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Network characterisation of end-linked poly(dimethylsiloxane) by ^{1}H-NMR-spin-spin relaxation

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Summary

Above the glass transition temperature ^{1}H-NMR-spin-spin relaxation curves of elastomers usually consist of two main components, a Gauss-like decay and a longer exponential decay. They can be attributed to inter-crosslink chains and free dangling chain ends, respectively, in accordance with basic ideas of the dynamics of polymer chains. By using an increasing amount of end-linking agent during the network synthesis of poly(dimethylsiloxane), the portion of the long decay is considerably reduced while the shape and the decay times remain approximately constant. This gives experimental evidence of the common classification of the decay components for the first time. Finally, the theoretical model for network dynamics used, which includes common phantom network properties and a concept of two independent motion scales, provides two mean correlation times and an average molecular mass of inter-crosslink chains.

Introduction

^{1}H-NMR-spin-spin relaxation (transversal relaxation) uses the static magnetic interaction of nuclear dipoles and its motional averaging for probing the dynamics of molecules. Therefore, the "contrast" in such an "NMR-picture" of polymers is given by differences in molecular mobility. It has been shown in some papers (1-5) that the transversal relaxation curves of several statistically crosslinked elastomers measured above the glass transition temperature T_g consist on principle of two components - in most cases of a main Gauss-like decay ("short component") and a longer exponential decay ("long component").

One aim of this paper is to provide the first experimental proof of the often assumed correspondence between the short component and the inter-crosslink chains on the one hand, and between the long component and the dangling chain ends on the other.

The quantitative analysis of the decay shape of the short component is carried out using an approved model (2,5-7) which makes use of common phantom network properties and of two scales of chain motion.

Our investigations of polymer networks by NMR are also connected with the aim of getting a tool for studying filled networks for practical purposes. In such systems the network characterization by the stress-strain behaviour, for instance, which has an excellent theoretical background for unfilled systems (look f. i. (8)), is at present only in the early stages (9).

Experimental section

Poly(dimethylsiloxane), with hydroxy groups at both chain ends, was end-linked by tetraethoxysilane in a usual manner in the presence of a tin octaneate catalyst.

The precursor chains synthesized by an anionic ring opening reaction of the cyclic tetramer octamethylcyclotetrasiloxane were characterized by the number average molecular mass M_n and the M_n-distribution (M_w/M_n = 1.65). The estimation of M_n was carried out using end group analysis of the hydroxy groups and by gel permeation chromatography. Both values are approximately equal. The siloxane networks investigated were synthesized using different ratios of functional groups of the crosslinking agent and the linear chains. This ratio r was changed from 0.5 to 2.0. Three networks PDMS 1, 2, and 3 (TABLE 1) were extracted and investigated by NMR.

The networks were controlled by sol-gel analysis (10) and uniaxial elongation and compression studies. The molecular mass between the junctions M_c was calculated using the rubber elasticity theory and the Mooney-Rivlin equation with structure factor A=1 which is possible as shown by (11) in the case of small deformations. The network characteristics are shown in TABLE 1.

TABLE 1

Characteristics of the samples used			
	PDMS 1	PDMS 2	PDMS 3
r	0.52	1.06	1.94
M_n, kg/mol	12.9	12.9	12.9
w_{sol}, weight%	4.9	1.8	0.9
w_{cyc}, weight%	3.4	3.4	3.4
M_c, kg/mol	18.7	13.6	10.8

The NMR experiments were carried out on a BRUKER SXP4-100 spectrometer working at a proton resonance frequency f_0=88MHz. The transversal magnetization decay was measured by a common Hahn spin echo technique. Relaxation curves are presented in Fig. 1. A very long exponential component with a decay time of about 100 ms and a portion of less then 1 % has already been subtracted. This component is attributed to small non-network molecules which are left after the extraction procedure and which can be reduced by annealing.

