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Analysis of deuterium NMR spectra of probe chains diffusing in a stretched polybutadiene network

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Abstract

Polybutadiene network was swollen with short perdeuterated network-like chains (PBD). Deuterium NMR spectra of these probe chains are measured as the rubber matrix is uniaxially elongated. Due to the presence of two kinds of deuterons (methylene and ethylene) and two possible configurations of monomer units (*cis* and *trans*) in PBD chains, composite NMR spectra are observed and analysed. They evidence for different orientational behaviour of *cis* and *trans* units. 'Rod-like' motional behaviour of the trans units leads to higher degree of orientational order than for the *cis* units.

Keywords: Deuterium NMR spectroscopy; Polybutadiene network; Orientational dynamics

1. Introduction

Deuterium NMR spectroscopy (^{2}H NMR) is known to be a powerful method in studying anisotropic systems [1]. This approach has been widely used during the last two decades in studying orientational order induced in various polymer networks under uniaxial constraint. These studies have been done both on labelled networks and on labelled swelling agents (good solvents or short network-like chains), used as NMR probes. Most investigations in this field have been performed on the polydimethylsiloxane (PDMS) networks [2,3] and on polybutadiene (PB) networks [4–9]. The observed segmental ordering has been interpreted in terms of a mean orientational field due to the cooperative effect of the segment–segment interaction (excluded volume interaction [10,11] and nematic like interaction [3,12]) in the uniaxially deformed networks. Therefore, all chains, network or free probe, within the matrix experience the mean field that induces a segmental alignment along the strain direction.

The conventional ^{2}H NMR spectra of deuterated PB networks consist of complex poorly resolved structures. Various reasons specific to the PB structures have the origin in the following:

(a) from the NMR point of view, two kinds of non-equivalent deuterons are distinguished in perdeuterated 1,4-polybutadiene: methylene deuterons, attached to the carbon atoms with a single bond (further: CD_2 component) and ethylene deuterons attached to the carbon atoms with a double bond (further: CD component), (b) *cis* and *trans* configurations of monomer units are generally presented in a PB chain due to the existence of unsaturated carbon atoms. The presence of these isomers increases the number of NMR lines, (c) the NMR spectra of PB consist of relatively broad lines due to the low segmental mobility at room temperature, in contrast with PDMS.

For all these reasons, the ^{2}H NMR spectra of PB networks under constraint become obviously more complicated and result in poorly resolved structures. To overcome this complexity, Gronski et al. [4–6] and later Menge et al. [7–9] have made this problem simpler from the NMR point of view by studying PB networks with selectively deuterated matrix or probe chains. In both cases, these authors have used PB chains labelled only on the methylene groups (CD_2 component) only. The single line of the CD_2

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component observed in the relaxed network, is split in two doublets when an uniaxial force is applied. These two doublet structures are related to *cis* and *trans* configurations of 1,4-butadiene monomer units [5].

In this communication we present the analysis of composite ^{2}H NMR spectra obtained by low molecular weight perdeuterated PB chains diffusing through an uniaxially stretched PB network. The experiments were performed at high temperature to increase the segmental mobility. Different orientational behaviour of chemically different C–D bonds along the probe chain was observed and discussed.

2. Experimental section

2.1. Sample preparation

Low molecular weight ($M_w = 4600$) perdeuterated polybutadiene chains (PBD), used as NMR probe, were synthesised by anionic polymerisation in a solution using *s*-butyllithium as the initiator. PBD chains possess approximately equimolar *cis*-1,4- and *trans*-1,4-configurational units and ca. 6% 1,2- monomer units. They were incorporated in a sample (20 × 8 × 1) mm^3 of a nonlabelled polybutadiene network, supplied by Michelin Rubber Company. Network chains containing 38% *cis*-1,4-, 51% *trans*-1,4- and 11% 1,2 monomer units were crosslinked by using dicumylperoxide. The average molecular weight between the crosslink junctions of the network was $M_c = 40000$. Labelled network-like chains were introduced in the network by diffusion at 308 K in a saturated of benzene. The sample was left in the equilibrium with the solvent vapours during 48 h, at constant temperature. Then the solvent was slowly removed and the sample was dried in vacuum at 308 K until its mass remained constant. The fraction of deuterated free chains in the network was estimated to be ~20 wt%. A schematic representation of the network sample swollen with probe chains in the relaxed and uniaxially deformed states (elongation ratio $\lambda > 1.00$) is given in Fig. 1.

