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Using nuclear spin correlation of residual quadrupolar interaction to probe orientation and dynamics of poly(butadiene) networks

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Summary

A new NMR method, based on nuclear spin correlations of residual dipolar/quadrupolar interactions, demonstrated by Callaghan et. al. (1), is used for the first time to study molecular orientation and dynamics of partially deuterated cis-1,4 poly(butadiene) networks. The polymer networks under deformation and swelling are studied. It is shown that the latter method can probe not only the most dominating orientation and dynamics of the networks but also the sub dynamics of the network due to network inhomogeneities.

Introduction

Macroscopic strain applied to elastomeric networks induces orientation to the constituent polymer chains. Several experimental techniques, such as rheo-optical and deuterium nuclear magnetic resonance, have been devoted to the study of the anisotropy at a molecular level in strained elastomers (2-6). These measurements allow access to a more direct determination of chain behaviour to that given by bulk stress-strain data.

Another NMR technique, which is a further development of the work done by Collignon et. al. (7), was recently demonstrated by Callaghan et. al. (1) that is suitable for the measurement of weak proton dipolar interactions in fluid polymers where rapid segmental dynamics pre-average the rigid lattice dipolar coupling. This method is especially applicable to polymer melts and networks, where such residual interactions can provide valuable information regarding molecular order and reorientational dynamics. The radio frequency pulse sequence which is employed in this study directly generates a nuclear spin correlation function, ß, which is zero in the absence of the dipolar/quadrupolar interaction and it is completely independent on all Zeeman dephasing associated with chemical shifts or magnetic inhomogeneity, and whose time dependence can yield both the magnitude and the fluctuation rate of the residual dipolar/quadrupolar interaction. However, this method developed by Callaghan et al. is rigorously valid only for a spin-pair system or for deuterium. Originally, Callaghan applied the method to a proton dipolar network and so the results have some degree of approximation.

In this paper, for the first time, we report the employment of the above mentioned ß function to deuterium nuclei of partially deuterated Poly(butadiene) in order to study the magnitude and the fluctuation rate of the residual quadrupolar interaction.

Besides of this method, there exist a lot of other 1D and 2D NMR methods to extract information about molecular dynamics in polymeric networks like dipolar correlation

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function developed by Kimmich and Grinberg (8) and NOE/MAS developed by Demco, Hafner and Spiess (9), which are in many aspects more advanced than the presented technique introduced by Callaghan et al.

Background

The ß function experiment (1) is composed of a single $90°_x$ pulse; solid echo sequences, $90°_x$ -τ- $90°_y$; and Hahn echos, $90°_x$ -τ- $180°_y$ and $90°_x$ -τ- $90°_x$, where, in the echo examples, τ is the time separating the rf pulses. In each case, it is allowed the density matrix that describe the nuclear spin ensemble will evolve under the influence of the two offset terms in the Hamiltonian. The details of these evolutions are well known (10). The superposition of above mentioned echoes and the single pulse, in order to create the ß function, is as follows.

$$\beta(t,\tau) = \left[S_1(t,\tau) - S_2(t,\tau) - S_3(t,\tau)\right]/2S_3(0,0) \qquad \textbf{(1)}$$

where

$$S_1(t,\tau) = 90^0_x - \tau - 90^0_y,\ S_2(t,\tau) = 90^0_x - \tau - 90^0_x,\ \ S_3(t,\tau) = 90^0_x - \tau - 180^0_y\ and\ S_3(0,0) = 90^0_x\ .$$

This superposition signal is obtained using a single pulse sequence under appropriate phase cycling conditions. As the time t=2τ corresponds to the instant that the magnetic precessions are refocused in the spin echo, at this particular moment the effect of Zeeman precession vanishes. Therefore, the function ß(2τ,τ) is well suited to investigate the weak dipolar interactions, quadrupolar interactions and their fluctuations without perturbations due to Zeeman effects. The exact expression for ß(2τ,τ) is derived as (11)

$$\beta(2\tau,\tau) = \exp\left\{-2\bar{Q}_2\,\tau_s^2\left[\exp(-\tau/\tau_s) - 1 + \tau/\tau_s\right]\right\} \times \sinh\left\{\bar{Q}_2\,\tau_s^2\left[1 - 2\exp(-\tau/\tau_s) + \exp(-2\tau/\tau_s)\right]\right\},\ \textbf{(2)}$$

where $\bar{\bar{Q}}_2$ is residual quadrupolar second moment and τ_s is slow correlation time of the isotropic slow segmental motion.

