Polymer Bulletin 37, 489–496 (1996)

Polymer Bulletin

# New aspects of transversal $^1$H-NMR relaxation in natural rubber vulcanizates

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Received: 16 January 1996/Revised version: 13 May 1996/Accepted: 2 July 1996

## Summary

Structure and dynamics of unfilled and carbon black filled natural rubber vulcanizates were investigated by means of transversal $^1$H-NMR-relaxation. A simple theoretical model including different motions in polymer network was extended by the discussion of an anisotropy parameter of segmental motion not only for the intercrosslink chains but also for the dangling ends. It makes characterization of the filling state of the network possible to approximate . The effect of increasing correlation times $\tau_f$ of the fast anisotropic local motion with reduction of the molecular mass of intercrosslink chains which was observed, but not cleared up in previous investigations is evidently smaller by using this modified model in accordance with the expectation of a local motion. The determined values of $M_c$ are in good agreement with the results of fits by using the unmodified relaxation function. $^{13}$C-NMR-spectra and stress-strain-experiments are leading in most cases to similar results, especially for $M_c$.

## Introduction

The possibility to study structural and dynamical parameters of polymer melts and networks by transversal relaxation of protons for temperatures well above the glass transition temperature $T_g$ is already well-known for a long time. A variety of publications (1-9) proved it impressively.

The shape of the decay of tranversal magnetization depends characteristically on the dominant motions of the spins. The mostly non-exponential relaxation decays can be understood on the basis of the so-called "tube-model". This model takes into account fast anisotropic segmental motions within the tube and slower motions along the tube (reptation) and of the tube itselfes (tube-renewal).

This approach was used consequently for intercrosslink chains; for dangling ends and "sol-chains" only isotropic segmental motions with corresponding relaxation times were discussed. The advantage of this simplified approach consists in a relatively simple fit-function and in the possibility of the determination of the molecular mass of intercrosslink chains $M_c$.

We always obtained the expected relaxation curves in experiments for intercrosslinked networks. The Gaussian-like decay at the beginning of the relaxation curve is related to the intercrosslink chains which are anchored on both sides to the network by chemical or physical (entanglements) crosslinks. Both exponential-like decays were assigned to dangling ends and "sol-chains and -molecules".

Nevertheless, there were systematical problems in some cases of fitting the relaxation curves.

In crosslinked networks a "sol"-part of the order of 2..5% was observed, the corresponding part of the curve was purely exponential. However, the related relaxation time $T_{2,sol}$ was often about a factor 10 longer compared to the fitted relaxation time $T_2$ of the remaining parts of network. This "sol"-part was correlated until now with non-network molecules, i.e. with additional substances or very short oligomer chains.

However, there is a problem of interpretation, if the decay of the relaxation curve at the very beginning, which is related to the intercrosslink chains, is equal to the decay time $T_{2,sol}$.

In such a case the "sol"-part seems to consist of relatively long polymer chains, because the rubber is mixed in a laboratory mill with only few additional substances, which might have a much longer $T_2$. Here the approach of a single $T_2$ in contrast to previous models using different $T_2$'s for the several parts of network seems to be justified.

The correlation time $\tau_f$ of the fast local motions should increase slightly with increasing crosslinking density. In (8) a much stronger dependence was detected, which could not be explained. In this paper we propose a solution of these problems by a modification of our previous model (1,2,6).

We consider not only the motion of the intercrosslink chains as an anisotropic one but for the dangling ends as well. This part of the polymer chains can move more freely, of course. However, the crosslink at one side of the dangling end leads to a hindrance of the motion giving rise to a non-fully isotropic segmental motion of which the anisotropy is smaller than that for the intercrosslink chains.

The modified model must work as well as the previous procedure in the determination of the other parameters, especially $M_c$.

It should be noticed here, that the discussion of an anisotropy parameter of segmental motion of "sol"-chains will be inpossible because of the expected very small value of this parameter!

