Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials

Kay Saalwächter

Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, Friedemann-Bach-Platz 6, D-06108 Halle, Germany

Received 9 August 2006
Available online 12 January 2007

Keywords: Residual dipolar couplings; Transverse relaxation; Double-quantum NMR; Polymer dynamics; Elastomers; Networks; Rubber; Swelling; Poly(isoprene); Poly(butadiene); Poly(dimethylsiloxane)

Contents

1. Introduction .......................................................... 1
2. Basic principles ....................................................... 3
  2.1. Multiscale chain dynamics and residual dipolar couplings ...... 3
  2.2. The static \(^1\)H multiple-quantum experiment .................. 5
    2.2.1. Basic principles ........................................... 5
    2.2.2. Conceptual details and data treatment .................... 8
    2.2.3. Advanced approaches .................................... 9
  2.3. Limitations of transverse relaxometry .......................... 9
  2.4. Comparison of DQ excitation schemes ............................ 11
3. Applications to elastomers ........................................... 13
  3.1. Chain order distributions and heterogeneities .................. 13
  3.2. Quantitative interpretation of residual couplings ............... 16
  3.3. Chain dynamics in elastomers: failure of the slow-motion model . 18
  3.4. Network swelling ............................................. 21
  3.5. Strained and oriented networks .................................. 23
4. Entangled melt dynamics .............................................. 24
5. Other applications .................................................... 26
  5.1. Grafted chains ................................................. 26
  5.2. Confined chains ............................................... 28
  5.3. Study of gelation ............................................... 29
6. Summary and conclusions ............................................. 30
Acknowledgments ......................................................... 32
References ............................................................ 32

1. Introduction

This article reviews the principles and applications of one of the currently most powerful NMR approaches for the characterization of chain motion in elastomers, entangled
polymer melts and related mobile polymeric systems well above the glass transition. Considering the ubiquitous applications of rubbers, as well as the industrial relevance of melt processing of polymers, the rheological behavior of soft polymeric systems is of central (technological) concern, yet the establishment of quantitative relationships between macroscopic properties and structure and dynamics at the molecular level remains an open challenge.

Melt-like polymer chains exhibit a complex hierarchy of dynamic processes, starting with very fast and local conformational rearrangements on the ps scale, and extending into the range of seconds for slow, diffusive and cooperative motions [1]. Fast local motions are the domain of NMR methods based on longitudinal spin relaxation of suitable nuclei such as protons or carbon-13, where the study of the relaxation dispersion over a large frequency range for the former via field-cycling methods [2–5] or the chemical resolution of the latter [6,7] are the basis of the most powerful strategies, and do not even require isotopic labelling. This class of methods is not covered here and the reader is referred to the cited literature.

Motions that involve a larger number of segments up to the level of whole chains dominate the mechanical properties of soft polymeric systems, emphasizing the need for NMR methods that are sensitive in the corresponding frequency range. Traditionally, transverse relaxation phenomena of protons or deuterons, or, equivalently, line shape analysis in the frequency domain, have been used for that purpose [8–20], and provided the starting point for more

Nomenclature

List of symbols, abbreviations and acronyms

ACF autocorrelation function

\(a(\psi)\) duty-cycle dependent scaling factor

AW Andersen–Weiss

BR butadiene rubber

\(C_{\infty}\) Flory’s characteristic ratio

\(C(t)\) orientation autocorrelation function

CPMG Carr–Purcell–Meiboom–Gill

DCC dipolar coupling constant

DCE dipolar correlation effect

DELM dipolar-encoded longitudinal magnetization

DLS dynamic light scattering

DQ double quantum

\(D_{\text{eff}}\) effective DCC (=\(D_{\text{stat}}/k\))

\(D_{G}\) residual DCC, Gaussian distribution average

\(D_{\text{res}}\) residual DCC

\(D_{\text{stat}}\) static-limit DCC

\(A_{t}\) inter-pulse spacing

FID free induction decay

\(H_{\text{DQ}}\) average (DQ) Hamiltonian

\(H_{J}\) (\(J\) coupling) Hamiltonian

\(I\) spectroscopic intensity

\(\hat{I}(t)\) raising/lowering spin operator

\(J\) scalar coupling

\(k\) scaling factor for the intra-segmental DCC

\(\kappa\) power-law exponent

LM longitudinal magnetization

\(M_{\text{eff}}\) effective static-limit second moment

\(M_{\text{res}}\) residual second moment

\(M_{c}\) network chain molecular weight

\(M_{e}\) entanglement molecular weight

\(M_{\text{me}}\) molecular weight between trapped entanglements

MAS magic-angle spinning

MQ multiple quantum

\(N\) number of statistical (Kuhn) segments

\(n_{c}\) number of pulse sequence cycles

\(n_{\text{DQ}}\) point-by-point normalized DQ intensity

NR natural rubber (poly(cis-1,4-isoprene))

\(P(\ldots)\) probability density

\(P_{2}(\ldots)\) second Legendre polynomial

PB poly(butadiene)

PDMS poly(dimethylsiloxane)

\(\text{phr}\) per hundred rubber

PS poly(styrene)

PS-\(b\)-PB PS-\(block\)-PB copolymer

\(\text{Pt(S-co-AMS)}\) poly(styrene-co-aminomethylstyrene)

\(\phi\) pulse phase

\(\phi_{\text{...}}\) integrated dipolar evolution phase

\(Q\) degree of volume swelling \(V/V_{0}\)

RDC residual dipolar coupling

REDOR rotational-echo double-resonance

SBR styrene–butadiene rubber

\(S_{b}\) dynamic order parameter of the polymer backbone

\(\sum_{\text{MQ}}\) multiple-quantum sum intensity

\(\sigma_{G}\) standard deviation of Gaussian distribution

SEDOR spin–echo double resonance

\(T_{2}^{*}\) apparent transverse relaxation time

\(T_{g}\) glass transition temperature

\(t_{p}\) 90° pulse length

\(t_{c}\) pulse sequence cycle time

\(\tau_{\text{DQ}}\) DQ evolution time

\(\tau_{d}\) disengagement or terminal relaxation time

\(\tau_{e}\) entanglement time

\(\tau_{f/s}\) fast/slow correlation time

\(\tau_{R}\) (longest entanglement-constrained) Rouse time

\(\tau_{z}\) z-filter time

WLF Williams–Landel–Ferry

ZQ zero quantum
specific developments that ultimately led to the introduction of multiple-quantum (MQ) spectroscopy.

