Chain orientation and dynamics of filled and unfilled poly(butadiene) networks studied by applying nuclear spin correlation of residual quadrupolar interaction

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Summary

Strength and fluctuation of nuclear quadrupolar interaction of filled, partially deuterated cis-1,4 poly(butadiene) networks under deformation are studied by implementing, for the first time, a new NMR method based on nuclear spin correlation of residual dipolar/quadrupolar interactions, demonstrated by Callaghan et. al. [1]. It is shown that this method can probe different dynamics and orientation of polymer chains in filled systems and the results are in good agreement with that reported in literature [17] for the same system but using another NMR methods. Furthermore, the effect of temperature on the quadrupolar interaction of unfilled cis-1,4 poly(butadiene) is studied by using the same method and the results are reported.

Introduction

Chain segment orientation in strained, filled and unfilled rubber is vastly studied since it provides information that is essential for the understanding of the insight of the material. In particular, such studies give access to a more direct description of the chain deformation than macroscopic data derived from stress-strain or swelling measurements. Hence, various techniques, sensitive to local properties, have been developed recently in this field. Among them several experimental methods, 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].

Recently, an another NMR technique, which is a further development of the work done by Collignon et. al. [7], was 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, β, 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 a previous paper [8], we reported the employment of the β function, for the first time, to deuterium nuclei in partially deuterated Poly(butadiene) in order to study the magnitude and the fluctuation rate of residual quadrupolar interaction. We have shown that if the polymer network contains regions with different chain dynamics, β function measurements can detect them and reflect as additional maxima to the major maximum.

In this paper, as a continuation of our previous work, we discuss the results of the β function measurements obtained from two systems. Firstly, it was applied to carbon black filled Poly(butadiene) networks, under deformation, in order to study the chain segment anisotropy in filled systems. Secondly, β function measurements were used to study the temperature effect on the unfilled polymer networks. By showing a narrow peak at very low time scales, which get broaden but does not disappear at high temperature, the latter study reveals that there exist network inhomogeneity in the unfilled samples. Since the same unfilled polymer is used to produce the filled samples, a narrow peak at low time scales, representing the network inhomogeneity, is observed also from the filled networks.

Background

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- $90°_x$ are the rf pulse sequences used in the β function experiment. τ is the time separating the rf pulses. A detailed description of the experiment can be found in the literature [1,8-10]. The superposition of above mentioned echoes and the single pulse, in order to create the β function, is as follows.

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

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 β(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 β(2τ,τ) is derived as [9]

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

where 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 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[11]

$$q^2 = \bar{Q_2} / \bar{Q_{2S}} \;. \tag{3}$$

It can be shown that [1] $Q_{2S} = (2/5)(\Delta\nu_S)^2$, where $\Delta\nu_S$ is the distance between the two maxima of the NMR powder spectrum [12] which can be measured below glass transition temperature T_g. For methylene deuterated poly(butadiene) it was found [13] that $\Delta\nu_S = 123$ kHz. The relation between ν_q and $\Delta\nu_S$ is [14] $\nu_q = \dfrac{4}{3}\Delta\nu_S$, which gives the value for ν_q

as 165 kHz. Fitting of the experimental data to equation (2) lead to estimate Q_2 and hence q can be determined using equation (3).

Experimental

A Varian INOVA 400 wide bore spectrometer (400 MHz proton frequency), operating at 61.3MHz for deuterons and at room temperature, was used to perform all NMR experiments. Spectra were obtained using a standard 90 radio frequency pulse of approximately 3 μs. The pulse sequence provided in reference [1] is used to conduct the β function measurements The deuteron measurements under mechanical deformation were performed by a simple stretching device perpendicular to the static magnetic field B_o. The aim of uniaxial stretching of the samples was to induce an orientation of the network chains. The stretching ratio was determined from the distance between two marks on the sample, before and after stretching. During the temperature variation experiments, it was allowed 15 minutes time to stabilize the temperature over the network while the temperature increase was 1 degree per 3 minutes. 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 [15] and NMR relaxation. Filled polymer samples were prepared using Carbon black N220 as the filler. Carbon black was incorporated by mixing the polymer, crosslinker and filler together in a mixer of rotating frequency of 60 min^{-1} for 10 minutes at a temperature of 50°C, and then the vulcanization procedure was applied. An Origin program was written to fit the experimental data to the theoretical $\beta(2\tau,\tau)$ expression. It was difficult to get the experimental data points which represent the initial positive slope of the narrow peak at low time scales because of the limitations of experimental pulse delay time. Therefore, we added the point (0,0) to all the data sets before performing the fitting procedure.