Since the aim here is to calculate the residual quadrupolar interaction ν_0, it is necessary to estimate the fraction q of the residual second moment to static second moment $\bar{Q}_{2S}$, which is certainly also the fraction of ν_0 / ν_q where ν_q is the static quadrupolar coupling constant. q is given by (12)

$$q^2 = \frac{\bar{Q}_2}{\bar{Q}_{2S}} \qquad \textbf{(3)}$$

It can be shown that $(1)\bar{Q}_{2S} = (2/5)(\Delta\nu_S)^2$, where $\Delta\nu_s$ is the distance between the two maxima of the NMR powder spectrum (13) which can be measured below glass transition temperature T_g. For methylene deuterated poly(butadiene) it was found (14) that $\Delta\nu_s$ =123 kHz. The relation between ν_q and $\Delta\nu_s$ is (15) $\nu_q = \frac{4}{3}\Delta\nu_s$ which gives the value for ν_q as 165 kHz.

Fitting of the experimental data to equation (**2**) lead to estimate $\overline{\overline{Q_2}}$ and hence q can be determined using equation (**3**).

Experimental

All NMR experiments were carried out on a Varian INOVA 400 wide bore spectrometer (400 MHz proton frequency) operating at 61.3MHz for deuterons and at room temperature. Spectra were obtained using a standard 90 radio frequency pulse of approximate 7 µs. The pulse sequence provided in reference (1) is used to conduct the ß function measurements The deuteron measurements under mechanical deformation were performed by a simple stretching device parallel to the static magnetic field B_o. The stretching ratio was determined from the distance between two marks on the sample, before and after stretching.

The partially deuterated poly(butadiene) was polymerised by a conventional Ziegler-Natta polymerisation with Toluene as the solvent to obtain high-cis microstructure (98%). The microstructure was determined by ^{13}C-NMR. Molecular weights were performed by gel permeation chromatography: M_n(D) = 25000 g/mol, M_w(D) = 120000 g/mol, U = 4.8 for the deuterated polymer. This polymer was mixed in a ratio 1:9 with a commercial non-deuterated poly(butadiene) BUNA cis 132 (M_n(H) = 120000 g/mol, M_w(H) = 450000 g/mol, U = 3.75). 1 phr dicumyl peroxide (DCP) was used as the crosslinking agent for network prepared. The samples were vulcanised in a vulcameter press at 145 °C and 100 bar for 1h. The resulting mean molar mass between two crosslinks, M_c = 6500 g/mol, was determined from mechanical stress-strain measurements (16) and NMR relaxation.

Results and Discussion

Since $ß(2\tau,\ \tau)$ starts from near to zero, reaches to a maximum value and then decays to zero with time, it is more appropriate for a fitting procedure. Because of the fact that this function exhibits a high degree of sensitivity to the precise nature of dynamics (expressed via correlation function), it is argued that this sensitivity is significantly greater than that found in the measured quantities for other NMR methods which provide information about the strength and fluctuation of dipolar/quadrupolar interactions (17).

$ß(2\tau,\ \tau)$ was investigated at different deformation ratios of the network, as shown in Figure 1 (a), (b) and (c). It is worth to state here that the maximum amplitude of $ß(2\tau,\ \tau)$ is a property which is independent of the interaction strength and which depends only on the functional form of time dependence (11, 17). Hence the observed maximum amplitude of the experimental $ß(2\tau,\ \tau)$ data will give an idea about the nature of the dominant dynamics in the network. It is also important to note that this height will be sensitive to all dynamical regimes, not just that prevailing at the observational time scale τ.

There exist additional broadened maximum at higher τ values (see Figure 1(a)) in addition to the major maximum. This broadened second maximum gets slightly narrower and moves to the left on τ axis at higher deformation ratios, as does the major maximum, as shown in Figure 1 (a), (b) and (c). The latter observation is due to the influence of deformation on the polymer chain dynamics and orientation. When a polymer network is uni-axially deformed, an overall orientation is induced on the polymer chains due to end-to-end vector constraint and due to the orientation of mean field (18). This orientation results in giving more solid like behaviour to the network, e.g. a higher residual interaction than that of undeformed network.