An important feature of the dynamics of cross-linked, tethered or entangled chains is the semi-local anisotropy. Fast motions such as Rouse modes are ultimately hindered by the presence of topological restrictions, and long-lived orientation correlations are induced. Their magnitude is directly linked to microscopic parameters such as the cross-link density, the entanglement length, or the "tube diameter", and their lifetime is related to parameters such as the terminal relaxation time or the disengagement time of the tube/reptation model. Consequently, knowledge about local order is highly relevant for the understanding of the material's rheological properties. Already more than 30 years ago, Cohen-Addad [8,16] and some time later yet independently Gotlib [9] had realized that the degree of local order is directly reflected in the transverse evolution of magnetization subject to residual motion-averaged tensorial NMR interactions.

The most straightforward observable is certainly the proton residual dipolar coupling, which renders transverse relaxation curves of long-chain polymers non-exponential since they are dominated by (coherently refocussable) dipolar dephasing. A multitude of often related theories has been presented over the years that address the central problem of describing the shape of relaxation curves and resonance lines, and separating the coherent dipolar effect from true spin relaxation induced by random thermal motion [11,14,17,20–25]. As will be shown below, MQ spectroscopy can help to test the validity of some important model assumptions. Conversely, transverse relaxation decays are notoriously featureless and influenced by a variety of factors, such that the use of multi-parameter functions based on strong model assumptions cannot be expected to provide proof of the validity of a model and may even lead to fitting artifacts.

The existence of "pseudo-solid" spin echoes represents one of the most direct proofs of residual dipolar couplings [26], yet their analysis until now remains mostly qualitative [27]. Improvements directed at a better separation of true transverse relaxation and residual couplings were achieved by clever combinations of Hahn and solid echoes [28–30] or by approaches based on stimulated echoes [31,32]. The former yields a build-up signal that is described by a sine–sine correlation function, also referred to as the "$\beta$" function. This function provides a more reliable basis for fitting, separation and extraction of meaningful parameters, as the coherent dipolar effect causes an intensity build-up, while dynamic effects cause the competing decay.

The essential advantage of MQ spectroscopy is now that it not only yields a build-up function that is essentially identical to the above mentioned sine–sine correlation, i.e., a build-up curve that is dominated by spin-pair double-quantum (DQ) coherences [33], but also that the same experiment provides access to a fully dipolar-refocussed multiple-quantum decay function which can be used to independently analyze the effect of dynamics on the measured data. In networks, where large-scale chain dynamics is mostly absent, the shape of the MQ decay is almost identical to the relaxation part of the DQ build-up signal, such that a temperature-independent normalized build-up function can be obtained that solely depends on the network structure. In this way, reliable information on the distribution of residual couplings, and thus on semi-local dynamic heterogeneity, becomes accessible.

This review is concerned with the foundations and recent applications of proton MQ spectroscopy to a variety of systems such as elastomers of different types, swollen gels and gelling systems, as well as free and confined polymer melts and chains tethered to copolymer blocks and surfaces. It should be emphasized, however, that the central concepts and advantages of MQ spectroscopy, in particular the distribution analysis in networks and the separation of structural and dynamic information, is directly and without any change in the experimental strategy applicable to deuterium. The absence of complications due to multiple coupled spins and the possibility of selective deuteration means that deuterium NMR studies will help to further extend our understanding of polymer dynamics.

2. Basic principles

2.1. Multiscale chain dynamics and residual dipolar couplings

The phenomenological starting point for the understanding of the relationship between polymer chain dynamics and NMR-detected local order is the orientation dependence of the dipolar (or quadrupolar) coupling, which is given by the second Legendre polynomial $P_2(\cos \theta)$. A priori, the angle $\theta$ is the orientation of the internuclear axis with respect to the magnetic field, which fluctuates rapidly and thus mirrors the segmental dynamics. In order to simplify the treatment, one can subsume local and very fast conformational rearrangements on the ps scale into a pre-averaged dipolar tensor. The joint number of monomer units that take part in this pre-averaging can be referred to as an "NMR submolecule" [21,22,24,34]; the associated tensorial interaction is therefore a semi-local quantity. It may be related to the statistical or Kuhn chain segment [35], and the analysis of motions within such a Kuhn segment is the domain of $T_1$ relaxometry and rotational isomeric states models. (Note that this submolecule definition resembles that of Breter [24,34], while in Cohen-Addad’s original work [21,22] it comprises a length scale up to the entanglement length.)

The pre-averaging embodies a rescaling of the static-limit dipolar coupling constant ($D_{\text{stat}}$) by a constant $k$, for which a model needs to be adopted (vide infra). Importantly, $\theta$ then takes on the meaning of the orientation of the local symmetry axis of motion rather
than an individual bond or internuclear vector orientation, and this symmetry axis can safely be assumed to be along the polymer backbone. The time dependence, \( \theta(t) \), therefore monitors orientation fluctuations of the polymer backbone. Its dynamics should be describable in terms of the classical theories of polymer dynamics [1], and its spatio-temporal distribution can be quantified in terms of a uniaxial order parameter. The characteristics of the uniaxial dynamics of \( \theta(t) \) is most conveniently described by the autocorrelation function (ACF) of the second Legendre polynomial,

\[
C(|t_a - t_b|) = \langle P_2(\cos \theta_a)P_2(\cos \theta_b) \rangle. \tag{1}
\]

\( C(t) \) basically gives the probability of finding a chain segment, that has been observed in a particular orientation \( \theta_a \) at time \( t_a \), again in the same orientation after the time \( t = |t_a - t_b| \) has passed. Most theoretical approaches describing NMR relaxation rely on a knowledge of this function.