Results and Discussion

The profile of β(2τ,τ) is well suited especially for the fitting procedures since it starts from near to zero, reaches to a maximum value and then decays to zero with time. β(2τ,τ) exhibits also a high degree of sensitivity to the precise nature of dynamics (expressed via correlation function) and 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 [8,10]. The maximum amplitude of β(2τ,τ) is a property which is independent of the interaction strength and which depends only on the functional form of time dependence [9, 10].

In a previous work, in which the $\beta(2\tau,\tau)$ was applied to the quadrupolar nuclei, we have shown that a $\beta(2\tau,\tau)$ experiment can results more than one maximum when there exists few different dynamics in a polymer network (e.g. inhomogeneous network). By fitting the theoretical $\beta(2\tau,\tau)$ function to these maxima, strength and fluctuation of the quadrupolar interaction in these different regions of the network are investigated [8]. In this section, we discuss the results obtained from the similar experiments conducted on filled and unfilled polymer networks.

Unfilled Polymer network

$\beta(2\tau,\tau)$ experiments were performed at different temperatures on unfilled Poly(butadiene) networks. The results are depicted in Figure 1. It is noted that results from each experiment contain two major maxima, a narrow maximum at short τ region and a broad maximum at longer τ region. A similar observation was reported [8] from a poly(butadiene) network which is incorporated with high amount (20%) of free chains. It was argued that the observed narrow maximum at low time scales is emerging from the highly swollen, less mobile part of the network, giving a high value for the residual quadrupolar coupling (ν_0 ~23 kHz), while the broad maximum at higher time scales represent the rest of the network.

However, in the present system there exist no free chains and therefore, we propose that the narrow maximum which give the dynamics of the less mobile part of the network is stemming from either the possible presence of crystallites or the network inhomogeneity. As shown in Figure 1, this narrow maximum is becoming broader as the temperature increases but does not disappear even at 338K revealing there exist no crystallites in the sample [19].

Therefore, the narrow maximum is solely reflecting the fluctuation of quadrupolar interaction of the less mobile chains in the inhomogeneous network. The broad peak represent the rest of the network. The effect of the temperature increase is common for whole network. As it can be seen from Figure 1, both maxima become broader and move to the lower time scales as the temperature increases.

The theoretical $\beta(2\tau,\tau)$ function is used to fit the experimental data. A sample fit is shown in Figure 2. The residual quadrupolar interaction ν_0 is calculated, for both narrow and broad maximum separately, using the values of fitting parameters and shown in Table 1.

Residual quadrupolar interaction ν_0 increases with decreasing temperature, due to the experience of an additional hindrance to the chain motion upon lowering the temperature. In other words, this analysis shows a monotonous increase in the value of Q_2 and hence in the

values of V_0 with the decreasing temperature. At the lowest temperature (250K), used in this
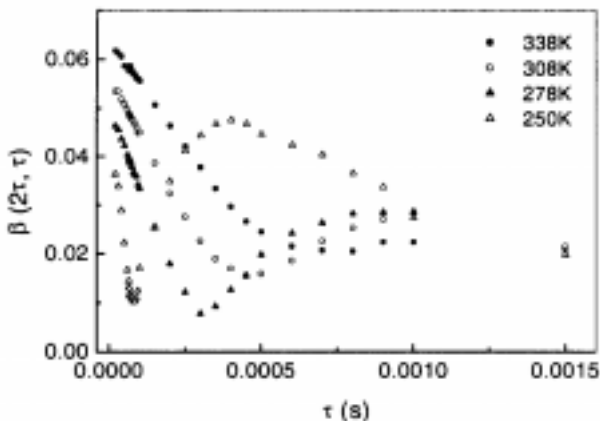

Figure 1. Experimental data obtained by employing $\beta(2\tau_f,\tau)$ experiment to unfilled cis-1,4 Poly(butadiene) network, at different temperature. As temperature decreases both maxima get narrower and moves to the left along time axis.
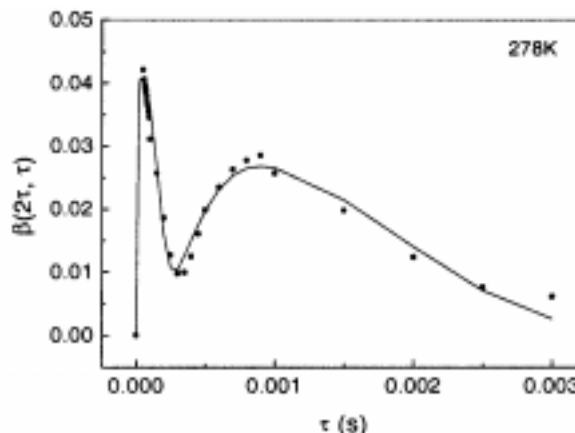

Figure 2. Sample fit of the theoretical curve to the data points.

study, the value of V_0 calculated from the narrow peak is very high and is near to the value of static quadrupolar coupling. Furthermore, in the whole temperature region it exhibits a considerably high value of V_0 than that merely observed for melts, indicating that a portion of the network is highly immobile due to network inhomogeneities.

