Polymer Bulletin 25, 365–371 (1991)

Polymer Bulletin

The effect of carbon black filling and cross-linking in stretched SBR networks: a ^{2}H-NMR study

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Summary

The line splitting $\delta\nu$ in ^{2}H-NMR spectra of deuterated benzene in stretched crosslinked SBR depended linearly on the classical stretch term α^2-1/α for samples with and without carbon black filling. The ratio LS = $\delta\nu/(\alpha^2-1/\alpha)$ was measured in dependence on the solvent fraction Φ. The extrapolated value L of this ratio at $\Phi = 0$ gave a linear dependence on the inverse molecular mass $1/M_c$ of inter-crosslink chains. This was expected according to a simple model of chain dynamics and offers a further NMR-method for M_c-determination even in filled networks. However, the slope of the $L(1/M_c)$-line increases with an addition of carbon black which indicates a higher molecular order. Three reasons for this could be discussed. However, one of them is preferable.

Introduction

A number of papers (for example (1-5)) have shown that the local segmental order in stretched deuterated elastomers can be monitored sensitively by a splitting $\delta\nu$ of lines in the ^{2}H-NMR spectrum. This is due to an anisotropy of molecular motion caused by a molecular order:

$$\delta\nu = (3/2)*q*P_2(\cos\Omega)*<P_2(\cos\theta(t))> \qquad (1)$$

q represents the static quadrupolar coupling constant which is of the order of 175 kHz. The angles in the second Legendre polynomials connect the direction of the C-^{2}H bond with the experimental coordinate system. Ω is the angle between the static magnetic field and the constraint axis and is 90° here. $\theta(t)$ is the time dependent angle between the C-^{2}H bond and the constraint axis. Since the time of the segmental motion is much less then the characteristic time 1/q the time average of the segmental location can be replaced by the spatial average. This average $<P_2(\cos\theta)>$ is called the order parameter S which is proportional to α^2-1/α (1-5). α is the stretching ratio. Furthermore, the ratio $LS = \delta\nu/(\alpha^2-1/\alpha)$ was found to be a function of the molecular mass M_c of the inter-crosslink chains. Taking into account Kuhn and Grün (9) one can derive (1,17,18)

$$LS = \delta\nu/(\alpha^2-1/\alpha) \sim 1/M_c \qquad (2)$$

Since deuterated samples with carbon black filling were not available we used the deuterated solvent C_6D_6 for probing the molecular order and M_c in accordance with (6-9). In order to eliminate the concentration dependence of LS, equation (2) must now be replaced by

$$L = \lim_{\Phi \to 0} LS \sim 1/M_c \qquad (3)$$

where Φ is the mass fraction of the solvent in the system of solvent plus polymer.

In this paper we use this technique in order to determine the dependence of the quadrupolar splitting on M_c and to probe the influence of carbon black filling on the segmental order in the network matrix of SBR. One might expect a higher order of polymer chains between filler particles. This should be visible in the splitting behavior of lines in the spectrum.

TABLE 1

Sample	G1	GF1	G2	GF2	G3	GF3	G4	GF4
Symbol for figures	○	●	△	▲	▽	▼	◇	◆
TMTD-S, phr	1.55	1.55	2.14	2.14	2.73	2.73	3.50	3.50
M_c(mech), kg/mol	15.2		11.2		9.2		7.3	
M_c(^{1}H-NMR), kg/mol	15.1	18.4	11.0	17.3	9.1	10.8	7.9	7.9
Carbon black, m%		33		33		33		33
Sample	G5	GF5	G6	GF6			GF41	GF42
Symbol for figures	⦶	⦷	□	■			⟠	⊕
TMTD-S, phr	4.45	4.45	5.67	5.67			3.50	3.50
M_c(mech), kg/mol	7.1		6.5					
M_c(^{1}H-NMR), kg/mol	7.5	7.7	6.1	7.2			8.8	7.7
Carbon black, m%		33		33			20	43

TMTD-S, phr - Tetra-methylthiuramdisulfide-sulfur mixture (25:1) in parts per hundred of rubber,

M_c(mech) - Mean molecular mass from stress-strain (mechanical) measurements (10),

M_c(^{1}H-NMR) - Mean molecular mass from ^{1}H-NMR-spin-spin relaxation measurements (11).