Fig. 1 gives a schematic representation of the orientation ACF for the case of long-chain polymer melts and networks. The first decay is associated with Rouse-type chain motions. This type of dynamics is ultimately constrained by entanglements or permanent cross-links, whereby a more or less developed plateau arises. In permanently cross-linked networks, the plateau is only weakly affected by slower, cooperative modes, while for entangled linear or end-tethered chains, reptation or arm retraction, respectively, provide effective mechanisms for further loss of correlation. The exact shape of the ACF depends on the complex hierarchy of free, constrained, and cooperative motions. Different models and approximations for the ACF, many of them based on the Rouse/reptation or tube models [1] have been discussed in the context of different NMR studies, yet no consensus has currently been reached on its exact shape.

The height of this plateau is given by the square of what is here defined as the order parameter of the polymer backbone,

\[
S_b = k \frac{D_{\text{res}}}{D_{\text{stat}}} = \frac{3}{5} \frac{r^2}{N}, \tag{2}
\]

where \( D_{\text{res}} \) is the residual dipolar coupling (RDC) that results as a time average over the fluctuations of the dipolar tensor covering the time until the plateau region is reached. The constant \( k \) describes the averaging due to very fast intra-segmental motions. As indicated by the right hand side of Eq. (2), \( S_b \) is related to the ratio \( r \) of the end-to-end vector \( r \) of the chain segment separating the constraints to its average, unperturbed melt-state value \( r_0 = r^2/r_0 \), and to \( N \), the number of statistical (Kuhn) segments between the constraints [38]. The latter provides the link to entanglement theories or theories of rubber elasticity, swelling [39], and stress-optical properties [40] of elastomers. The \( 1/N \)-relationship is very well supported by a variety of NMR experiments, to be addressed below.

Due to the lack of timescale separation, \( S_b \) or, equivalently, \( D_{\text{res}} \) is not easily accessible in polymer melts or lowly cross-linked systems, while a model-free determination of \( D_{\text{res}} \) is feasible for the case of elastomers [36]. In this case, it is possible to fully remove the effect of dynamics from the experimental observables, whereby reliable information even on the distribution of \( D_{\text{res}} \) is attainable. The fitted quantity always represents an average over multiple inter- and intra-segmental dipolar couplings, which means that only an apparent spin-pair \( D_{\text{res}} \) is obtained. It is often given in terms of the related (van Vleck) second moment \( M_{2\text{res}} \),

\[
M_{2\text{res}} = \frac{9}{20} D_{\text{res}}^2. \tag{3}
\]

Thus, \( S_b^2 = M_{2\text{res}}/M_{2\text{eff}} \), when we include the pre-averaging by local conformational rearrangements in an effective rather than static rigid-lattice second moment,

\[
M_{2\text{eff}} = \frac{9}{20} \left( \frac{D_{\text{stat}}}{k} \right)^2. \tag{4}
\]

This, as well as \( D_{\text{eff}} = D_{\text{stat}}/k \), is of course a model-dependent quantity. Note that the occasional neglect of \( k \) is a subject of some confusion in the literature.

The effect of distributions of \( D_{\text{res}} \) on a simple, purely dipolar free-induction decay as well as the corresponding spectra is demonstrated in Fig. 2. Generally, distributions of \( D_{\text{res}} \) lead to a disappearance of characteristic oscillations, but it is important to realize that intermediate-timescale motions and the resulting intensity relaxation have the same qualitative effect, such that a reliable differentiation between the two is not straightforwardly possible. In a variety of works [17,22,23,41–45] proton or deuterium relaxationdecays or lineshapes of elastomers have been analyzed in terms of \( P(r) \), a Gaussian distribution of end-to-end distances between cross-links. In terms of the normalized \( r^2 = r^2/r_0^2 \), \( P(r) \) is given by

\[
P(r) = \frac{4}{\sqrt{\pi}} \left( \frac{3}{2} \right)^{3/2} r^2 \exp \left\{ -\frac{3}{2} r^2 \right\}. \tag{5}
\]
Gaussian statistics is a cornerstone assumption in most theories of polymer dynamics, and it is important to appreciate its potential effect on the measured data. Using Eq. (2), the distribution of $D_{\text{res}}$ is easily obtained as

$$P(D_{\text{res}}) = \frac{2}{\sqrt{27}D_{\text{res}}^{3}} e^{-3D_{\text{res}}/2D_{\text{res}}}.$$  \hspace{1cm} (6)

This is a gamma distribution, whose positive distribution-averaged $D_{\text{res}}$ is directly related to its standard deviation, $\sigma_{D_{\text{res}}}^2 = \frac{D_{\text{res}}^2}{3}$. It should be kept in mind that $P(D_{\text{res}})$ neglects any influence of a potentially serious network chain polydispersity. The solid line in the inset of Fig. 2b may be referred to as “super-Lorentzian”, and its observation in deuterium spectra of elastomers was interpreted as a confirmation of the relevance of Gaussian statistics [41,44,45]. Below, evidence will be presented that suggests that this conclusion is in fact not fully correct.

2.2. The static $^1H$ multiple-quantum experiment

2.2.1. Basic principles

The pulse sequences of the experiments to be discussed in the following are schematically depicted in Fig. 3, and details are given in the cited literature. Many of the results reported herein have been obtained using simple low-field equipment, which was shown to yield data of almost the same quality as a modern high-field spectrometer [47]. The major effects on the NMR observables are dipolar in nature and thus field-independent, and the loss of chemical resolution due to the low field or the absence of MAS does not pose a serious restriction when single-component systems or materials with large mobility contrast (such as block-copolymers) are to be investigated. Intensities are always obtained either by simply measuring the initial FID amplitude, or by signal integration after FT, provided there is sufficient chemical-shift resolution at high field.