However, the broad peak results a lower V_0 value which is supposed to represent the normal network. For example, the V_0 value deduced from the broad peak, at 293K, is comparable with the literature reported results for the similar network. τ_s values derived from fittings were expected to be decreasing at lower temperatures. We must exercise some caution in trying to interpret τ_s in terms of network dynamics. Also the τ_s values show only less dependency of the magnitude of Q_2. However, it is not obvious what kinds of temperature

Broad peak

Temperature (K)	τ_s (s)	q	V_0 (kHz)	τ_s (s)	q	V_0 (kHz)
250	.0001	.96	158.4	.07	.063	10.4
278	.0167	.80	132.0	.02	.030	4.9
294	.0169	.59	97.3	.03	.023	3.8
308	.0190	.52	85.8	.06	.020	3.3
338	.0580	.51	84.1	.11	.018	3.0

Filled Network

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 [16]. This orientation results in giving more solid like behaviour to the network, e.g. a higher residual interaction than that of undeformed network.
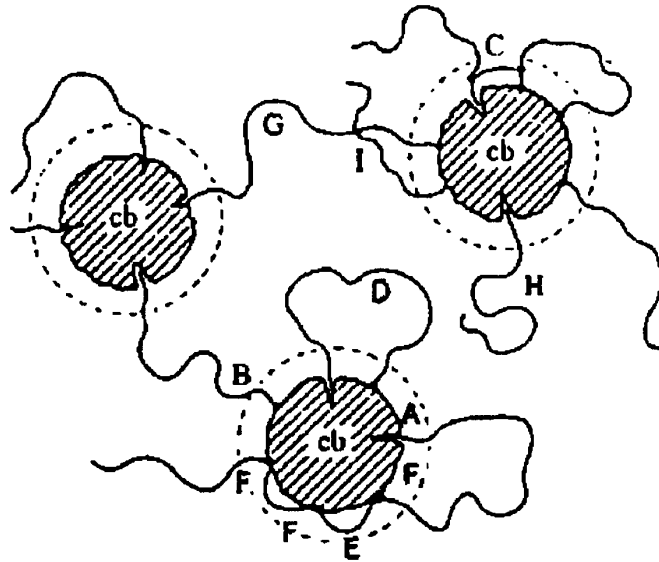

Figure 3. Model of the filler-elastomer interactions, **cb**: carbon black. **A**: physical attachment. **B**: chemical attachments. **C**: cross-linked rubber chain. **D**: loose fold. **E**: tight fold. **F**: multiple adsorptive attachments. **G**: inter-particle tie chain. **H**: cilium. **I**: entanglements (from reference 17).

However, in the filled polymer networks, applied macroscopic deformation does not affect the chains closely attached to filler particles to the same degree as it does the remaining chains [17]. Figure 3 shows schematically the various possibilities of polymer chain attachments to the filler particles. Chain segments E, F and D are not affected directly by the macroscopic deformation

Carbon black (N220) filled cis-1,4Poly(butadiene) was used in this study. For the same filled network, in an earlier work [16], we have reported that the effective crosslink density of the chains not in the vicinity of the carbon black particles to be 1600 g/mol. This can be compared with the stress-strain measurements [15]. It has also shown that the crosslink density of the chains closely attached to the carbon black particles is 1100g/mol. This slightly higher density of crosslinks is consistent with the chains being attached to the filler particles and these contacts acting as extra crosslink points.