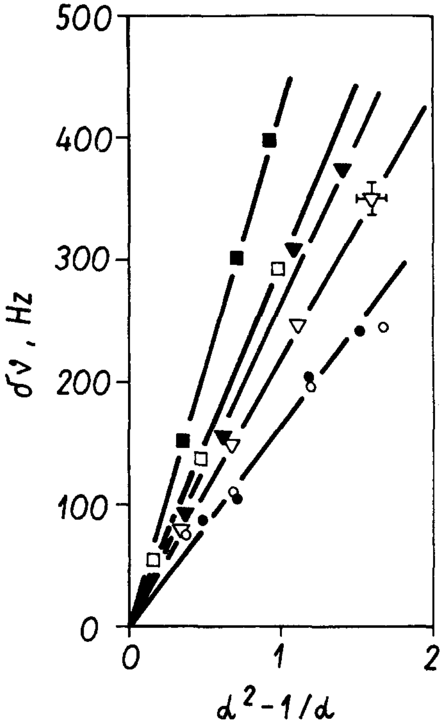

Fig. 1:
Quadrupolar splitting δν of the C_6D_6-line in dependence on α^2-1/α for some samples with $\Phi\approx0.08$ (for symbols - look to TABLE 1).

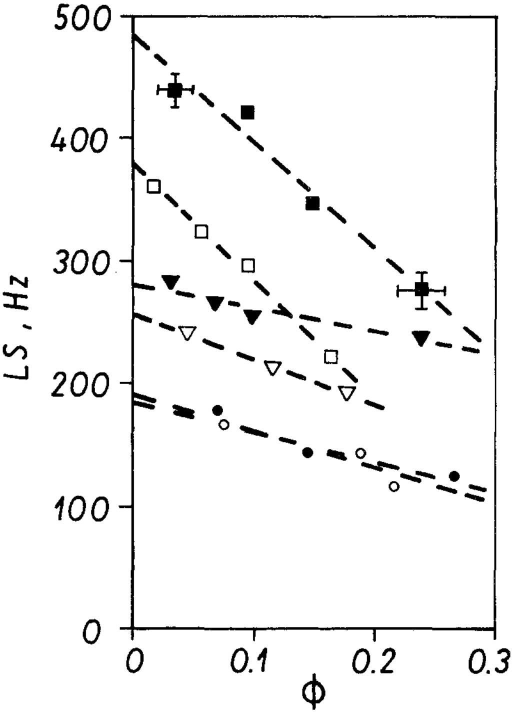

Fig. 2:
Typical dependence of the slope LS on the fraction Φ of C_6D_6 for the same samples as in Fig. 1.

Experimental

Our experiments make use of statistical crosslinked long precursor chains ($M_n \approx 74$ kg/mol) of conventional statistical styrene-butadiene rubber (SBR). This material was described in more detail in (11). A brief characterization gives TABLE 1. All NMR-spectra were measured on a BRUKER SXP4-100 spectrometer at 300 K and 13.81 MHz. Samples of about 3 x 1.5 x 45 mm^3 were gripped by ceramic jaws. One of these jaws was fixed at the bottom of the NMR-tube. The other could be drawn along the tube. The stretching ratio was determined by measuring the distances between several markers on the sample with an accuracy of ± 0.1 mm.
The mass fraction of the solvent was evaluated by a conventional weighing procedure. The content of solvent was constant during the NMR-measurement (less then 2 hours).