The advantages of the MQ experiment are best appreciated by comparison with a simple dipolar FID of a spin-pair, as for instance detected in a Hahn (not solid!) echo experiment. The echo intensity, $I_{\text{echo}}$, is related to $\phi_{\text{echo}}$, the net phase factor (see Fig. 3a), by

$$I_{\text{echo}} = e^{2\pi i \Delta \phi} I_{\text{echo}}^0.$$  \hspace{1cm} (7)

Fig. 2. (a) Distribution functions, $P(|D_{\text{res}}|)$, for residual dipolar coupling constants, $D_{\text{res}}$, with a common average value $D_{\text{res}}/2\pi = 100$ Hz. $\sigma_G$ denotes the standard deviation of a Gaussian distribution. (b) Relaxation functions calculated from Eqs. (7) and (8) using the distributions in (a). The inset shows the corresponding spectra after Fourier transformation. Data replotted from Ref. [37].
\[ I_{\text{echo}}(\tau_{\text{echo}}) = \langle \cos \phi_{\text{echo}}(\tau_{\text{echo}}) \rangle, \]  
(7)

The time-dependent phase factor \( \phi_{\text{echo}} \) (in radians) associated with purely dipolar time evolution reads

\[ \phi_{\text{echo}}(\tau_{\text{echo}}) = \frac{3}{2} D_{\text{eff}} \int_0^{\tau_{\text{echo}}} P_2(\cos \theta_i) \, dt. \]  
(8)

The time dependence of \( \theta_i \) reflects the full hierarchy of motions ranging from orientation fluctuations of the Kuhn segment to large-scale cooperative modes. Assuming all modes up to the length scale of the fixed topological constraints in a permanent network to be fast, the integral in Eq. (8) simply reduces to \( S_b \). As sketched in the upper left of Fig. 4, one would in this case expect to observe purely dipolar FIDs (or spectra) characterized by a well-defined residual dipolar coupling, \( S_b D_{\text{eff}} \). This scenario will be referred to as the “quasi-static” or “fast-motion” limit.

In practice however, there will always be some contribution of molecular motion on the timescale of the experiment. The explicit time dependence of \( \theta_i \) must therefore be considered, and phenomenologically, a damping of the dipolar FID (or a broadened spectrum) is observed. This is sketched at the lower left of Fig. 4. Note that in a dipolar-refocussed solid-echo-type experiment in the absence of motion leading to relaxation, the net phase would be the difference of two equal terms (see Fig. 3a) and thus simply be zero. Consequently, the echo duration dependent signal would then be equal terms (see Fig. 3a) and thus simply be zero. Consequently, the echo duration dependent signal would then be equal terms (see Fig. 3a) and thus simply be zero. Consequently, the echo duration dependent signal would then be equal terms (see Fig. 3a) and thus simply be zero.

While the term “multiple-quantum” experiment implies a conceptually complicated experiment, its theoretical treatment is in fact rather compact when the arguments are restricted to simple spin pairs. In most general terms, time evolution occurs under a pure dipolar DQ Hamiltonian [46].

\[ H_{\text{DQ}} = -\frac{a(\psi)}{2} \sum_{i<j} D_{\text{eff}}(i,j) P_2(\cos \beta_{ij})(I^0_i I^{(j)}_+ + I^{(j)}_+ I^0_i). \]  
(9)

Note that the duty-cycle dependent scaling factor \( a(\psi) \) is usually absorbed into the time axis and neglected in the following for clarity [37]. Focussing on a single pair interaction, the corresponding intensity build-up of DQ coherence, \( I_{\text{DQ}}(\tau_{\text{DQ}}) \), is obtained as

\[ I_{\text{DQ}}(\tau_{\text{DQ}}) = \langle \sin \phi_{\text{DQ1}} \sin \phi_{\text{DQ2}} \rangle. \]  
(10)

where the phase factors \( \phi_{\text{DQ1}} \) and \( \phi_{\text{DQ2}} \) for different average Hamiltonian and thus exhibit a different prefactor.

A salient advantage of the MQ experiment is now that a simple change in the 4-step DQ filtration phase cycle of the receiver provides access to a reference intensity,

\[ I_{\text{ref}}(\tau_{\text{DQ}}) = \langle \cos \phi_{\text{DQ1}} \cos \phi_{\text{DQ2}} \rangle, \]  
(12)

which simply comprises all magnetization that has not evolved into DQ (or, more precisely, \( (4n+2)\)-quantum) coherences. In the spin pair limit, it just comprises dipolar-encoded longitudinal magnetization (DELM), which can also be used for separate analysis [49].

---

**Fig. 4.** Comparison of the results of “conventional” experiments (dipolar or quadrupolar spectra and the corresponding shift-compensated FIDs) and an MQ experiment for the cases of isolated spins or spin pairs without relaxation and real elastomers. The given relations describe the form of the signal function for the ideal, “quasi-static” case without relaxation.
The sum of the two possible signal functions $I_{\Sigma MQ}$ is

$$I_{\Sigma MQ}(\tau_{DQ}) = \langle \sin \phi_{DQ1} \sin \phi_{DQ2} \rangle + \langle \cos \phi_{DQ1} \cos \phi_{DQ2} \rangle.$$  

(13)

This is a fully dipolar refocussed intensity that decays only as a result of molecular motion that renders $\phi_{DQ1} \neq \phi_{DQ2}$. The phenomenological behavior of the signal functions $I_{DQ}(\tau_{DQ})$ and $I_{\Sigma MQ}(\tau_{DQ})$ for the quasi-static and real cases is shown at the right side of Fig. 4.

It turns out that in networks, the relaxation contributions to $I_{DQ}(\tau_{DQ})$ and $I_{\Sigma MQ}(\tau_{DQ})$ are nearly equal, such that the effect of molecular motion on $I_{DQ}(\tau_{DQ})$ can be removed by point-by-point division to give $I_{\Delta DQ}$, the so-called normalized DQ intensity (not to be confused with the “trivial” and customary normalization of experimental intensities to, for example, the full intensity after a 90° pulse):

$$I_{\Delta DQ}(\tau_{DQ}) = I_{DQ}(\tau_{DQ}) / I_{\Sigma MQ}(\tau_{DQ}).$$  

(14)

This now carries only structural information, and can be analyzed in the quasi-static limit even in terms of distributions of $D_{\text{res}}$. The approach is easily validated by the observation that $I_{\Delta DQ}(\tau_{DQ})$ is independent of temperature over an interval exceeding 100 K, as is shown in Fig. 6.