Regions with different dynamics can present in a network if it is not homogeneously vulcanised, i.e. the network is not fully homogeneous. We argue that if the polymer network contains regions with different chain dynamics, ß(2τ, τ) can detect them and reflect as additional maxima to the major one, as can be seen in Figure 1. This additional maxima can be either side of the major maximum, depending on their dynamics.

Also it is important to note that in order to derive the expression (**2**) it was used the exponential correlation function $C(t) = \overline{Q_2}\exp(-t/\tau_s)$ and this is related to the isotropic slow chain motion, or in other words, to the long-range center-of-mass motion. However, the hierarchy of motions and their correlation functions are well described by Callaghan et. al. (11).

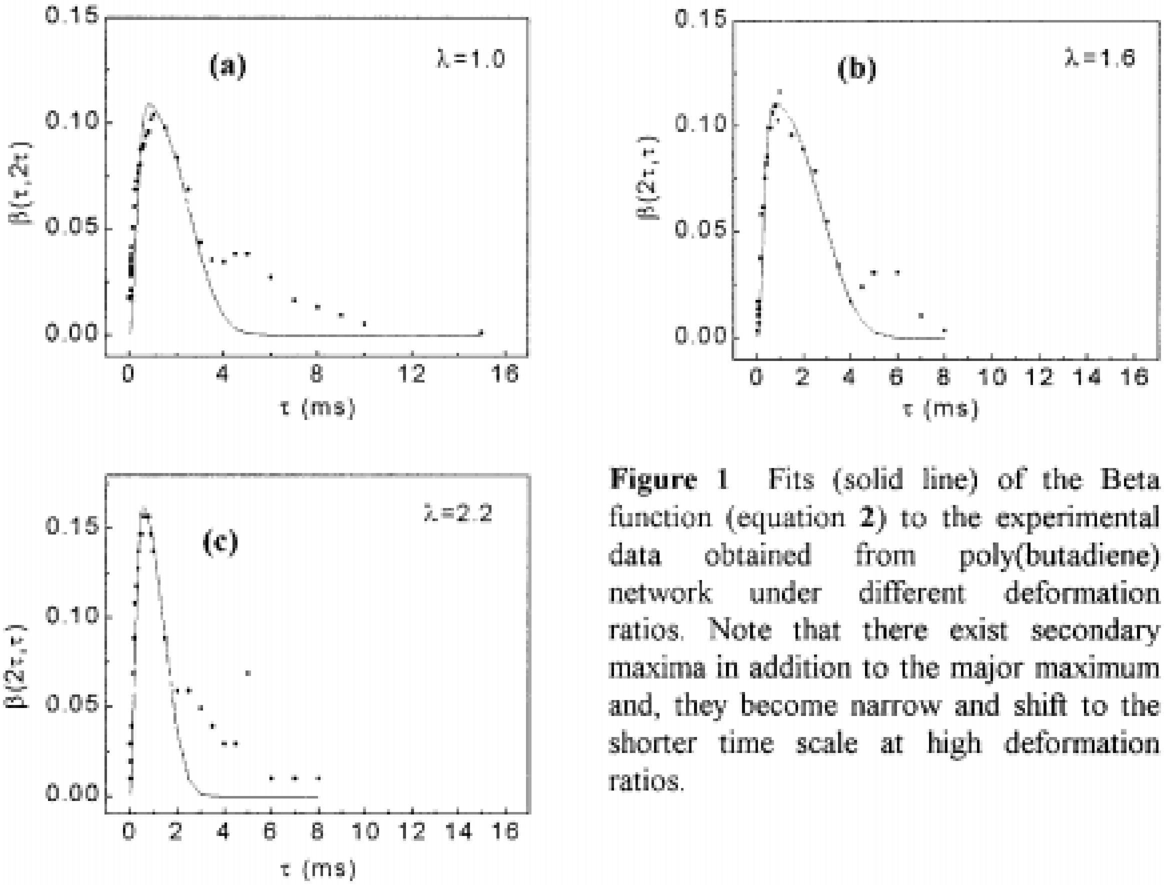
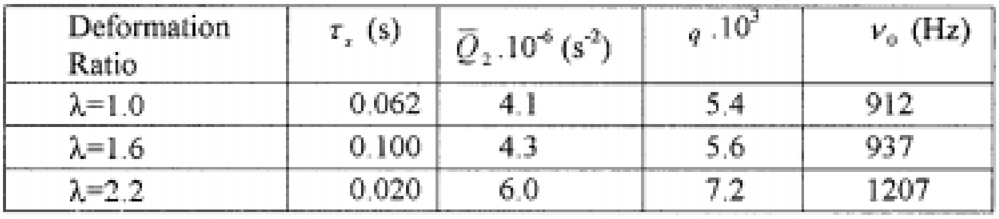


Figure 1 Fits (solid line) of the Beta function (equation **2**) to the experimental data obtained from poly(butadiene) network under different deformation ratios. Note that there exist secondary maxima in addition to the major maximum and, they become narrow and shift to the shorter time scale at high deformation ratios.