## Experimental

The samples of series 1 were provided by the University of Freiburg/Breisgau (Germany), Institute of Macromolecular Chemistry (preparation by Degussa AG), whereas series 2 came from the University Regensburg, Institute of Polymer Physics (preparation by POPPE & CO, Gießen). The support of Prof. Gronski and Prof. Göritz in having the possibility to use these samples for our measurements is gratefully acknowledged.

Previous investigations of transversal relaxation, results of $^{13}$C-NMR-spectroscopy and stress-strain-experiments already existed for series 1.

The composition and the conditions of vulcanization of the samples of series 1 are shown in Tab. 1. The temperature of vulcanization was 155 °C.

The composition of the samples of series 2 is shown in Tab. 2. Samples of four vulcanization times (uncrosslinked, 30 min, 44 min, 58 min) and consequently four crosslink degrees were made from the row material. The temperature of vulcanization was 120 °C.

The routine NMR relaxation experiments were carried out on a solid-state NMR spectrometer BRUKER SXP 4-100 (resonance frequency for protons: 90 MHz) equipped with a SMIS-console. Experiments for comparison were done on a high field NMR spectrometer VARIAN Unity 400 (resonance frequency for protons: 400 MHz).

To eliminate the influence of inhomogeneities of the magnetic field and of chemical shift the transversal magnetization decay was detected by the common HAHN spin-echo technique. In dependence on the available amount of sample material we obtained a signal-to-noise ratio of 1000 to 10000 by 16 scans, which is absolutly necessary to analyse the relaxation curves by using a model with a large number of parameters.

The measurements were performed at 60 °C. At that temperature, neither vulcanization continues nor aging happens. The influence of physical entanglements compared with chemical crosslinks is small and effects of crystallization can be excluded at this temperature.

The comparison of different relaxation curves showed the good reproducibility of the results. Nevertheless the samples of one series were always measured one after the other in order to decrease the variation of environmental influences furthermore.

| | unfilled samples | samples with 10 phr carbon black N220 | samples with 50 phr carbon black N220 |
|---|---|---|---|
| SMR | 100 | | |
| $S_8$ | 0.8 / 1.0 / 1.2 / | 1.4 / 1.6 / 1.8 / 2.0 | / 2.2 / 2.4 |
| CBS | 0.8 / 1.0 / 1.2 / | 1.4 / 1.6 / 1.8 / 2.0 | / 2.2 / 2.4 |
| corresp. crosslink. time[min] | 18 / 22 / 21 /<br>20 / 20 / 20 /<br>20 / 19 / 19 | 15 / 15 / 14 /<br>14 / 14 / 14 /<br>14 / 14 / 14 | 12 / 11 / 11 /<br>10 / 10 / 10 /<br>10 / 10 / 10 |
| ZnO | 3 | | |
| StS | 1 | | |
| sample | 1, ..., 9 | 19, ..., 27 | 10, ..., 18 |

Table 1: Composition (phr) and conditions of vulcanisation of the samples of series 1

| | |
|---|---|
| RSS1 | 100.0 |
| ZnO active | 6.0 |
| stearinacid | 0.5 |
| CBS | 0.5 |
| sulfur | 5.0 |

Table 2: Composition (phr) of the series 2

# Theory

## Model of polymer network:

Since the transversal $^1$H-relaxation is determined by the dipolar magnetic interaction of protons, one can conclude from the averaging of this interaction to the motion of the protons. Different experimentally observed components of the relaxation decay originate from protons in parts of the molecule owing to different characteristic times and anisotropies of motion.

Figure 1 should give a coarse survey about the components of network producing separate signals of relaxation.