In the absence of relaxation effects, $I_{\Delta DQ}(\tau_{DQ})$ is given by Eq. (10) with equal phases, $\langle \sin \phi_{DQ}^2 \rangle$. Under the assumption of static Gaussian statistics for the associated interaction frequency $\omega \sim \phi_{DQ}/\tau_{DQ}$, which is approximately provided by the powder average (see Fig. 5), the second-moment approximation of the DQ build-up reads

$$I_{\Delta DQ}(\tau_{DQ}) = \frac{1}{2} \left( 1 - \exp \left\{ -\frac{8}{9} M_{\text{res}}^2 \tau_{DQ}^2 \right\} \right)$$

$$= \frac{1}{2} \left( 1 - \exp \left\{ -\frac{2}{5} D_{\text{res}}^2 \tau_{DQ}^2 \right\} \right).$$  

(15)

A comparison of this result with the powder-averaged signal $\langle \sin \phi_{DQ}^2 \rangle$, Eq. (10), as well as experimental data is shown in Fig. 6. The strong oscillations of the powder-averaged spin-pair signal are not very apparent in experimental data, which is a consequence of multiple couplings, as evidenced by multi-spin simulations (see Fig. 20). In particular this latter comparison shows that Eq. (15) approximates the build-up function of a monomeric unit very well up to $I_{\Delta DQ} = 0.45$. Equating this value with Eq. (15) yields a definition of an operationally defined fitting limit,

$$\tau_{DQ}^{\text{max}} = 2.4 / D_{\text{res}},$$  

(16)

that should always be enforced to minimize systematic errors. When more complicated functions comprising distributions or correlation times (see Section 3.3) are used for fitting, $\tau_{DQ}^{\text{max}}$ must be iteratively adjusted to the current best-fit value of $D_{\text{res}}$.

A distribution of residual couplings, which is in the simplest case related to the chemical heterogeneity (e.g., styrene–butadiene rubber, SBR), lead to deviations from the inverted Gaussian shape. The most general approach is to use Eq. (15) as the kernel function in a regularized inversion of the distribution interval, and details and limitations are discussed in Ref. [37]. For narrower spreads of frequencies, one can assume the shape of the distribution function to be Gaussian (see Fig. 2), whereby the distribution integral over Eq. (15) can be evaluated analytically, giving

$$I_{\Delta DQ}(\tau_{DQ}) = \frac{1}{2} \left( 1 - \exp \left\{ -\frac{4 \sigma_G^2 \tau_{DQ}^2}{\pi \tau_{G}^2 \tau_{DQ}^2} \right\} \right) \left( \sqrt{1 + \frac{2}{3} \sigma_G^2 \tau_{DQ}^2} \right)$$  

(17)

$D_G$ and $\sigma_G$ are the average apparent RDC constant and the standard deviation, respectively. Note that fits to this function make physical sense only as long as $\sigma_G$ is substantially smaller than $D_G$. For samples with clear-cut bimodality, stable fits of weighted two-component superpositions of Eqs. (15) or (17) are also possible. For completeness, I also give the the second-moment approximation to the Hahn echo decay function, Eq. (7),

$$I_{\text{echo}}(\tau_{\text{echo}}) = \exp \left\{ -\frac{9}{40} D_{\text{res}}^2 \tau_{\text{echo}}^2 \right\}.$$  

(18)
2.2.2. Conceptual details and data treatment

Following the established rules of coherence order selection [50], the acquisition of a reference intensity that forms the full complement of $I_{\text{DQ}}(\tau_{\text{DQ}})$ is only possible for DQ coherence selection using a 4-step phase cycle $(x, y, -x, -y)$ of the carrier phase difference $\Delta \Phi$ (see Fig. 3). Then, the receiver phase cycle is $(x, -y, x, -x)$ for $I_{\text{DQ}}(\tau_{\text{DQ}})$ and $(x, x, x, x)$ for $I_{\text{ref}}(\tau_{\text{DQ}})$. These phase cycles in fact select all coherences of order $(4n + 2)$ and $(4n)$, respectively, and many higher coherence orders do indeed play a role, since the average DQ Hamiltonian, Eq. (9), excites all $2n$ coherence orders. An important consequence of long-time spin dynamics spanning the full Liouville space of even quantum orders is the equal intensity partition among $I_{\text{DQ}}(\tau_{\text{DQ}})$ and $I_{\text{ref}}(\tau_{\text{DQ}})$. This means that $I_{\text{nDQ}}(\tau_{\text{DQ}})$ in networks always attains a long-time intensity plateau at 50% (the same holds for isolated pairs, but not for finite odd-numbered clusters such as methyl groups). This is shown in Fig. 7. Note that $I_{\text{nDQ}}(\tau_{\text{DQ}})$ becomes unreliable at longer evolution times, where $I_{\text{DQ}}(\tau_{\text{DQ}})$ has decayed to a very low level.

Spin counting experiments [46], which are based on a discrete smaller-step incrementation of $\Delta \Phi$ and subsequent Fourier transformation over this phase dimension, can be used to assess the effect of higher-quantum coherences on the measured intensities [37]. The data plotted in Fig. 7 gives convincing evidence that higher-quantum orders are indeed not important until well into the plateau region of the proton nDQ build-up curve of a typical rubber. The initial rise. Note that transverse relaxation data, which gives convincing evidence that higher-quantum orders are indeed not important until well into the plateau region of the proton nDQ build-up curve of a typical rubber. The initial rise.

So far the simplified assumption that the investigated material consists only of elastically active network chains has been made. Usually, additional components such as short dangling chains, sol, or some solvent may be present. The dynamics of these components are usually isotropic on rather short timescales, such that no observable dipolar coupling remains. These parts are therefore detected only in the reference experiment, and thus form more slowly decaying long-time tails of $I_{\text{SMQ}}(\tau_{\text{DQ}})$. In order for the normalization approach to be successful and to observe a 50% intensity plateau for $I_{\text{nDQ}}(\tau_{\text{DQ}})$, it is necessary to remove these contributions by suitable fitting and subtraction of the tails. Tails are also observed in $T_2$ relaxation curves; they are schematically shown in Fig. 4.

