineshapes. So far, these 2D techniques have been demonstrated on nematic liquid crystals that produce large and well-separated ^{2}H quadrupolar splittings. The purpose of this work is to test the applicability of ^{2}H-^{13}C NMR correlation spectroscopy on a rubbery system such as PI.

Experimental

The experiments were conducted on a rubbery network. The polyisoprene (PI) polymer was prepared by anionic polymerisation of deuterated (99%) monomers in hexane by standard high-vacuum techniques at ambient temperature. Molecular weights M_w and weight distributions M_w/M_n were measured independently by low angle laser light scattering and size exclusive chromatography (M_w = 220 kg/mol and M_w/M_n = 1.02). The network was prepared by crosslinking with 1 phr dicumyl peroxide (DCP) in bulk for 1 h at 145 °C and 100 bar. The mean molar masses between two crosslinks M_C was determined to be 6.6 kg/mol by swelling, NMR and stress-strain experiments. At room temperature the system is well above the glass transition temperature (Tg is about -65 °C measured by DSC).

The NMR data were collected on a Bruker Avance DSX-400 spectrometer (equipped with a 7 mm triple-resonance MAS probe), and on a Chemagnetics Inifinity-400 instrument (equipped with a 4 mm triple-resonance MAS probe). The S/N ratios in the ID ^{13}C and 2D ^{2}H-^{13}C experiments did not improve by employing ^{2}H decoupling. Therefore, experiments involving carbons were acquired without ^{2}H decoupling. All NMR experiments were performed at ambient temperature and under "static" (non-spinning) conditions.

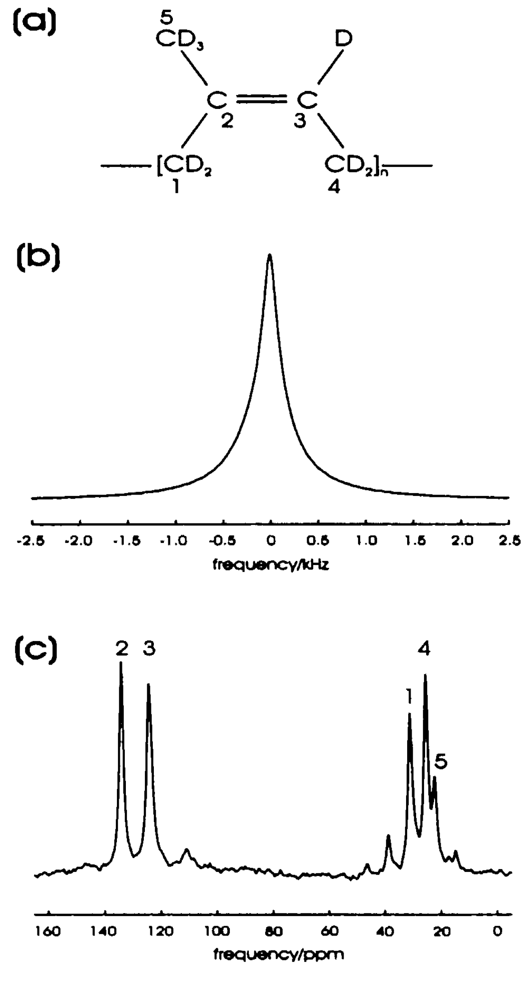

Figure 1. **(a)** Structure of the repeat unit in perdeuterated *cis*-1,4-PI showing the atomic labelling. **(b)** One-dimensional ^{2}H spectrum of perdeuterated PI. **(c)** One-dimensional ^{13}C spectrum of perdeuterated PI obtained without ^{2}H decoupling.

Results and discussion

Figure 1c shows the 1D ^{13}C spectrum of perdeuterated PI. There are five well-resolved intense signals originating from the five non-equivalent carbon sites in this rubber (cf. Fig. 1a). The other less intense peaks are produced by material from the crosslinking process. As discussed above, the ^{2}H signals from the four CD_n groups (where n is equal to 1, 2 or 3) in PI overlap completely with each other (cf. Fig. 1b). A standard inversion-recovery (IR) experiment was used to estimate the ^{2}H T_1 relaxation, and the recovery of the polarization required a multi-exponential fit with three time constants of 77 ms, 4.5 ms, and 0.7 ms. This suggests that there are (at least) three different types of deuterons with different mobility. It is tempting to identify these ^{2}H spins with the methyl, methylene, and methine groups in PI. In the following, we will confirm this by ^{2}H-^{13}C correlation spectroscopy.

