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^{1}H-NMR-spin-spin relaxation in cross-linked SBR with and without carbon black filling

G. Simon[1],* B. Götschmann[1], D. Matzen[2], and H. Schneider[1]

[1]Department of Physics, Technical University »Carl Schorlemmer« Leuna-Merseburg, DDR-4200 Merseburg, German Democratic Republic
[2]Kombinat Chemische Werke BUNA, DDR-4212 Schkopau, German Democratic Republic

Summary

For the first time ^{1}H-NMR-spin-spin relaxation curves of a chemically crosslinked statistical copolymer of styrene and butadiene (SBR) with and without carbon black filling are interpreted in terms of a dynamical model which includes two correlation times typical for flexible polymers and which makes use of common phantom network properties. The residual second moment of the magnetic dipolar interaction of spin pairs in network chains gives average molecular masses M_c for unfilled SBR and SBR which is filled with carbon black. All the parameters of the model used are selfconsistent and in good accordance with the results of stress-strain experiments.

Introduction

It has been shown in several papers (for example in (1-9,17)) that ^{1}H-NMR-spin-spin relaxation is a very useful tool for characterizing the network structure and dynamics of common elastomers.
Above glass transition temperature T_G network chains are represented by a fast relaxing quantum of magnetization of about 80 % ; the relaxation curve component has a Gauss-like decay form (4,8,9). The fast relaxation was proved to be connected with a residuum of the second moment of the static dipolar interaction which is left by an anisotropy of segmental motion in an inter-crosslink chain (10). The residual second moment is directly connected with the number Z of Kuhn statistical segments in an inter-crosslink chain (11,12). Therefore, one of the most interesting results for

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*To whom offprint requests should be sent practical application is the possibility of determining Z or, furthermore, of determining the average molecular mass M_c of the inter-crosslink chains. This was sucsessfully used in (9) for poly(dimethylsiloxane) networks.

In this paper the "^{1}H-NMR-tool" is now applied to a widly used elastomer, to a statistical copolymer of styrene and butadiene. The NMR-M_c values (M_c(NMR)) for unfilled SBR show good accordance with the M_c values of stress-strain experiments (M_c(mech)).

Experimental section

The composition of SBR was determined from ^{1}H- and ^{13}C-NMR spectra of uncrosslinked SBR in solution. It consists of 62 mass% of 1,4-cis-poly(butadiene), 11 mass% 1,2-poly(butadiene) and 27 mass% poly(styrene) which is statistically distributed. The molecular masses were determined by GPC and are M_w ≈ 223 kg/mol and M_n ≈ 74 kg/mol. The samples used here were mixed from SBR by adding 3 phr (3 parts to 100 parts of rubber) zinc oxide, 1 phr stearic acid, 1 phr phenyl-β-naphthylamin and a tetra-methylthiuramdisulfid-sulfur (TMTD-S) mixture (25:1) for crosslinking. In filled samples the amount of carbon black (PM 100) was 50 phr (about 20 vol%). Each filled sample (named GF) has an unfilled partner (G). The portion of crosslinking agent and the M_c(mech) values of unfilled samples according to (13) are reported in TABLE 1. The M_c values were evaluated using the theory published in (14).

TABLE 1

Sample	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10
TMTD-S, phr	1.55	1.75	2.14	2.73	3.49	4.45	5.67	6.94	7.75	10.0
M_c, kg/mol	15.2	13.8	11.1	9.2	7.3	7.1	6.5	5.1	4.7	3.5

The vulcanization was carried out at 145 °C for 20 minutes (G10 60 minutes). The transversal magnetization decays of the protons were measured on a BRUKER SXP4-100 spectrometer (88 MHz) using a common Hahn spin echo technique.