Multicomponent fits of transverse relaxation data are always subject to potentially uncontrolled interdependencies of individual fitting parameters, in particular when the exact functional forms of the components are unknown. The MQ experiment has some features that provide a more reliable separation of different components in the case of permanent elastomers [51].

Singly exponential tails, as observed in our work on dry and swollen PDMS networks [37,52] are easily identified by straight lines in a semi-logarithmic plot of $I_{\text{SMQ}}(\tau_{\text{DQ}})$, see Fig. 8a. Notably, the amount of the mobile contributions changes with temperature, which indicates its origin to be from partially hindered dangling chains: larger and larger fractions of such chains appear isotropically mobile when the entanglement effect on their ends is reduced by arm retraction processes. Fitting and subtracting them, and using Eq. (14), leads to $I_{\text{nDQ}}(\tau_{\text{DQ}})$ curves such as the ones in Fig. 6 that are temperature independent over the whole investigated range.

In the case of styrene–butadiene rubber, and sometimes also butadiene rubber and natural rubber, a second, more rapidly decaying component of $I_{\text{SMQ}}(\tau_{\text{DQ}})$ (or $I_{\text{ref}}(\tau_{\text{DQ}})$) appears. Since these polymers are less mobile (=closer to $T_g$ at common experimental temperatures), this component may be associated with dangling chains ($B$), while the long time tail is attributed to low molecular weight sol components ($C$). The associated value of $T_\infty^{C}$ is usually long enough to be reliably fitted and subtracted.

Due to the similarity of its apparent $T_\infty^{B}$ to the long-time decay of actual multiple-quantum coherences in $I_{\text{DQ}}(\tau_{\text{DQ}})$ and $I_{\text{ref}}(\tau_{\text{DQ}})$, it is often not possible to simply subtract a second exponential tail. The trick to solve this problem is based on the notion that $I_{\text{DQ}}(\tau_{\text{DQ}}) = I_{\text{ref}}(\tau_{\text{DQ}})$ in the long-time limit. As shown in Fig. 8b, the $B$ fraction is more reliably identified and fitted in a semi-logarithmic plot of $I_{\text{ref}}(\tau_{\text{DQ}}) - I_{\text{DQ}}(\tau_{\text{DQ}}) - Ce^{-2\tau_{\text{DQ}}/T_\infty^{C}}$ vs. $\tau_{\text{DQ}}$, where the interval over which the $B$ component decays linearly is substantially prolonged. With $B$ determined, the final formula for $I_{\text{SMQ}}(\tau_{\text{DQ}})$ is thus

$$I_{\text{SMQ}}(\tau_{\text{DQ}}) = I_{\text{DQ}}(\tau_{\text{DQ}}) + I_{\text{ref}}(\tau_{\text{DQ}}) - Be^{-2\tau_{\text{DQ}}/T_\infty^{B}} - Ce^{-2\tau_{\text{DQ}}/T_\infty^{C}},$$

(19)
where \( B \) and \( C \) are the fraction of dangling and sol chains, respectively. The fraction \( A \) of network chains is easily obtained as \( A = 1 - B - C \) when \( I_{\text{ref}}(\tau_{\text{DQ}}) \) is normalized to 1 for \( \tau_{\text{DQ}} = 0 \).

It should be mentioned that the amplitudes, and to a larger extent, the apparent relaxation times of the contributions \( B \) and \( C \), are affected by the long-time performance of the pulse sequence, which in turn depends on the rf homogeneity, the quality of the spectrometer setup, and other factors. This is probably the reason why solvent and dangling-chain contributions cannot be separated in the case of PDMS, where the apparent relaxation times of the contributions, however, the initial rise of \( I_{\text{DQ}}(\tau_{\text{DQ}}) \) is only weakly affected even when the mobile contributions are not modelled and subtracted precisely [51].

2.2.3. Advanced approaches

When the network chain content is known already or not of central interest, the isotropically mobile contributions can also be removed by appending a second fixed DQ excitation/reconversion sequence block before the actual incremented DQ pulse sequence [37]. The nested phase cycle is constructed such that DQ coherences (that arise only from the network fraction) are selected by the first block, while the second block is used to probe either \( I_{\text{DQ}}(\tau_{\text{DQ}}) \) or \( I_{\text{ref}}(\tau_{\text{DQ}}) \). The success of this procedure is shown in Fig. 9a.

Of crucial importance is the period \( \tau_z \) between the two parts of the experiment, during which spin exchange may occur. The DQ pre-selection of course excites segments associated with different orientations of the RDC tensor with respect to \( B_0 \) with different efficiency, which means that the isotropic powder average, needed for an unambiguous analysis of the final build-up curve, is broken. This effect is demonstrated in Fig. 9b for the case of \( \tau_z = 0 \). In order to avoid such complications one can just use a value of \( \tau_z \) on the order of 100 ms to ensure complete re-equilibration. Note that for experiments with short \( \tau_z \) it is important to construct the phase cycle such that only coherences of order 0 (mostly longitudinal magnetization and some ZQ coherences that result from two consecutive DQ transitions) are retained during this interval.

A powerful experimental strategy, yet to be used in actual applications, is to monitor the recovery of the isotropic powder distribution by incrementing \( \tau_z \) (see Fig. 9c). Flip-flop-mediated spin diffusion or slow reorientations of the RDC tensor are possible processes explaining the behavior, and temperature-dependent studies can be used to differentiate between the two scenarios. Considering that slow reorientations are probably absent in permanent elomers (vide infra), spin diffusion is the most likely candidate. Thus, using spin diffusion coefficients that can be estimated from \( T_2 \) experiments [54], one could gain access to the length scale of correlated RDC tensor orientations, or the size of regions of different cross-link density in heterogeneous rubbers.