Some preliminary strain experiments were also performed. Under uniaxial mechanical deformation parallel to the static field of the spectrometer, it was found that the linewidth, second moment, and asymmetry of the ^{2}H spectra increased with increasing deformation ratio (not shown). We were, however, not able to induce a splitting in the ^{2}H spectrum.

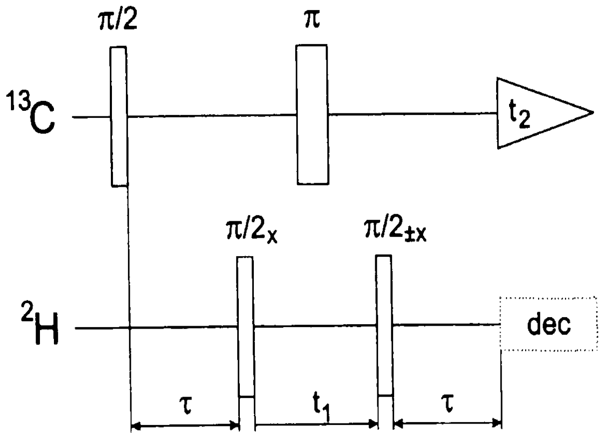

Figure 2. Pulse sequence for 2D ^{2}H-^{13}C heteronuclear multiple-quantum spectroscopy. The ^{2}H decoupling during t_2 is optional.

There are several ways of implementing the 2D ^{2}H-^{13}C correlation experiment. Initially, we tried to use the method reported by Auger et al. (16,17). A key step in this approach is a ^{2}H-^{13}C cross-polarization (CP) sequence that transfers ^{2}H magnetization to the ^{13}C spins by utilizing heteronuclear (dipolar) spin-spin couplings (the pulse sequence and the phase cycle are available on the web: http://www.ens-lyon.fr/STIM/NMR).

For an undeformed rubbery system the efficiency of the CP step is mainly determined by the heteronuclear isotropic J_{CD} couplings and the ^{2}H $T_{1\rho}$ relaxation rates. In less mobile systems, it is also necessary to take into account the residual quadrupolar and ^{2}H-^{13}C through-space dipolar couplings (17,18). Since the CP contact time needs to be of the order of the inverse of the spin-spin coupling strength, this accounts for the fact that CP times of more than 10 ms are required for effective polarisation transfer in the undeformed network ($^1J^{-1}_{CD} \approx 45$ ms in PI). Unfortunately, the ^{2}H $T_{1\rho}$ relaxation time in PI is rather short (about 4 ms). Therefore, we must use contact times of 4 ms or less, and it turned out that this is not long enough to obtain significant polarisation transfer from deuterons to carbons. This is not particularly surprising, hence this experiment is tailored to work in systems with large residual couplings (and where the distributions of couplings may also be large). Another approach for achieving ^{2}H-^{13}C correlation is based on the HMQC (19,20) pulse sequence in Fig. 2. This experiment has been described in detail elsewhere (19,20) and is particularly suitable when the residual couplings are small (or, in the extreme case where only the isotropic J_{CD} couplings remains). Here, only the essential features are briefly outlined. The first two pulses excite heteronuclear multiple-quantum (MQ) coherences which evolve during t_1 under the ^{2}H quadrupolar and ^{2}H chemical shift interactions. The ^{13}C π pulse at the center of the evolution period refocuses ^{13}C chemical shifts and ^{2}H-^{13}C spin-spin couplings. Reconversion of the MQ coherences into detectable ^{13}C magnetization is accomplished by the last ^{2}H π/2 pulse and the subsequent delay. The signal is finally observed during t_2 as it evolves under the ^{13}C chemical shift interaction. If necessary, ^{2}H decoupling may be employed during the detection period. For the simple case of an isolated ^{2}H-^{13}C two spin system, a density operator analysis is straightforward (21). After the basic two-step phase cycle which involves signal subtraction one obtains the following expression for the observable difference time signal

$$\Delta S(t_1,t_2) \equiv S_+(t_1,t_2) - S_-(t_1,t_2) \propto \sin^2 2\omega_{CD}\tau \cos\omega_Q t_1 \exp(i\omega_{CS} t_2)$$

where ω_{CD}, ω_Q and ω_{CS} are the ^{2}H-^{13}C spin-spin, ^{2}H quadrupolar and ^{13}C chemical shift frequencies, respectively. A 2D signal matrix is built up by repeating the experiment for many different values of t_1. This experiment yields a spectrum in which the ^{2}H resonances in the first dimension (ω_1) are correlated with the ^{13}C chemical shifts in the second dimension (ω_2).