2.2. NMR background

The ^{2}H NMR spectra depend on the way the (tensorial) quadrupolar interactions affixed to each C–D bond are averaged by molecular motions. In the presence of fast, anisotropic molecular motions the quadrupolar interaction is partially time-averaged to a non-zero value. Such a residual interaction splits the NMR line into a doublet of Lorentzian lines. In the particular case of fast uniaxial motions around a symmetry axis (that can be induced by an uniaxial force applied to the sample), the doublet spacing $\Delta\nu$ is given (in frequency units) by:

$$\Delta\nu = \nu_Q \overline{P_2(\theta(t))} |P_2(\Omega)| \qquad (1)$$

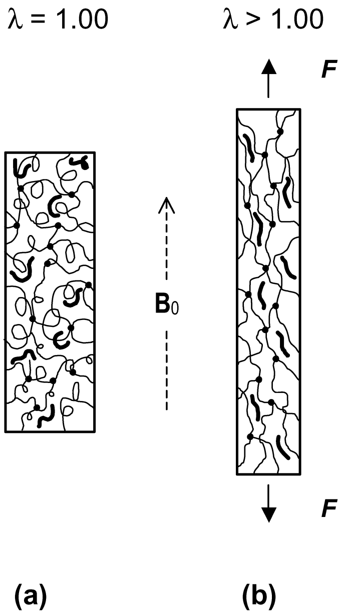

Fig. 1. Scheme of a network swollen by probe chains in (a) relaxed state and (b) uniaxially deformed state. The extension ratio λ is defined as $\lambda = l/l_0$; l and l_0 being the lengths of uniaxially deformed and relaxed sample, respectively. F is the applied force and B_0 the static magnetic field.

where $P_2(\theta)$ is the second order Legendre polynomial:

$$P_2(\theta) = \frac{3\cos^2\theta - 1}{2}, \qquad (2)$$

ν_Q denotes the static quadrupolar coupling constant, $\theta(t)$ is the instantaneous angle between the C–D bond and the symmetry axis and Ω the angle between the symmetry axis and the static magnetic field ($\Omega = 0°$ in our experiments). The overbar in the Eq. (1) denotes a time averaging over motions faster than the characteristic time ν_Q^{-1}; for C–D bonds in deuterated PB, $\nu_Q \approx 150$ kHz for the CD$_2$ component and $\nu_Q \approx 180$ kHz for the CD component. The $\overline{P_2(\theta)}$-term in the Eq. (1) is the order parameter, S, describing the mean degree of the orientational order of the chain segments (that is, the degree of motional anisotropy). In the fast motion limit, the spectral linewidth of each component of the doublet structure depends on the spin–spin relaxation time T_2 and is usually small enough with respect to the value of the splitting $\Delta\nu$, leading to well resolved spectra. In a macroscopically oriented system, the spectrum consists of a doublet structure for each C–D bond, which gives directly access to the order parameter S, according to Eq. (1).

2.3. NMR measurements

NMR measurements were performed on a Bruker AM400 spectrometer, operating at 61.4 MHz ($B_0 = 9.4$ T). The force applied to the sample was parallel to the static magnetic field B_0 (Fig. 1(b)), so that the angle $\Omega = 0°$ in Eq. 1. The sample was constrained at room temperature with a device described in previous papers [6,13] and its elongation was measured by the use of a microscope. The sample was placed in the spectrometer magnetic field (B_0) after 20 min in order to reach a steady state of the constraints. The sample was then thermostated at 60 °C during 15 min prior to NMR measurements and the temperature was controlled by a Bruker variable temperature unit BVT100 (± 1° C regulation). This temperature was intended to increase the segmental mobility of the probe chains in the PB network, in order to reach the motional narrowing regime. This leads to a well-adapted splitting to linewidth ratio and then to the spectra with resolved lines.

3. Results and discussion

In Fig. 2, experimental ^{2}H NMR spectra of the PBD chains diffusing in the polybutadiene network are presented (left side) using the same sample in the relaxed (elongation ratio $\lambda = 1.00$) and uniaxially deformed ($\lambda > 1.00$) states.