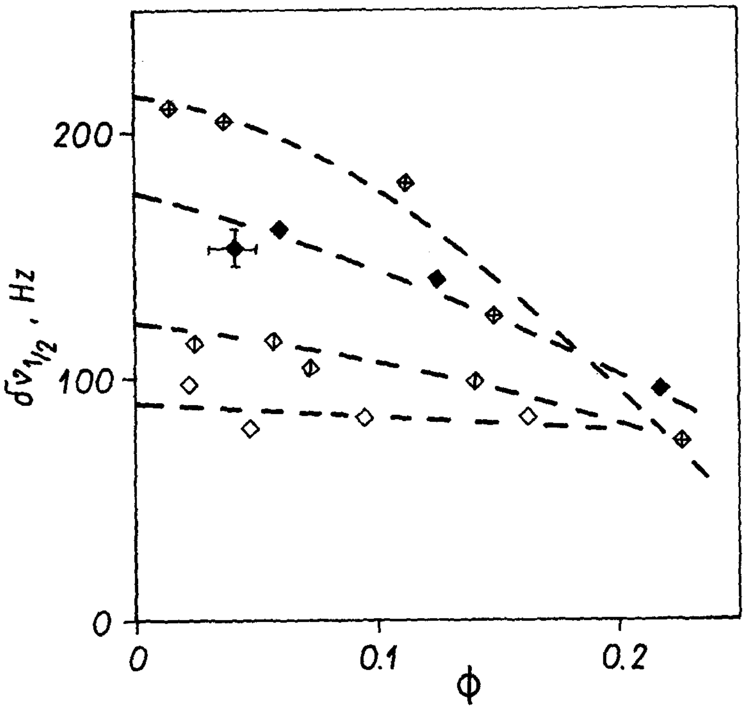

Fig. 3:
Line width at half height $\delta\nu_{1/2}$ of samples G4, GF4, GF41 and GF42 in dependence on the C_6D_6 fraction Φ.

Results and discussion

For some typical samples which were swollen in C_6D_6 Fig. 1 demonstrates that the splitting $\delta\nu$ depends linearly on α^2-1/α for filled as well as for unfilled samples in the range of small deformations ($\alpha<1.5$). In order to get the result L of formula (3) the splitting was measured in dependence on Φ (Fig. 2). An additional result of these experiments can be taken from Fig. 3. The line width at half height of resonance lines decreases with an increase of Φ. This was expected and occurs for the same reason as the decrease of line splitting with an increase of Φ. By an increase of the solvent fraction the mobility of the whole system increases, resulting in a lowering of the residual quadrupolar interaction (8).
Fig. 4 shows the extrapolated line width at half height for $\Phi=0$ in dependence on the filler content. One can assume that this line width is inverse proportional to the segmental mobility. The same quantitative behavior of the mobility was found by ^{1}H-NMR relaxation measurements (11).
The values of L are plotted in Fig. 6 in dependence on $1/M_c$(^{1}H-NMR). Obviously, L is linearly dependent on $1/M_c$.

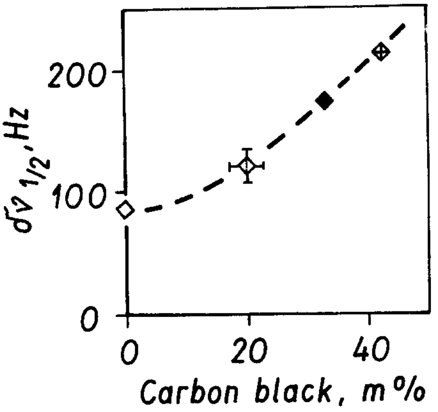

Fig. 4:
Line width at half height for $\Phi=0$ in dependence on the mass fraction of carbon black (samples of Fig. 3).

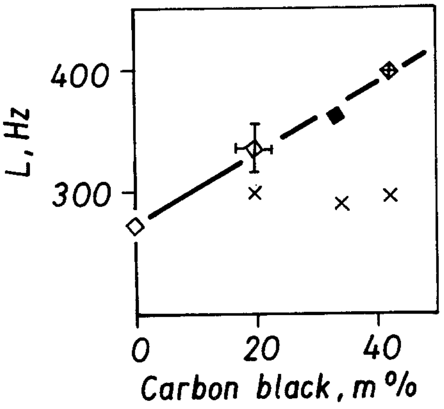

Fig. 5:
Slopes L and L_p (x) in dependence on the mass fraction of carbon black ($\Phi=0$, samples of Fig. 3).