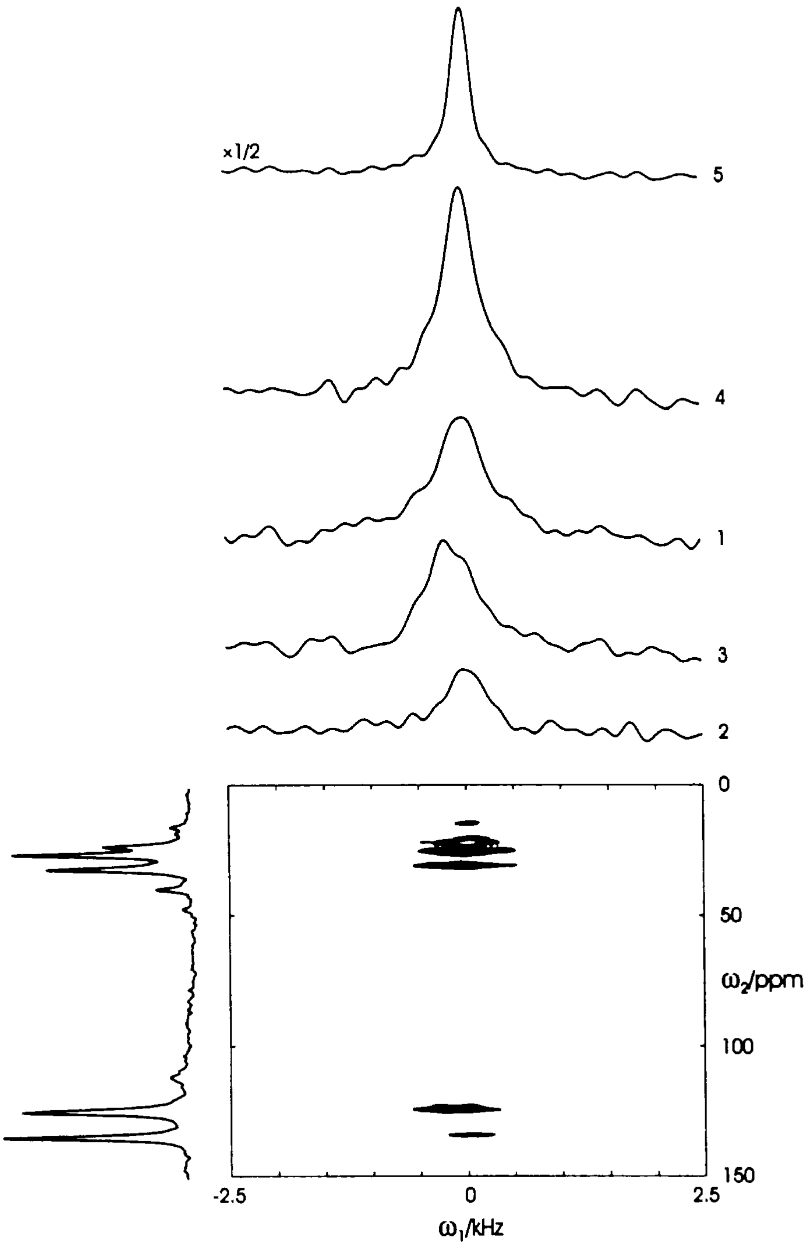

Figure 3. Two-dimensional ^{2}H-^{13}C HMQC spectrum of perdeuterated PI obtained as the sum of 2 spectra with τ = 8 ms and 6 ms, resp., and without ^{2}H decoupling. The traces taken parallel to ω_1 show the individual ^{2}H signals. Fourty-five time-data points in t_1 were acquired with increments of 50 μs. For each t_1 point, 1600 transients were averaged with a recycle delay of 3 s. The broadening in the deuterium dimension is 100 Hz. Quadrature detection in t_1 was obtained using the States-TPPI method.