2.3. Limitations of transverse relaxometry

As mentioned, Hahn echo experiments are a popular alternative to MQ experiments in rubber applications. In the framework of the Andersen–Weiss theory [55], the echo intensity \( I_{\text{echo}}(\tau_{\text{echo}}) \) can be evaluated from Eqs. (7) and (8) on the basis of a slow-motion model for the RDC tensor reorientation process. That is, only an exponential long-time decay of the correlation function in Fig. 1, with a decay time of \( \tau_s \), is explicitly considered [11]. This yields a three-parameter fitting function for the network component (A):

\[
I_{\text{echo}}(\tau_{\text{echo}}) = \exp \left\{-\frac{9}{20} D_{\text{ref}}^2 \tau_s^2 \left[ e^{-\tau_{\text{echo}}/\tau_s} + \frac{\tau_{\text{echo}}}{\tau_s} - 1 \right] \right\}.
\]
$T_{2A}$ should phenomenologically parametrize the influence of the initial fast decay of the correlation function, and is often neglected. As will be unambiguously proven in Section 3.3, the slow-motion model is incorrect, yet since it is still rather popular \cite{13,15,18,56}, the serious limitations inherent in the use of Eq. (20) must be emphasized \cite{53}.

Using proton Hahn-echo experiments at 400 MHz proton frequency in combination with Eq. (20), Luo et al. \cite{56} have studied residual dipolar couplings in a series of styrene–butadiene rubber filled with different amounts of carbon black and silica. In agreement with earlier work in the field, their data was interpreted as indicating a substantial increase of the effective cross-link density with increasing filler content (Fig. 10a). This, however, is an artifact related to fitting ambiguities resulting from parameter interdependencies, which is directly proven by the observation of a contradictory trend when the same samples are investigated at 20 MHz and analyzed in the same way (Fig. 10b). Therefore, slight field-dependent changes in the shape of the relaxation curves, which are of course not covered by the model underlying Eq. (20), bias the fitting results into different directions. The origin of the (weak) field dependence is as yet unclear, yet molecular motion in combination with susceptibility contrast around nanoscopic void spaces appears to be a possible candidate \cite{57}.

In fact, the rubber matrix turned out to be virtually unaffected by the presence of filler, as clearly corroborated by proton MQ experiments conducted on the same sample series at 500 MHz \cite{51}, see Fig. 10c. In this graph, both the average RDC from a regularization analysis, and results from a single-parameter fit using Eq. (15) are given, and as expected for distributed quantities, the values differ due to the way the average is taken. Notably, as shown in Fig. 10d, fitting the 20 MHz data with the static-limit fitting function Eq. (18) yields the same results. The corresponding fits are of course only poor representations of the actual data (since no distribution is explicitly accounted for), but they do provide a stable average over the existing RDC distribution. In conclusion, Eq. (20) should not be used for the analysis of Hahn echo experiments on elastomers.

Another, even more subtle artifact in RDC determinations arises when elastomers with different chemical functionalities are investigated by proton Hahn-echo relaxometry at high magnetic field \cite{58}. At Larmor frequencies of a few hundred MHz for protons, a limited chemical shift resolution makes it possible to detect RDCs specifically for the resolved resonances even in static spectra. Along these lines, Steren et al. \cite{59} have claimed weaker RDCs associated with the olefinic proton methine resonance in natural rubber when compared to the RDCs detected at the (overlapped) CH$_2$/CH$_3$ signal positions. The effect can be inspected for the resolved Hahn echo data plotted in Fig. 11. These observations are again in marked contrast to the results of MQ experiments \cite{60}, which indicate virtually identical $D_{eq}$ (see Section 3.2).

The explanation is as follows: the methine resonance comprises a single proton that is primarily coupled to neighboring methene and methyl protons rather than its own kind one monomer unit away (for a proof see the 2D DQ correlation spectrum in Ref. \cite{58}). Apart from...
the dipolar couplings between CH and CH$_2$/CH$_3$, the chemical shift separation of 3.5 ppm amounts to 1750 Hz at 500 MHz, which clearly exceeds the average dipolar coupling of a few hundred Hz experienced by the CH group. Since the homonuclear dipolar and the chemical shift difference Hamiltonians do not commute, the homonuclear dipolar coupling is effectively averaged to the weak coupling limit by the chemical shift difference [61]. This amounts to a factor of 2/3 for the apparent dipolar coupling, in agreement with the observation of the Hahn echo decay at high field.

When the chemical shift difference is effectively removed by either performing experiments at low Larmor frequency or by using a repetitive pulse sequence that provides rapid shift refocussing, the strong coupling limit applies and the factor 2/3 disappears. The Baum/Pines MQ experiment, which we apply in a repetitive fashion ($n_c$ incrementation) at high field for exactly this reason, does provide this rapid refocussing, as chemical shifts are compensated over a single cycle. Alternatively, CPMG experiments can be performed, where of course always the last echo of an incremented train needs to be Fourier-transformed to obtain a spectrum. The results in Fig. 11 nicely show that the CPMG-detected initial decay of CH and CH$_2$/CH$_3$ magnetization is indeed almost identical. Note that this result is not much dependent on the pulse spacing in the CPMG trains; slight differences arise only for the apparent $T_2$ values of the sol contributions detected at the different resonances (this may well be a genuine effect related to the fact that the fast segmental averaging process that ultimately leads to similar RDCs and causes this $T_2$ decay has different local geometries).

In summary, MQ spectroscopy has been found to be the most reliable tool for the analysis of elastomer microstructure, as it intrinsically avoids artifacts related to non-dipolar effects on the analyzed build-up functions. Further, as a genuine advantage, it provides access to the RDC distribution, which in the case of Hahn echoes is always masked by effects of intermediate motions.

### 2.4. Comparison of DQ excitation schemes

As an alternative to the lengthy Baum/Pines sequence presented above, one may simply use a two-pulse segment ($\pi_2$) for MQ excitation and reconversion. Transverse magnetization created by the first pulse then undergoes free dipolar evolution (as in a Hahn echo experiment), and after $\tau_{\text{DQ}}$, the resulting two- and higher-spin antiphase coherences are converted into various MQ coherences by the second pulse. Free dipolar evolution during $\tau_{\text{DQ}}$ features the common prefactor of 3/2, rendering the build-up quicker, yet less efficient as to the excitation of higher-order coherences than the Baum-Pines sequence. When just spin pairs are considered, the theory discussed in Section 2.2.1 is fully valid apart from this multiplicative correction. In order to improve the long-time performance of the two-pulse sequence, a refocussing $\pi$ pulse needs to be added in the center, and the version with equal phases.