In Fig. 1 only some of the relaxation curves are shown in order to give a clear illustration. The measuring temperature T = 130 °C was chosen in order to increase the differences

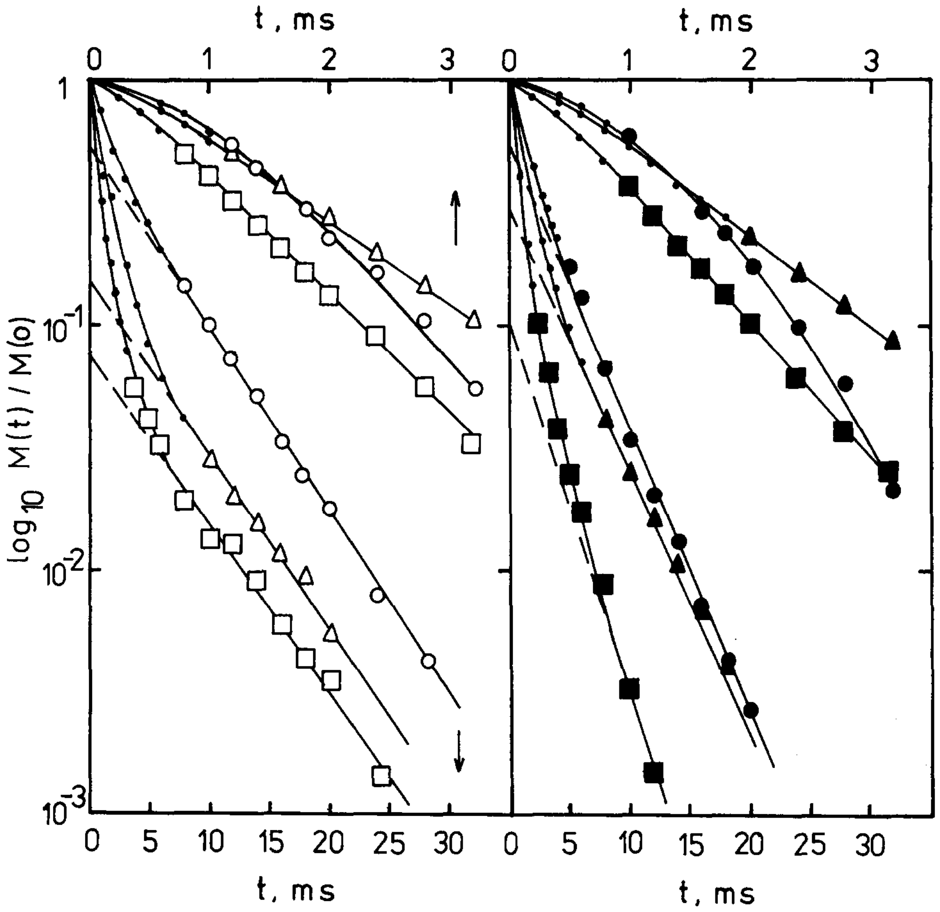

Fig. 1: Relaxation curves of unfilled samples G0 (○), G2 (Δ), G7 (□) and of filled samples GF0 (●), GF2 (▲), GF7(■). The upper curves show the separated and normalized Gauss-like component. According to formula (1) the fitted function (full lines) correlate excellently with experimental values (symbols and (•)), the correlation coefficient is about 0.98.

between the curves and to emphasize the influence of chemical crosslinks. A very long, clearly exponential component of only about 5 % and with a decay time of $T_2 \approx 10$ ms for filled and $T_2 \approx 20$ ms for unfilled samples has already been subtracted. This component can be attributed to small non-network molecules which can be extracted (e. g. sol fraction, admixtures) (9). The remaining exponential tail of about 15 % belongs to dangling chain ends as was also proved in (9).

Data analysis and discussion

In accordance with (4,5,8,9,17) the relaxation curve of the transversal magnetization at $T > T_g+100$ K can be described by the following decay function:

$$M(t) \doteq A*\exp(-t/T_{2,f}-q*M_2*\tau_s^2*(\exp(-t/\tau_s)+t/\tau_s-1)) + B*\exp(-t/T_{2,f}). \quad (1)$$