For $\lambda = 1.00$, the spectrum consists of two lines with a relative intensity ratio close to 1:2. The distance between the two lines (220 Hz or 3.58 ppm) corresponds to the difference in chemical shifts of the two kinds of deuterons presented in PBD chains. The line of lower intensity is attributed to the CD component, while the other corresponds to the CD_2 component.

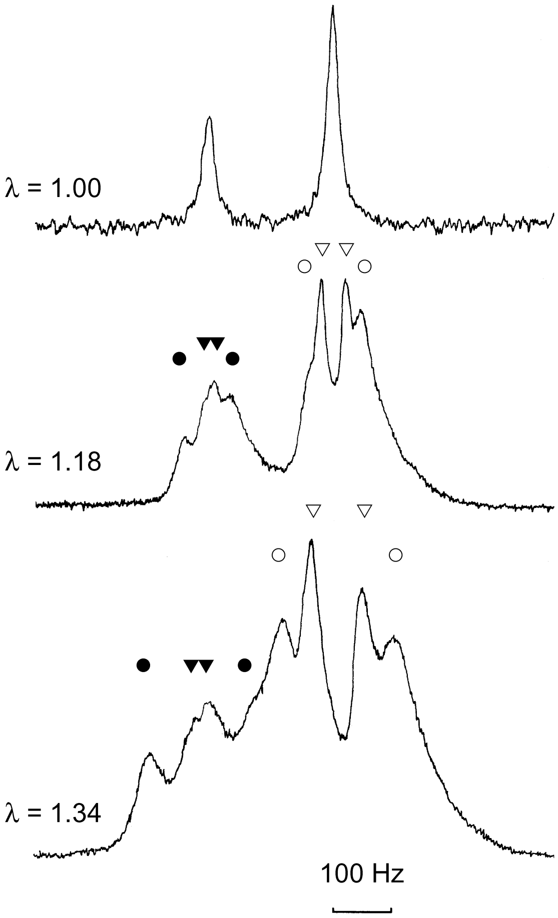

Fig. 2. ^{2}H NMR spectra of PBD probe chains diffusing through the PB network observed for various extension ratio λ. Left side: experimental spectra; right side: calculated spectra. The doublets are assigned as following: (a) *cis* units-CD_2 component (▽), (b) *cis* units-CD component (▼), (c) *trans* units-CD_2 component (○) and (d) *trans* units-CD component (●).

When the sample is uniaxially stretched ($\lambda > 1.00$), both lines split into different doublet structures. However, these structures are not easy to distinguish and should be analysed in details here. For $\lambda = 1.18$, the line of CD_2 component splits into two doublets: the internal one (symbol ▽) is the best resolved and corresponds to anisotropic motions of the CD_2 bonds in *cis* monomer units [5,6]; the external one is less resolved (symbol ○) and is associated with reorientational motions of the CD_2 bonds in *trans* monomer units [5, 6]. The weak overlap of these doublets structures leads to an asymmetric lineshape due to a slight difference in chemical shifts for deuterons of *cis* and *trans* units [14]. Note that this difference is very small in comparison with that one observed between chemical shifts of the CD and CD_2 components and cannot be observed in relaxed network, the lines being too broad. An additional factor that might also contribute to the asymmetric lineshape of doublet structures is the inhomogeneity of the magenetic field associated with the diamagnetic effect related to the specific macroscopic shape of the sample [15].

The line of the CD component also splits in two doublet structures for $\lambda = 1.18$: a weakly defined internal doublet with a small splitting (symbol ▽) and a better resolved external doublet (symbol ●). These two doublet structures are associated with anisotropic motions of the CD bonds in *cis* and *trans* monomer units, respectively.

All the observed doublet spacings increase with increasing λ, therefore, the spectral shape strongly changes at higher deformations. As shown in Fig. 2, for $\lambda = 1.34$ the spectrum becomes more complex due to overlapping resonance: the doublet of CD component (●) overlaps with the doublet of CD_2 component (○).