A convenient way to optimize ^{2}H-^{13}C HMQC experiments is to perform reduced (t_1 = 0) 1D experiments in which the time delay τ is varied. From such experiments, we found that the optimal τ value is 6 - 8 ms for PI. Experimental difficulty in this case arises from the relatively fast ^{13}C T_2 relaxation, which strongly attenuates the signal intensity during the excitation/reconversion time periods. Figure 3 shows a HMQC spectrum of perdeuterated PI. The 2D map clearly demonstrates that it is possible to exploit isotropic J_{CD} couplings for polarization transfer in a rubbery system like PI. Information about the dynamics of the deuterated sites is obtained by extracting cross-sections parallel to the ω_1 axis that pass through the ^{13}C resonances in ω_2. It is seen that the weakest correlation peak originates from the quaternary carbon (C2), as it is not directly bonded to any deuteron. For this carbon, the polarization must be mediated by long-range spin-spin couplings, including both through-bond and through-space couplings. The 2D spectrum recorded with $\tau = 2$ ms (not shown here) exhibits a smaller correlation peak from the quaternary carbon. If it is assumed that the major axis of the field gradient tensor coincides with the C-D axis and the asymmetry parameter is negligible then the expression

$$D_{CD} = \frac{\mu_0}{4\pi} \frac{\gamma_C \gamma_D h}{6\pi^2 r^3 \left(\dfrac{e^2 qQ}{h} \right)} \Delta\nu_D = 0.01447 * \Delta\nu_D$$

is valid (22), where $\Delta\nu_D$ is the deuterium quadrupolar splitting, r is the C-D distance (0.109 nm), the γ's are the gyromagnetic ratios and (e^2qQ/h) is the deuterium quadrupole coupling constant (165 kHz). From the deuterium linewidths it is known that the deuterium quadrupolar splittings are less than 500-800 Hz. This shows that the absolute values of all one-bond through-space couplings are less than 7-12 Hz. A typical one-bond isotropic J_{CD} coupling is around 20-25 Hz, which proves that $J_{CD} >> D_{CD}$ in polyisoprene.

As expected, the slice through C5 is by far the narrowest one (the full-width-at-half-height, FWHH, linewidth is around 240 Hz) indicating very high mobility of the CD_3 group. Note that the dynamics of this moiety involves the overall chain motion as well as the rapid methyl group rotation. The broadest ^{2}H slice is produced by the deuteron at position 3 (FWHH linewidth $\approx$ 650 Hz), showing that the methine group is somewhat less mobile than the others. The FWHH linewidths for the slices through C1 and C4 are 550 Hz and 420 Hz, respectively.

Tab. 1: Lineshape analysis for the individual ^{2}H traces from the 2D HMQC

Site	Linewidth/Hz (τ = 6 ms)	Linewidth/Hz (τ = 8 ms)	Linewidth/Hz (τ = 2 ms) *Signal-to-noise-ratio worse
1 (CD_2)	550	540	810
4 (CD_2)	440	400	640
3 (CD)	670	600	620
5 (CD_3)	240	250	250

This may be interpreted as a small difference in segmental mobility for the two methylene groups. The difference is, however, too small to make any conclusive statements. According to these results there seems to be three types of deuterons in PI with different dynamics: (i) the CD_3 group (most mobile), (ii) the CD_2 groups (intermediate mobility), and (iii) the CD group (seems to be the least mobile). However, the differences between the CD_2 and the CD are very small and at a worse signal-to-noise ratio even a bit contradictory. Based only on the lineshape analysis of the 2D projections any conclusion about different mobility of CD and CD_2 groups could be hardly derived. But, this correlates nicely with the three-component recovery of the polarization observed in the ^{2}H IR experiment discussed above.

We have also estimated the ^{13}C T_1 relaxation rates, and the spin-lattice relaxation times were found to decrease in the following order: C5 (T_1 = 4.5 s), C4 (T_1 = 1.6 s), C1 (T_1 = 1.3 s), and C3 (T_1 = 1.0 s).

These results (all together) further strengthens our conclusions concerning the segmental dynamics in Polyisoprene networks.

Conclusions

The segmental mobility in poly(isoprene) has been investigated by ^{2}H and ^{13}C NMR spectroscopy. The conclusions of our study may be summarized as follows:
First, the small residual CD couplings can be utilized for polarization transfer between ^{2}H and ^{13}C spins in a mobile solid polymer. This makes it possible to correlate the ^{2}H resonances with the ^{13}C chemical shifts in a 2D experiment, and thus allows the extraction of the individual ^{2}H signals. Second, the experimental data obtained from the 2D correlation spectrum indicates that the segmental mobility of the C-D vectors in perdeuterated PI seems to decrease in the following order: 5 (the CD_3 group), 4 and 1 (the CD_2 groups), and 3 (the CD group). Finally, the conclusions are fully consistent with ^{2}H and ^{13}C T_1 relaxation data.
The results shown in this paper demonstrate the potential of ^{2}H-^{13}C NMR correlation spectroscopy in rubbery systems. Further work on mechanically deformed rubber networks using this approach is currently in progress.

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