Deformation Ratio	τ_s (s)	$\overline{Q}_2 . 10^{-6}$ (s^{-2})	$q . 10^3$	ν_0 (Hz)
λ=1.0	0.062	4.1	5.4	912
λ=1.6	0.100	4.3	5.6	937
λ=2.2	0.020	6.0	7.2	1207

Table 1 Results from the fitting of experimental data to the equation.(**2**).

The results of the fittings are shown in Table 1. Residual quadrupolar interaction ν_0 increases with increasing of the deformation, due to the experience of an additional hindrance to the chain motion upon stretching. In other words, this analysis shows a monotonous increase in the value of $\overline{Q_2}$ and hence in the values of ν_0 with the increasing deformation. τ_s values derived from fittings were expected to be decreasing with raising deformation ratio, however, the number of available deformation ratios are too less to observe a clear trend. We must exercise some caution in trying to interpret τ_s in terms of network dynamics. We are equally forced to acknowledge that this parameter may be required to reproduce the observed shape of the beta-function ß(2τ, τ) because of the inherent weakness in simplistic two-spin assumption. Also the τ_s values show only less dependency of the magnitude of $\overline{Q_2}$. However, it is not obvious what kinds of deformation dependent dynamical processes are responsible for the behaviour of the correlation (1).

In Figure 2(a), the results of the ß(2τ, τ) experiment obtained from a polymer network which was swollen to a higher degree by incorporating protonated free chains(M_n=1800 g/mol) are depicted. The amount of free chains inside the network is approximately 20 wt%. A narrow maximum was observed in the short time scales (short τ values). This region was expanded and fitted to the ß(2τ, τ) as shown in Figure 2(b). As expected the fitting resulted in a high value of residual quadrupolar interaction (ν_0 ~23 kHz) indicating a highly solid like behaviour. Indeed, the polymer sample was more solid like by the appearance and it is easily breakable by bending. This gives an additional evidence for the reliability of employing ß(2τ, τ) function to study the exact dynamics and orientation of polymer chains.

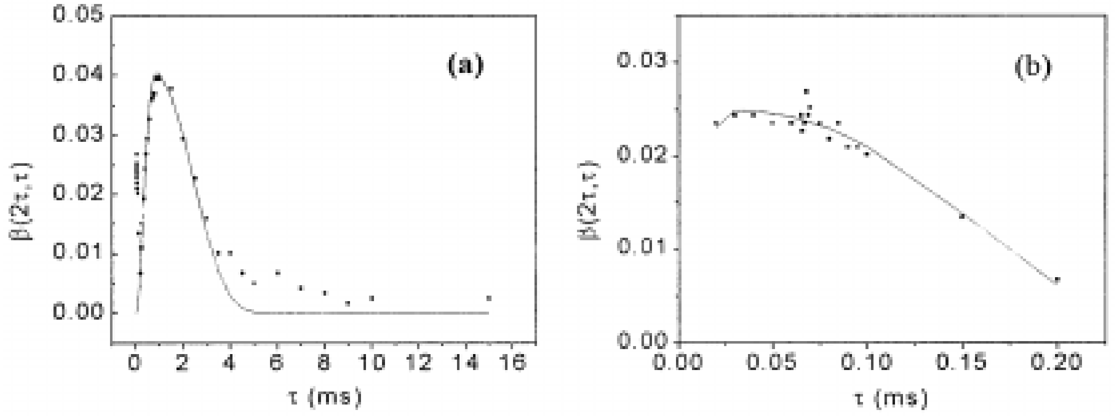


Figure 2 (a) Fit of the Beta function (equation 2) to the experimental data obtained from poly(butadiene) network which is incorporated with high amount (20 wt%) of free protonated poly(butadiene) chains (b) The fit for the peak at very small time scale shown in (a).

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