It is depicted in Figure 4 the results from $\beta(2\tau,\tau)$ experiments on filled networks at different deformation ratios, λ. In general, there exists two maxima, one at short time scale and the other at long time scale, as observed from the unfilled network. Filled network is prepared using the same unfilled polymer mixing with the filler. Therefore, the network inhomogeneities, as discussed in the above section, are unavoidable. In fact the narrow maximum observed in the filled polymer is similar to that of unfilled polymer. Having these evidences, we argue that the narrow maximum observed in the $\beta(2\tau,\tau)$ experiments on

filled polymer is due to the network inhomogeneities and therefore, we focus on the observed broad maximum in order to understand the effect of the filler on rubber.
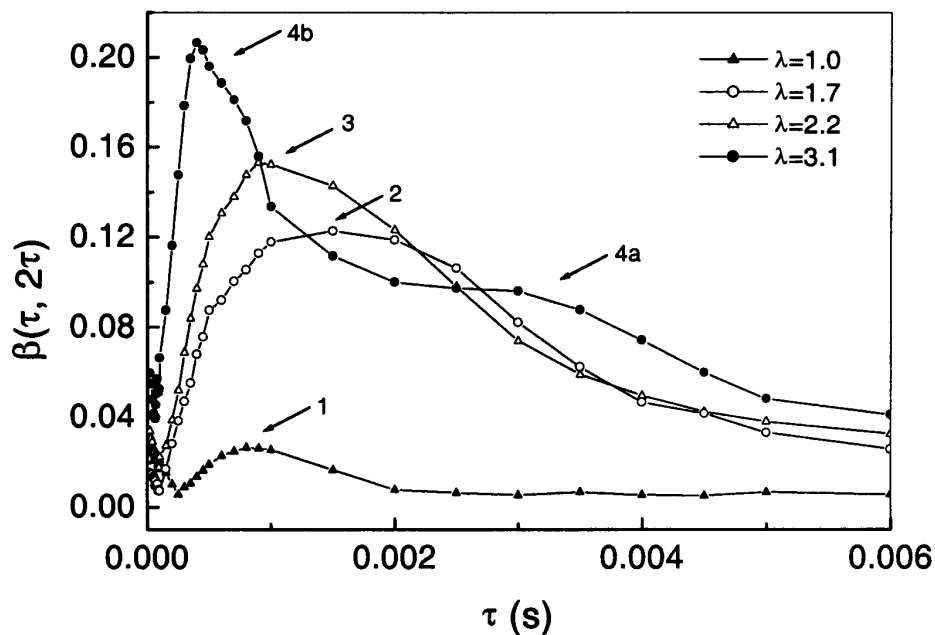

Figure 4. Experimental data obtained by employing $\beta(2\tau,\tau)$ experiment to corbon black filled cis-1,4 Poly(butadiene) network, at different deformation ratios. There exist two maxima at λ=3.1. The lines connecting data points are only to guide the eye.

The second maximum observed from the filled polymer is broader than that of the unfilled network. In the filled network, as discussed above, the polymer chains in the vicinity of the filler experience more hindrances than that of the polymer chains far away from the filler particles. Since these hindrance to the chains is having a distribution, it reflects as a broad maximum in the $\beta(2\tau,\tau)$ experiment. As the deformation ratio increase up to λ=2.2, this peak is getting broader and the maximum point is moving to the shorter time scales, revealing that the network experiences an overall orientation. We have shown [16,18] that this induced overall orientation on the polymer chains is due to the end-to-end vector constraint and due to the orientation of mean field. Furthermore, we have shown [17] that the polymer chains in the vicinity of filler experience an orientation of the mean field only at very high deformation ratios (e.g. λ>3.0) of the network. This effect can be clearly observed in $\beta(2\tau,\tau)$ experiments too. As shown in Figure 4, when λ is increased to a value of 3.1 the broad peak suddenly get narrower and move further to the lower time scale because now a fraction of the chains experiences high topological constraints from the filler as well as the induced orientation of the mean field. Table 2 shows the results of the fitting of $\beta(2\tau,\tau)$ to the experimental data obtained from the filled polymer network.

As the deformation ratio increases, the residual quadrupolar interaction constant increases due to the hindrance of the motion experience by the chain segments due to the end-to-end vector constraint. At a higher deformation ratio (λ=3.1), as discussed above, the chain segments in the vicinity of filler are highly oriented and results the peak 4b while the rest of the network results the peak 4a. The residual quadrupolar interaction of this highly oriented segments is almost twice as that of the normal network (see Table 2).

Table 2. The results obtained by fitting the theoretical $\beta(2\tau,\tau)$ function to the experimental data of filled network, at different deformation ratios

Peak number	τ_s (s)	q	ν_0 (kHz)
1 (λ=1.0)	.080	.022	3.7
2 (λ=1.7)	.070	.024	3.9
3 (λ=2.2)	.030	.025	4.1
4b (λ=3.1)	.006	.047	7.8
4a (λ=3.1)	.110	.013	2.2

This reasonable agreement with the results of other studies on filler-polymer interactions reveals the suitability of $\beta(2\tau,\tau)$ experiments to probe dynamics and orientation of polymer networks.

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