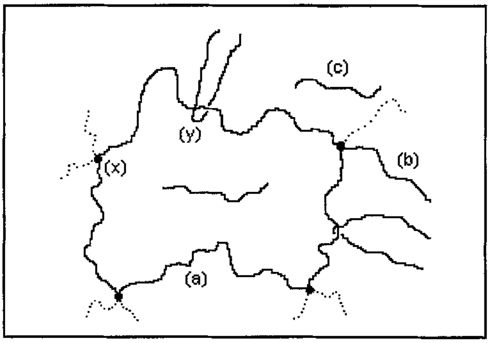

Fig. 1: Main ingredients of an elastomer network

Besides intercrosslink chains (a), dangling ends (b), "sol-molecules" or "sol chains" (c) and chemical crosslinks (x), there are physical loops -entanglements- (y), the influence of them is dependent on temperature. The entanglements will be taken into consideration later on.

Based on the "tube-model" of de Gennes (10) three typical kinds of motions may be distinguished.

First, a fast local motion of segments (abc) has to be considered (correlation time $\tau_f \approx 10^{-9}$ s). Its small motional anisotropy due to the limited "tube" and the fixing of the intercrosslink chains and the dangling ends on chemical crosslinks or entanglements respectively leads to a small non-averaged part of the second moment $q^*M_2$ ($q \approx 10^{-4}$ for segments of intercrosslink chains, $q' \approx 10^{-5}$ for dangling ends) of the dipolar interaction in the "rigid lattice" at temperatures below $T_g$.

On the other hand reptation (chain fold fluctuation) and tube renewal motions are expected. These motions are able to reduce the remaining dipolar interaction furthermore. A separation of these two slow isotropic motions (correlation time $\tau_s \approx 10^{-3}$ s) by means of analysis of relaxation curves is not possible.

## Correlation and relaxation:

The basic ideas of the interpretation of the relaxation of the transversal magnetization of protons in polymer networks for temperatures well above $T_g$ ($T > T_g + 120$ K) should be described in a frame of a modified single chain model (1-8).

In the case of strong topological restriction in networks the dynamics of chains looks like the dynamics of a single chain which is fixed on both ends. Another assumption is that the chains

consist of N free rotating KUHN-segments with single spin-pairs (11).
The correlation function of the anisotropic motion of spins in networks is given by

$$G(\tau) = M_2 * [(1 - q) * \exp(- \frac{\tau}{\tau_f}) + q] * \exp(- \frac{\tau}{\tau_s}) \qquad .(1)$$

In our experiments the assumptions $\tau_f \ll \tau_s$ and $q \ll 1$ are always fulfilled.
For the fast motion $\omega_0\tau_f <\approx 1$ holds true whereas for the slow motion $\omega_0\tau_s \gg 1$ is valid. Therefore the magnetization decay for the first term of Eq. (1) is exponential and can be expressed by the BPP formula

$$\frac{1}{T_2} = \frac{1}{3} M_2 * \tau_f * [3 + \frac{5}{1+(\omega\tau_f)^2} + \frac{2}{1+(2\omega\tau_f)^2}] \qquad ,(2)$$

but for the second term the Anderson-Weiss-formula has to be applied

$$M(t) \sim \exp\{ - \int_0^t G(\tau)\,(\tau - t)\,d\tau \} \qquad .(3)$$

Finaly, the total magnetization decay resulting from the correlation function (1) is given by

$$M_N(t) \sim \exp\{ - \frac{t}{T_2} - q*M_2 * \tau_s^2 * [\exp(- \frac{t}{\tau_s}) + \frac{t}{\tau_s} - 1]\} \qquad .(4)$$