A and B are the magnetization portions of inter-crosslink chains and dangling chain ends, respectively. The mean correlation times τ_f and τ_s represent the fast local segmental motion and the slower motion of larger molecular parts, respectively. $M_2 = 1.45*10^{10}$ s^{-2} is the second moment of the static magnetic dipolar interaction in the rigid lattice which can be measured at temperatures below T_g by the common relaxation function

$$M(t) = M(0)*\exp(-M_2*t^2/2). \quad (2)$$

If chains are fixed at both ends the τ_f-motion is anisotrpic at $T > T_g$. This gives a residual $M_{2,r} = q*M_2$ which cannot be averaged by this motion. As a result, a slower motion with τ_s is detectable which can be "felt" by a further reduction of $q*M_2$. For dangling chain ends q is equal to zero.
According to the common BBP-theory (15) we will assume that

$$T_{2,f} = M_2*\tau_f*(3+5/(1+y^2)+2/(1+4*y^2))/3 \quad (3)$$

where $y = 2*\pi*f_0*\tau_f$, $f_0 = 88$ MHz and $\tau_f \approx 10^{-9}$s.
It is possible from q to calculate the number Z of Kuhn statistical segments between the junctions of a network chain if this chain behaves like a Gauss chain with free rotating segments and if intermolecular interactions are excluded (phantom network properties) (11):

$$Z = 3/(5*q^{1/2}). \quad (4)$$

For real networks q must be replaced by $q-q_0$ (5,8). Here, $q-q_0$ stands for the temperature independent chemical network. q_0 is measured for the uncrosslinked reference sample, representing the temperature dependent "physical" network. All q-values are average values resulting from a natural distribution of network chain length.

In general, the molecular mass M_c of inter-crosslik chains of homopolymers can be evaluated by the relation

$$M_c = Z*M_u*c_\infty/N \qquad (5).$$

where N is the number of backbone bonds in a basic ("monomeric") unit, M_u is the molecular mass of this unit and c_∞ is the number of backbone bonds in a Kuhn statistical unit.

M_c is not easily available for statistical copolymers because the constant $K = M_u*c_\infty/N$ is unknown. However, K can be evaluated for unfilled SBR samples from M_c(mech) by a plot M_c(mech) as a function of $M_c(NMR) = K*Z$ (Fig. 2). The best fit is achieved for K = 137 g per statistical unit.

Using $\langle M_u/N\rangle_{bb}$ = 18 g as an average value which takes into account the portions of the bonds of the constituents in the backbone chain (bb), it follows for SBR that $c_\infty = 7.6$.

The good linearity of the M_c plot in Fig. 2 points to the validity of the model used to connect NMR parameters and molecular dynamics.

The calibration in Fig. 2 can now be used for determining the M_c values of the samples filled with carbon black. These values are also plotted in Fig. 2. Inspite of an general error for all M_c values of about 15 %, the tendency points to an M_c which is about 15 % higher than that for unfilled samples. Obviously, the filler disactivates a part of the crosslinking agent.

For long polymer chains which are crosslinked statistically one can expect that the portion of dangling chain ends B/(A+B) can be determined by the equation

$$B/(A+B) = M_c/M_n. \qquad (6)$$

In equation (6) it is assumed that one dangling chain end usually has an average molecular mass of $M_c/2$.

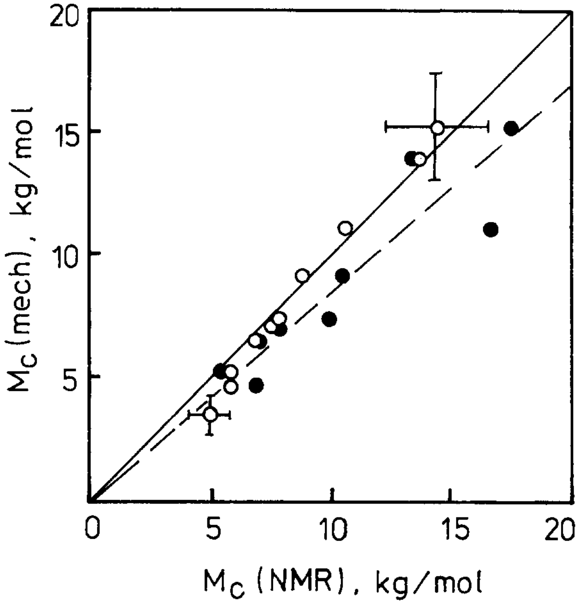

Fig. 2: M_c(mech) as a function of M_c(NMR) for unfilled samples (o), M_c(NMR) of filled samples as a function of M_c(mech) of their unfilled partners (●). Sample G10 does not have a filled partner.