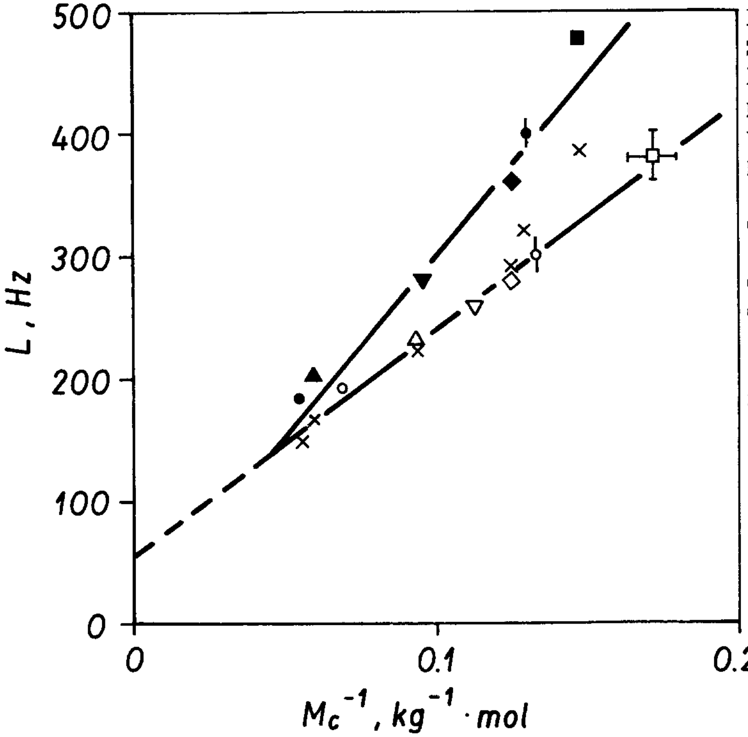

Fig. 6:
Slopes L and L_p (x) in dependence on the mean reciprocal molecular mass $1/M_c$ of intercrosslink chains according to formula (3) and formula (5) respectively.

However, the slope of the straight line for filled samples is steeper than that for unfilled samples and runs into the line of unfilled samples at low crosslink density. If one lengthens the straight line of unfilled samples (dashed line) it cuts the L-axis above zero. This is reasonable because of the presence of entanglements ($M_n > M_{critical}$).

The steeper slope indicates a higher order in filled samples. Fig. 5 shows that the order is increased continuously by an increase of the filler fraction.

In (12) similar ^{2}H-NMR measurements were carried out on deuterated short butadiene oligomers in stretched vulcanizates of natural rubber. No such significant increase of line splitting in filled samples was found. This led to the belief that a microscopical inhomogeneous distribution of stress which is caused by bridging molecules between filler particles exists in filled samples and that the mobile oligomers tend to avoid these regions of higher free energy.

In contrast to (12) we used highly mobile and consequently all over the sample present solvent molecules and we are led to the belief that the increased line splitting in filled samples could have three reasons:

1. The polymer network matrix is bound physically (13) and chemically (14) to active carbon black and forms bridges between the filler particles. If we assume that the carbon black particles are rigid and therefore could not be stretched, the measured stretching ratio α for filled samples must be replaced by a higher stretching ratio α_p of the polymer matrix. A simple model which assumes a line of alternate carbon black and polymer matrix pieces gives

   $$\alpha_p = (\alpha-\Phi_R)/(1-\Phi_R) \qquad (4)$$

   where Φ_R is the volume fraction of carbon black. This leads to a correction of the L-values for filled samples. The new value L_p can be calculated by a simple approximation if $\alpha < 1.5$ and $\Phi < 0.3$ (our case):

   $$L_p = L*(\alpha^2-1/\alpha)/(\alpha_p{}^2-1/\alpha_p) \approx L*(1-\Phi_R). \qquad (5)$$

   Therefore, the increase of L with an increase of the carbon black fraction in Fig. 5 and the steeper slope for filled samples in Fig. 6 seem to be a consequence of the greater inner stretch α_p. The consequence of the α-correction is demonstrated in both of the figures by crosses.
2. Carbon black clusters (15) become uniaxial deformed by an uniaxial stress and form an additional order.
3. ^{1}H-NMR-spin-spin relaxation studies (11,13,16) and Fig. 3 and 4 show that the incorporation of filler particles very clearly decreases the segmental mobility. This corresponds formally with a decrease of the temperature and leads consequently to an increase of the line splitting (17).

According to Fig. 5 and Fig. 6 we would now conclude that the main reason for the apparent higher order in filled samples is the greater inner stretch of the polymer matrix compared to the lower outer stretch of the sample. A further support for point 1. could be expected by a systematic investigation of highly filled samples at higher elongations ($\alpha > 1.5$). According to formula (4) one can expect deviations in the linearity of the function $\delta v(\alpha^2 - 1/\alpha)$. Some preliminary experiments show this.

Point 2. and 3. seem to have either no or only a weak influence on the order of the system.

Nevertheless, an investigation of deuterated networks which contain a carbon black filling would be very useful for immediate observation of the polymer chain order and for comparison with our experiments with a deuterated solvent.

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Accepted November 15, 1990 C