In our former papers this magnetization behaviour was assigned only to the motion of the intercrosslink chains, whereas in the dangling ends an isotropic fast segmental motion was considered, i.e., q' was neglected in the expansion of Eq. (5) for the rest of the network.
However, even the small anisotropy of the segmental motion in dangling ends can be measured. The related parameter of anisotropy q' is as expected clearly smaller than q.
One simplification is nessesary: a separate discussion of the correlation time of slow motions ($\tau_s'$) is not possible because already the exact finding of $\tau_s$ is not easy due to the width of the distribution of $\tau_s$. Therefore we set $\tau_s' = \tau_s$. The discussion of an anisotropy parameter of the segmental motion in the sol-fraction q" is impossible because the related part of the relaxation curve is pure exponential and thus q" will be non-measureable small.
The total relaxation function is therefore

$$\begin{aligned} M(t) = {} & A * \exp\{ - \frac{t}{T_2} - q*M_2 * \tau_s^2 * [\exp(- \frac{t}{\tau_s}) + \frac{t}{\tau_s} - 1]\} + \\ & B * \exp\{ - \frac{t}{T_2} - q'*M_2 * \tau_s^2 * [\exp(- \frac{t}{\tau_s}) + \frac{t}{\tau_s} - 1]\} + \\ & C * \exp\{ - \frac{t}{T_{2,sol}} \} \end{aligned} \qquad .(5)$$

The fractions A, B and C representing the parts of the magnetization of the protons in intercrosslink chains, dangling ends and sol-fraction correspond in first approximation to the molecular mass parts.
Based on GOTLIB's idea (2) of the factor q as the ratio between the second moments well above the glass transition temperature and for the rigid lattice, respectively, the averaged molecular mass of intercrosslink chains $M_c$ can be determined. The influence of physical entanglements for real networks is taken into consideration by the correction of the value of q by a quantity $q_0$, which is measured for uncrosslinked systems and can be extrapolated from the representation of crosslink

density over the content of crosslinker. It follows

$$M_c = \frac{3}{5 * \sqrt{q-q_0}} * c_\infty * \frac{M_{ru}}{N} \qquad (6)$$

$M_{ru}$ / N is the molecular mass of one monomer unit per number of backbone bonds in one unit. The quantity $c_\infty$ is the number of backbone bonds in one KUHN-segment.

The problems of determination of the second moment of the rigid lattice are discussed in detail in (8).

## Data analysis

### Anisotropy of the segmental motion in dangling ends:

Figure 2 shows transversal $^1$H-relaxation curves for unfilled samples of natural rubber of different series. A sol fraction $C_{sol}$ of 2% has already been subtracted.

It is obvious that the general form of the relaxation curves differs in dependence on the observed rubber. It should be noted that the content of crosslinker and consequently the density of crosslinks manifests itself not only in the shape of the decay. The crucial quantity is the value of the correlation time of slow motions $\tau_s$. This quantitity determines essentially the relation of the initial decay and the decay corresponding to dangling ends.

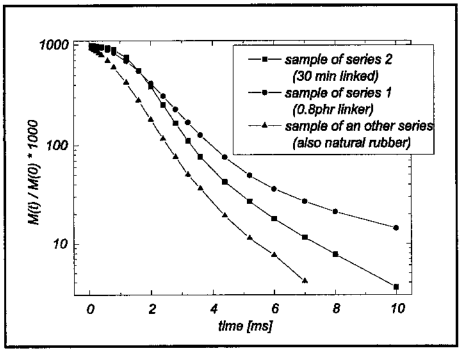

Fig. 2: Relaxation curves for unfilled samples of natural rubber of different series (there are generally three classes of curves which are different in the relation of the initial decay and that of the middle part. The sol fraction $C_{sol}$ is substracted.)

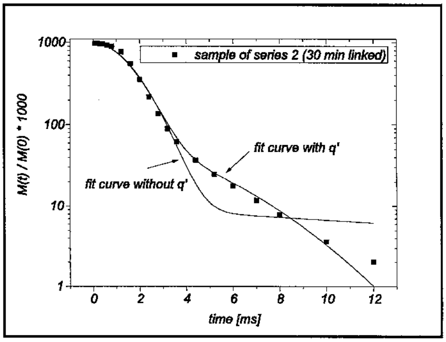

Fig. 3: Comparion of the measured relaxation curve of transversal magnetization of a sample of series 2 (natural rubber) with fit curves by using the unmodified model without consideration of anisotropy of segmental motion in dangling ends as well as by using the Eq. (5). The "Sol"-part is already substracted.