In order to confirm this analysis, a simple model is proposed to calculate the spectra by superposing four doublets of Lorentzian lines, each of them being associated with a specific deuteron (CD and CD_2 components in *cis* and *trans* units). To make this approach realistic, the area of these doublets reproduce the population of isomers in the PBD probe chains (equimolar ratio *cis*-1,4-/*trans*-1,4-monomers). Then, the parameters of the simulation are the doublet spacing $\Delta\nu$ and the half height linewidths of the Lorentzian components (see Table 1(a)). This leads to the calculated spectra shown in Fig. 2 (right side) and a good agreement is observed with the experimental ones confirming the qualitative analysis developed above.

Clearly, the fact that the measurements were performed at 60 °C leads to a higher spectral resolution, the doublet components being significantly narrrower than those observed at room temperature [5].

According to Table 1(a), the quadrupolar splittings $\Delta\nu$ of

Table 1

(a) Calculated quadrupolar splittings for the PBD chains (*cis* and *trans* units) diffusing in uniaxially stretched PB network (uncertainty is ±4 Hz) and half height linewidths in parentheses. (b) Orientational order parameters ($S = \Delta\nu/\nu_Q$)

Elongation ratio (λ)	(a) Splitting $\Delta\nu$ (Half-height linewidth) Hz			
	Cis		*Trans*	
	CD	CD_2	CD	CD_2
1.18	20 (28)	40 (24)	82 (28)	90 (30)
1.34	36 (54)	84 (38)	180 (52)	190 (52)
	(b) Orientational order parameter ($S/10^{-4}$)			
	Cis		*Trans*	
	CD	CD_2	CD	CD_2
1.18	1.1	2.7	4.6	6.0
1.34	2.0	5.6	10.0	12.7

CD and CD_2 components of *trans* units are similar for both values of λ. On the other hand, the splittings measured on the *cis* units are much lower than on the *trans* units; moreover, they are rather different for the CD and CD_2 component and this difference increases with increasing λ, (ratio equal to 2.00 for $\lambda = 1.18$ and to 2.33 for $\lambda = 1.34$). These data suggest that the degree of orientational anisotropy remains higher for *trans* units than for *cis* units as network is uniaxially elongated. Additionally, for the *cis* units, the CD component exhibits a lower degree of motional anisotropy than the CD_2 one. Finally, note that the lower resolution of the CD component in *cis* units could be related to restricted motions. This results in a lower splitting to linewidth ratio.

The values of the mean of orientational order parameters S are given in Table 1(b). These values are somewhat lower (~30%) than those given for the CD_2 component in reference [5] on a similar system. This difference is not surprising since our measurements are performed at a higher temperature so that the motional time averaging process may be more efficient. Moreover, our measurements have been done with a higher probe chain concentration that in reference [5], using a PB matrix of lower crosslink density. According to the work reported in references [3] and [9], these experimental conditions tend to decrease the value of S.

Different behaviour of *cis* and *trans* units has to be related to the different shape factors and configurations of these two isomeric states. The local geometry of the units has been obtained from molecular modelling and given in Fig. 3. Clearly, the *trans* units exhibit a 'rod-like' structure and then should be slightly more oriented than the *cis* units in the nematic-like field induced inside the stretched PB network. Therefore, the anisotropy of orientational fluctuations -and so the mean degree of order- are expected to be slightly more pronounced for the *trans* units.

It would be also reasonable to consider that internal motions contribute to the observed averaging effects. One may speculate that fluctuations (or rotations) around the single bond between CD_2 components of two neighbouring monomer units take place. As shown in Fig. 3, note that the local molecular chain axis (dashed line) goes diagonally through the *trans* monomer units whereas it is parallel to the double bond for the *cis* units. Then the angles between the corresponding C–D bonds and the local chain axis are different in the *cis* and *trans* units; moreover, in the *trans* unit these angles are very similar for the two kinds of bonds, contrary to the case of the *cis* unit. Under these conditions, the mentioned internal fluctuations (with a magnitude dependent on the nature of the isomeric unit) may produce different time motional averaging in *cis* and *trans* units and also may contribute to differentiate the residual interactions observed on the CD_2 and CD components of the *cis* units.