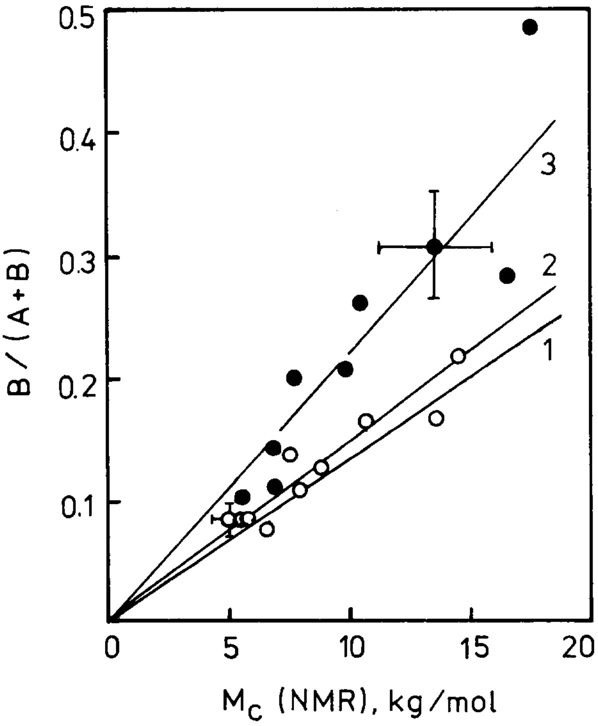

Fig. 3: Portion of the dangling chain ends as a function of M_c(NMR) for unfilled samples (o) and filled samples (●). According to formula (6) numbers 1, 2 and 3 correspond to M_n= 74, 69 and 43 kg/mol, respectively.

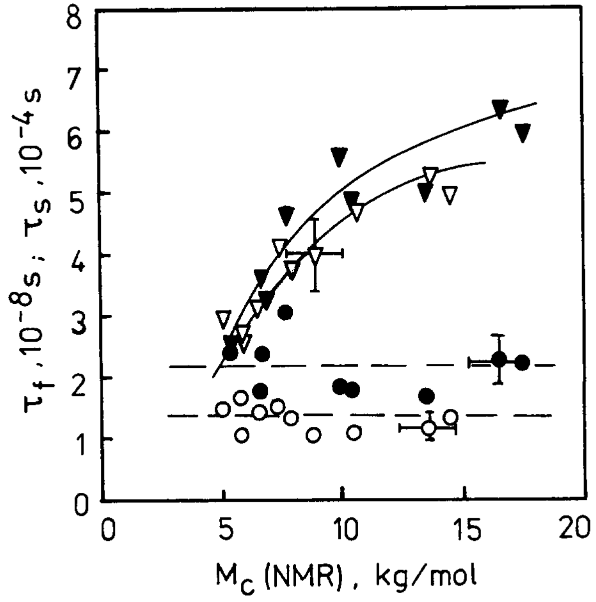

Fig. 4:
Correlation times as a function of M_c(NMR).
τ_f: ○ unfilled,
● filled.
τ_s: ▽ unfilled,
▼ filled.

Since B/(A+B) ≈ = 0.55 is rather high for the uncrosslinked samples the dangling chain ends should be free of entanglements in crosslinked samples. This is supported by the measured constance of B/(A+B) at temperatures between 76 °C and 150 °C. From Fig. 3 it can be assumed that some polymer chains are cracked during the mixing and crosslinking procedure. M_n seems to decrease from 74 to about 69 kg/mol for unfilled samples and to about 43 kg/mol for samples filled with rigid particles of carbon black.

In Fig. 4 the correlation times τ_f and τ_s are shown as a function of M_c(NMR). Obviously, every motion in filled SBR is slower than in unfilled SBR. The incorporation of rigid particles makes this very plausible. The independence of the local correlation time τ_f of M_c further supports the theoretical model used.

If τ_s is assumed to represent fluctuations of inter-crosslink chains the increase of τ_s with M_c is a result of scaling. The values of the correlation times correspond with the two maxima of the typical distribution function of correlation times of flexible polymers in solution (10^{-8}s and 10^{-3}s) (16).

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