Therefore, three classes of relaxation curves can be subdivided. The classification can often be made for $\tau_s > 3$ms, 3ms $> \tau_s > 1$ms and $\tau_s < 1$ms. All three classes should be described using the well-known model which was successfully presented in some publications of our group (3-8).

Most of the curves, particularly these of the second and the third class where the initial decay of the relaxation curve is approximately equal or shorter compared to the decay of the intermediate component do not make problems in the analysis. But there are curves like the first one in Fig. 2, where the initial decay is longer than that one, which is correlated to dangling ends, and therefore the model is refused.

Fig. 3 shows the first relaxation curve of Fig. 2 as well as the fit curve by using the unmodified model and the fit curve by using Eq. (5). A sol fraction $C_{sol}$ of 2% with a relaxation time $T_{2,sol}$ of 19 ms for the crosslinked samples has been subtracted. Fig. 3 shows very clearly the discrepancy between the experimental decay and the fit curves, which have been obtained, if the segmental motion in the dangling ends looks like an isotropic motion and only an anisotropic one for intercrosslinked chains is discussed (3-8). It should be noted, that an apparent "better" fit in the semi-log plot can be obtained using the model without q', but on the expense of a much poorer fit in the initial part of the decay which would become obvious in a linear plot only.

The initial decay is remarkably slower than that part of the relaxation curve which is related to the dangling ends. Whereas the opposite constellation being understandable the present curves cannot be described sufficiently without adding an anisotropy parameter q'.

Here the fact should be emphasized that the determined value of $T_2$ is in good agreement with that of the sol fraction $T_{2,sol}$. This suggests the conclusion to discuss for all parts of network the same segmental mobility $\tau_f$ and therefore only one relaxation time $T_2$ ($T_2 \approx T_{2,sol}$) for "dry" networks (that means networks without solvents including protons).

Furthermore it must be noticed, that the accessibility of the anisotropy parameter q' depends on the shape of the measured relaxation curve. If the Gaussian like part of the initial slope is well shaped (as for instance for the relaxation curve in Fig. 3) which is correlated to very slow motions ($\tau_s > 3$ ms), q' can be determined with good accuracy. The discussion of q' is even absolutely necessary! In the other case ($\tau_s < 3$ ms) there are few problems in the exact determination of $T_2$. These problems influence the other fit parameters as well. The reason is the following: until now the middle part of the relaxation curve (dangling ends) was considered as "$T_2$-source" but this procedure now is practicable not due to the case $q' \neq 0$. Unlike this it is possible to determine $T_2$ from the decay of the sol-fraction in case of "dry" networks. If the value of anisotropy of the segmental motion in intercrosslink chains $q^*M_2$ is relatively small ($q^*M_2 < 1$ ms$^{-2}$, fulfilled always for weakly crosslinked samples), the decay in the sol fraction is comparable to the initial decay of the relaxation curve. In reality a comparison of both independently determined averaged relaxation times seems to be useful and with it the estimation of a "true", that means a global value. If there are highly crosslinked samples ($q^*M_2 > 1$ ms$^{-2}$), the initial decay fails as "$T_2$-source".

After determination of $T_2$, as described above, the fit with constant $T_2$ results in reproducable values of the other parameters, which are comparable to those determined by other procedures, i.e. using the model without q'. In case of networks containing solvent molecules it is essential to remove the related long exponential tail of the relaxation curve! This tail must not be confused with sol fraction! Therefore it is absolutely necessary to record as many as possible of points in the relaxation curve and extending the echo-time up to seconds.

## Discussion of parameters:

We are going to discuss the structural and dynamical parameters of networks determined by using Eq. (5) as well as observed quantities of unfilled and carbon black filled vulcanizates of natural rubber (contents in Tab. 1).