Data analysis and discussion

It is clear from the theoretical point of view that inspite of $T>T_g$ the local motion of polymer chain segments is anisotropic if the chains are fixed at both ends by chemical junctions or physical entanglements (6). It was proved in (12) by a combination of some ^{1}H- and ^{13}C-NMR spectroscopic methods that a broadening of lines for 1,4-cis-poly(butadiene) of high molecular mass (entangled chains) originates from this motional anisotropy.

In (1,5,7) it was shown that a model assuming an anisotropic local motion of network chain segments leads to a Gauss-like relaxation function due to a residual static magnetic dipolar interaction of protons. This relaxation function changes to an exponential one with a considerably longer decay time if one chain end is not fixed, such as for dangling chain ends.

This theoretical point of view is now supported directly by our experiments on end-linked PDMS. With an increasing amount

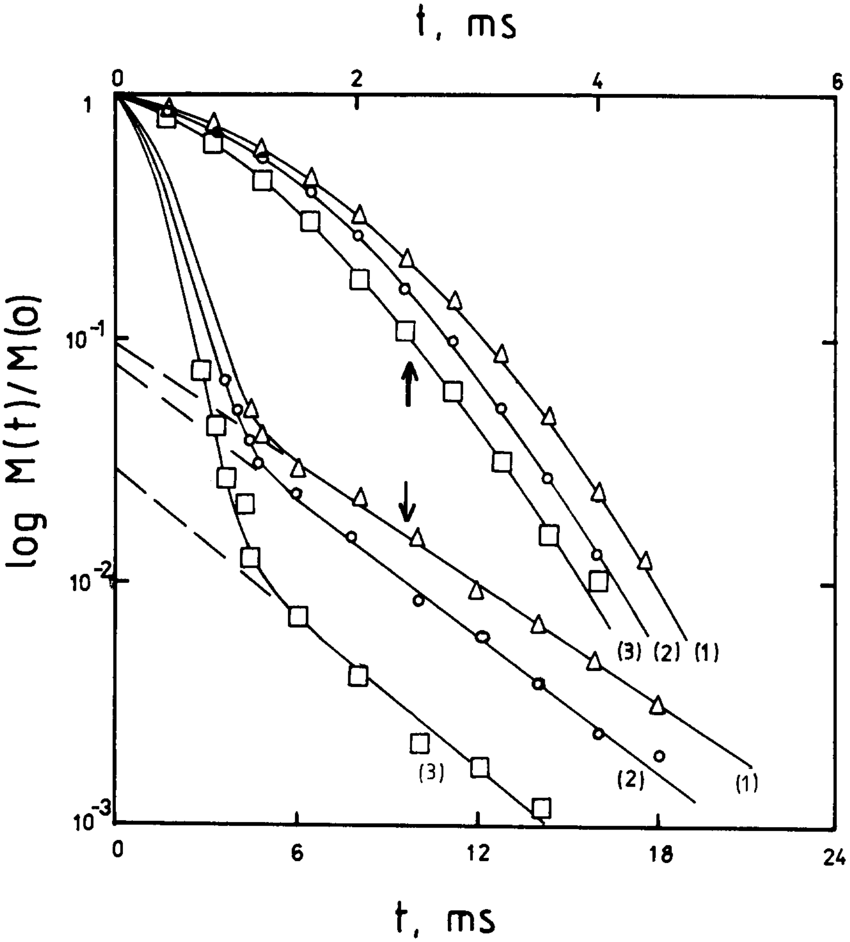

Fig. 1: ^{1}H-NMR-spin-spin relaxation of PDMS 1, 2, 3 at T=303K. The full lines are fitted curves according to formula (1). The upper curves represent the short component. The exponential tail is subtracted.

of crosslinking agent (sample 1 to 3), the portion of the exponential tail is reduced three times down to 3% whereas its decay time and the decay time of the short component (inter-crosslink chains) are approximately constant. The expected vanishing of the tail is not achieved in spite of an over-stoechiometric amount of linking molecules (sample 3). The reason may be that these molecules can react with each other and/or the four-functionality of the linker is reduced to a three-functionality.