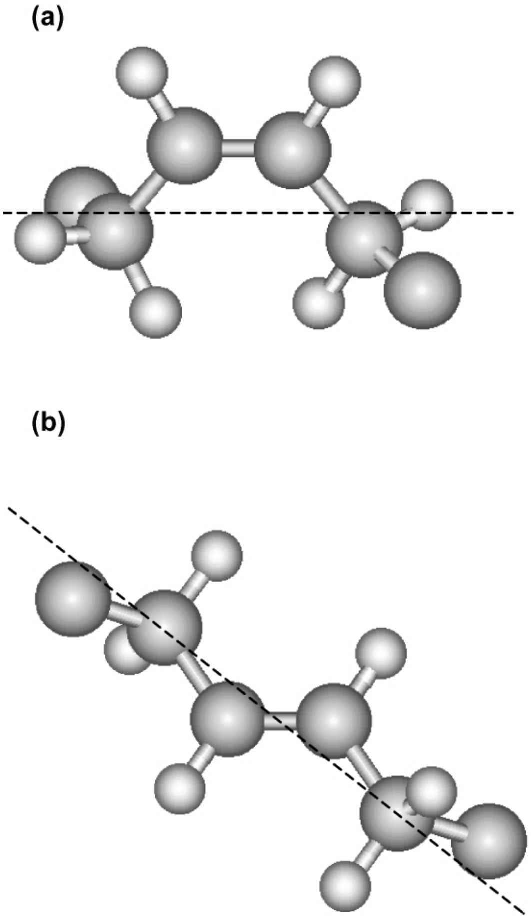

Fig. 3. Structure drawings of (a) *cis* and (b) *trans* conformational units of the PBD chain. The dashed line represents the local molecular chain axis.

This work points out the relevance of spectral data that can be obtained by introducing a small degree of anisotropy inside amorphous or/and disordered polymeric materials. It clearly emphasises the different behaviour of the *cis* and *trans* units of the PBD, both for the CD and CD_2 components. This should be correlated to the effect of shape factors and geometrical conformations in the presence of an orientational field. Finally, it seems that the study of residual (quadrupolar) interactions which can be observed on slightly constrained polymer chains, instead of the study of only chemical shifts or relaxation times, appears as a new NMR spectroscopic dimension leading to a strong enhancement of the knowledge of the physical chemistry properties of soft amorphous polymers. This approach could be very useful for a better understanding of the behaviour of probe chains diffusing in (nano)structured domains made of confined polymers (block copolymers, nanocomposites…) wherein a field of constraint is intrinsically presented [16–18].

References

[1] Spiess HW. Annu Rev Mater Sci 1991;21:131.

[2] Deloche B, Samulski ET. Macromolecules 1981;14:575.

[3] Deloche B, Sotta P. Deuterium NMR in rubbery materials. In: Litvinov VM, Prajna PDe, editors. Spectroscopy of rubbers and rubbery materials. Shawbury: Rapra Technology LTD; 2002. p. 557.

[4] Gronski W, Stadler R, Jacobi MM. Macromolecules 1984;17:741.

[5] Jacobi MM, Stadler R, Gronski W. Macromolecules 1986;19:2884.

[6] Jacobi MM, Abetz V, Stadler R, Gronski W. Polymer 1996;37:1669.

[7] Ries ME, Brereton MG, Klein PG, Ward IM, Ekanayake P, Menge H, Schneider H. Macromolecules 1999;32:4961.

[8] Menge H, Hotopf S, Schneider H. Polymer 2000;41:4189.

[9] Ekanayake P, Menge H, Ries ME, Brereton MG. Macromolecules 2002;35:4343.

[10] Brereton MG, Ries ME. Macromolecules 1996;29:2644.

[11] Depner M, Deloche B, Sotta P. Macromolecules 1994;27:5192.

[12] Sotta P, Deloche B. Macromolecules 1990;23:1999.

[13] Deloche B, Beltzung M, Herz J. J Phys Lett (France) 1982;43:763.

[14] Tanaka Y, Takeuchi Y, Kobayashi M, Tadokoro H. J Polym Sci: Part A-2 1971;9:43.

[15] Sotta P, Valić S, Deloche B, Maring D, Spiess HW. Acta Polym 1999; 50:205.

[16] Valić S, Deloche B, Gallot Y, Skoulios A. Polymer 1995;36:3041.

[17] Judeinstein P, Rault J, Alonso B, Sanchez C. J Polym Sci.: Polym Phys 2001;39:645.

[18] Valić S, Deloche B, Gallot Y. In preparation.