The correlation time of slow motion $\tau_s$ was determined to $\tau_s \approx 2$ ms in the limits of precision for all samples and was fixed afterwards in favour of a stable fit. Probably the values of $\tau_s$ underlay a wide distribution, however, this cannot be derived from the shape of relaxation curve.

Fig. 4 shows the dependence of the anisotropy of segmental motion in intercrosslink chains expressed in $q^*M_2$ on the amount of crosslinker. The values $q^*M_2$ are increasing with the content of crosslinker as expected; the value for the uncrosslinked sample represents the contribution of entanglements in chains ($q_0{}^*M_2$). The determination of the second moment of the rigid lattice $M_2$ is described in detail in (8). For the samples used here the following values are relevant: $M_2 = 0.8^*10^{10}$ s$^{-2}$ (unfilled samples), $M_2 = 1.0^*10^{10}$ s$^{-2}$ (10phr filled samples), $M_2 = 1.1^*10^{10}$ s$^{-2}$ (50phr filled samples).

It will become clear on closer inspection that a "$q_0$-correction" for black carbon filled samples with $q_0$ of an unfilled sample fails. On the other hand an extrapolation to $q_0$ for filled samples according to Fig. 4 is hardly possible. So in case there are unfilled uncrosslinked samples the following procedure is offered. The following relation valid exists between the number of crosslinks $\mu$ in a volume unit and the molecular mass of intercrosslink chains $M_c$, if the assumption tetrafunctionality of the crosslinks is correct (12)

$$\mu \sim \frac{\rho}{M_c} * (1 - \frac{M_c}{M_n}) \qquad (7)$$

$M_n$ is the molecular mass of initial chains, which are not linked, $\rho$ is the density of the rubber. According to Eq. (6) the uncorrected values of $M_c$ (without $q_0$-correction!) are determined and used in Eq. (7) first. The values of the crosslink density $\mu$ obtained in this way are shown in Fig. 5.

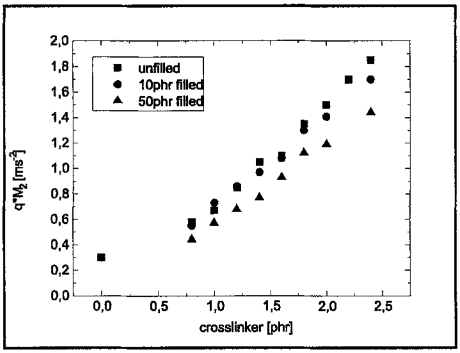

Fig. 4: $q*M_2$ in dependence on thecrosslinker content

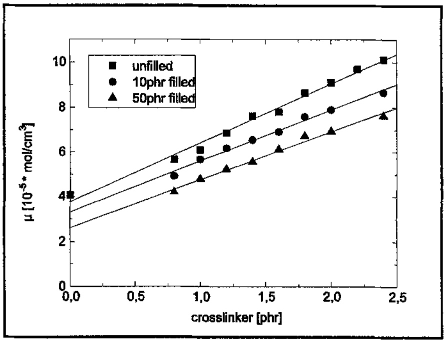

Fig. 5: Crosslink density $\mu$ determined from values of $M_c$ by using values of q from Fig. 4

The good linearity of crosslink density $\mu$ over the content of crosslinker shown in the graphical representation of Fig. 5 makes it possible to extrapolate to $\mu_0$ for filled uncrosslinked samples. From these values of $\mu_0$ at first uncorrected $M_c$ and in addition $q_0$ can be calculated in a reverse procedure by extrapolation of the curves in Fig. 5. It is remarkable that the measured values of $q_0$ for the unfilled uncrosslinked sample are in good agreement with the extrapolated one.