Another interesting and supporting fact is that the portions of components of relaxation curves do not change from 303 K up to 443 K. This indicates that physical constraints are not visible or neglible in our end-linked PDMS. The stress-strain behaviour supports the last. The corresponding coefficient of the Mooney equation is nearly zero in the case of small deformations. Common statistically crosslinked networks which contain a large number of physical restrictions show a significant dependence on temperature in their transversal relaxation (1,2). In particular, the portion of the long component increases considerably with increasing temperature and tends to a final value - chain ends are freed from physical entanglements.

In accordance with (1,5), the relaxation curve of the transversal magnetization at $T>T_g$ will now be treated quantitatively using the decay function

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

Here

A, B - magnetization portions of inter-crosslink chains and dangling chain ends, respectively,

$f(t/\tau_s) = \exp(-t/\tau_s) + t/\tau_s - 1$,

$T_2 = 1/(M_2*\tau_f)$,

τ_f, τ_s - mean correlation times of the fast local segmental motion and the slow motion of larger molecular "scales", respectively,

M_2 - second moment of the dipolar interaction in the rigid lattice ($T<T_g$),

$q = M_{2,r}/M_2$, portion of M_2 left by an anisotropy of the τ_f motion in an inter-crosslink chain.

In accordance with (6,13) it is possible from q to calculate the number Z of statistical segments between the crosslinks of a network chain if this chain behaves like a Gauss-chain with free rotating statistical segments and if intermolecular interactions are excluded (phantom network properties):

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

For statistically crosslinked polymers q must be replaced by

$q-q_\infty$ (2,5) where the temperature dependent q_∞ represents the "physical" network and can be measured for an uncrosslinked sample. However, as mentioned above for our PDMS, the q_∞ value is nearly zero.

Using the number of backbone bonds in a statistical segment of PDMS $c_\infty = 6.0$ (14) one can calculate the molecular mass M of the inter-crosslink chains

$$M = Z*M_u*c_\infty/N \qquad (3)$$

where N is the number of backbone bonds in a basic (monomeric) unit of PDMS and M_u is the molecular mass of this unit.

It is clear from the formulae (1) - (3) that M is not exactly equal to the common M_c. The q-value for each inter-crosslink chain is rigorously replaced by an average q (2,5,6) producing M in formula (3). However, M ist almost equal to M_c if the mass distribution is small. Moreover, the correspondence of M and M_n espatially for the stoechiometric sample PDMS 2 supports this approach. It is a subject of further work to show the exact relation between M and M_c.

TABLE 2 shows all parameters of equation (1) for all samples. The second Moment $M_2 = 5.0*10^9 s^{-2}$ was measured at $T<T_g$ by the common transversal relaxation curve for amorphous polymers (15) $M(t) = M(0)*\exp(-M_2*t^2/2)$. The common fit correlation coefficient is about 0.96.

The average molecular mass M_c from stress-strain experiments accords well with our M values. It has not been possible up to now to explain in exact terms the weak variation of molecular masses with different amounts of crosslinking agent. It can be a consequence of the chemical reaction order of PDMS precursors with a molecular mass distribution and/or of

TABLE 2

	PDMS 1	PDMS 2	PDMS 3
A	0.90	0.92	0.97
B = (1-A)	0.10	0.08	0.03
τ_f (10^{-8}s)	3.73	4.41	4.73
τ_s (10^{-3}s)	26	18	11
q (10^{-4})	0.74	0.89	1.31
M (kg/mol)	15.5	14.1	11.5
M_c(kg/mol)	18.7	13.6	10.8

homoreaction of the crosslinking agent providing short chains. The almost constant value of τ_f shows that for our samples both a variation of M and an increase of temperature do not significantly influence the local correlation time.

An idea of the time scale of the junction fluctuation gives τ_B which is about 10^6-times greater than τ_f. However, for PDMS a further interpretation of τ_B is not reasonable because of a fit uncertainty in equation (1) resulting from the relation $(q*M_2)^{-1/2} \approx t_d < \tau_B$ where t_d is the typical decay time. From this it follows that $\tau_B^2 * f(t/\tau_B)$ is almost independent of τ_B.

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