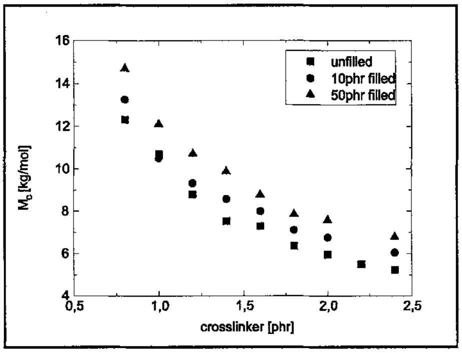

Fig. 6: $M_c$ after correction with the extrapolated parameter of anisotropy $q_0$ for filled samples

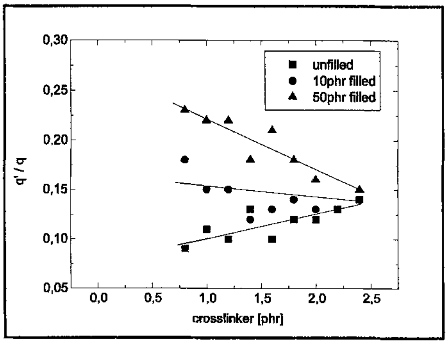

Fig. 7: Ratio q/q' in dependence on content of crosslinker and filler

Larger molecular masses of intercrosslink chains $M_c$ and therefore smaller densities of crosslinks $\mu$ (Fig. 6) are observed for filled systems . These differences could be understood on the one hand as a disability of crosslinking by presence of rigid particles of carbon black. On the other hand one may conclude that the crosslinking in filled systems is more heterogeneous than in unfilled systems. Therefore, the obtained network is not a "statistical" network - it must be calculated with very wide distributions of $M_c$. Another possibility to explain the problem is, that $q*M_2$ is determined as too small for such crosslink densities even in case of an equal number of crosslinks in unfilled and filled systems because the segments in long intercrosslink chains do not feel the anisotropy. The

questions of the decrease of molecular mass with increasing filling need further experiments.
Fig. 7 shows the dependence of the relation q'/q on the content of crosslinker. The quantity q'/q depends strongly on the content of filler. The differences decrease with increasing crosslinking.
In our opinion there is a possibility to understand why the anisotropy of motion of dangling ends (q') decreases with respect to the anisotropy of network chains (q) as a function of crosslinker content in the case of filled rubber whereas the reverse is true for unfilled samples. There is another situation in filled rubber compared to unfilled rubber. Carbon black filler by its chemical activity captures chains on its surface especially of dangling ends. Therefore, the amount of q' for filled rubber is already larger compared to unfilled and cannot be increased as strong as in the case of unfilled samples. Thus the ration q'/q decreases with increase of crosslinker content.
Despite of the large error of these values, q'/q may be suitable to estimate the filling state of an unknown system. Investigations along this line are in progress.

## Conclusion

We presented a critical analysis of the shape of decay of the transversal magnetization in polymer networks and the development of a simple theoretical model, using the Kuhn-Grün chain model, the Gotlib ideas, the basic NMR relaxation models of BPP and Anderson-Weiss and extensions as the separation of the influence of the "physical" and "chemical" networks.
Many experimental facts necessitated the introduction of an anisotropy parameter of segmental motion not only for the intercrosslink chains q but also for dangling ends q'. This must be done in particular for the class of those relaxation curves which are characterized by a correlation time of slow motions $\tau_s > 1$ms.
The classification of relaxation curves in three classes is important for the selection of the fit function. In case of large values of $\tau_s$ ($\tau_s > 1$ms) it is necessary and profitable to take q' into consideration.
However, depending on the signal-to-noise ratio and on the shape of the relaxation decay, it might be advantageous to use a simplified model (without q') rather than getting an unstable fit due to too many parameters.
Important network parameters such as the molecular mass of intercrosslink chains, the portions of these chains, of dangling chain ends and of sol molecules, and typical correlation times are nevertheless stable. The additional parameter makes the characterization of the filling state of the network possible.

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