---

**Fig. 10.** Proton residual dipolar couplings measured in SBR as a function of filler loading, given in per hundred rubber (phr). (a) and (b) Hahn-echo relaxometry at 400 and 20 MHz, both using Eq. (20) for data analysis, (c) static DQ spectroscopy at 500 MHz, (d) single-parameter fits to 20 MHz data using Eq. (18). Sol and dangling chain contributions were always subtracted before fitting. Data replotted from Ref. [53].

**Fig. 11.** Proton transverse relaxation data of the resonances of NR that are resolved at 500 MHz. For the CPMG experiments, the $\pi$ pulse spacing $\Delta_n$ is given in the legend. Data replotted from Ref. [58].
(\frac{\pi}{2}) - \tau_{DQ}/2 - (\pi) - \tau_{DQ}/2 - (\frac{\pi}{2})$, has shown the best performance in our experiments.

The short two-pulse segment has the decisive advantage that it provides access to strong, even rigid-limit dipolar couplings on the order of 10 kHz. In this regime, the intensity decays almost completely during a single cycle of the Baum/Pines sequence, whose minimum duration is around 50 µs under favorable conditions (short pulses, short phase switching times). The two-pulse segment has been used extensively in many applications of MQ spectroscopy by the Aachen group. They are reviewed in Ref. [62], and Refs. [49,63,64] are the most detailed accounts of applications to elastomers. However, these papers do not go into too much detail as to the actual data treatment, the fitting procedure and its limitations (they are particularly vague about the essential prefactor in the functions used for fitting). In this section, I therefore present some as yet unpublished results concerning a detailed comparison of the two alternative experiments, theoretically as well as experimentally.

The most important difference between the two experiments is that dipolar time-reversal is not possible with the two-pulse segment. The sign of the average Hamiltonian of the Baum/Pines sequence, Eq. (9), is easily inverted by a 90° shift of the carrier phase. This provides the possibility of assembling a fully dipolar refocussed sum intensity $I_{EMO}(\tau_{DQ})$, to be used for point-by-point normalization and removal of relaxation effects. This strategy may not be straightforwardly applicable to the two-pulse segment, where an additional intensity decay occurs due to the homogeneous nature of free multi-spin homonuclear dipolar evolution. The same effect is also responsible for the well-known inability of the solid echo to refocus multiple dipolar couplings. The Baum/Pines experiment in turn can in that sense be compared to a magic-sandwich echo [65], which does provide full dipolar time reversal.

Fig. 12 shows build-up data based on 6-spin simulations of a part of a poly(butadiene) chain fluctuating rapidly (fast, quasi-static limit) with an order parameter of 0.01 (see [60] for details). The lines are for the Baum/Pines MQ experiment, where it is seen that the DQ (more precisely: $2Q + 6Q$) build-up curve reaches the expected intensity plateau at 50% of the full magnetization. In the absence of motion $I_{DQ}(\tau_{DQ})$ therefore equals $I_{DQ}(\tau_{DQ})$, and $I_{EMO}(\tau_{DQ}) = I_{ref}(\tau_{DQ}) + I_{DQ}(\tau_{DQ})$ is always unity (full dipolar "echo"). To the contrary, $I_{DQ}(\tau_{DQ})$ excited by the two-pulse segment does not reach the 50% limit, and $I_{ref}(\tau_{DQ}) + I_{DQ}(\tau_{DQ})$ is subject to notable homogeneous dephasing. A normalization may nevertheless be attempted, and it is seen that, apart from oscillations arising from the limited number of simulated spins, $I_{DQ}(\tau_{DQ})$ also approaches 0.5. As expected from the higher prefactor of free dipolar evolution, this curve rises faster than $I_{DQ}(\tau_{DQ})$ of the Baum/Pines sequence, and their initial parts coincide once the time axis is scaled by 3/2.

These observations are quantitatively reproduced in the corresponding experiments, see Fig. 13. Here, the decay of $I_{EMO}(\tau_{DQ})$ from the Baum/Pines experiment is mainly caused by molecular dynamics, while for the two-pulse segment, a strong additional dephasing is apparent. This means that information about dynamic timescales cannot straightforwardly be extracted from the latter experiment. Consequently, Demco and coworkers have introduced the analysis of the fully shift- and dipolar-refocussed decay of a mixed magic-sandwich echo [66] as the appropriate means to assess dynamic timescales in elastomers [48]. Their theory provides a basis for the more reliable joint analysis of intensity build-up and decay in the Baum/Pines MQ experiment discussed in Section 3.3.
The build-up of $I_{DQ}(\tau_{DQ})$ of the two-pulse segment is delayed at intermediate times, in accordance with dephasing effects that cannot be normalized away completely. This means that single-parameter fits using Eq. (15) with the correct prefactor yield lower values of RDCs. Fits may well be restricted to the very initial rise, yet a bias towards large values must be expected for networks with broader distributions of residual couplings. As is however apparent from the observation of an intensity plateau at $I_{DQ} = 0.5$, the arguments concerning an equal intensity distribution among $4n + 2$ and $4n$ higher-order coherences over $I_{DQ}(\tau_{DQ})$ and $I_{ref}(\tau_{DQ})$ remain valid, whereby the analysis of $I_{ref}(\tau_{DQ}) - I_{DQ}(\tau_{DQ})$ proposed in Section 2.2.2 should also be a good way of performing the important extraction of the mobile fraction. This aspect is crucial, because when $I_{DQ}(\tau_{DQ})$ is to be fitted without point-by-point normalization, its intensity scale must be adjusted to network components only. Otherwise, an uncontrolled average over network chains and non-coupled sol is obtained.

Initial build-up data from the two-pulse segment is commonly fitted to the first parabolic term $\sim D_{res} \tau_{DQ}$ in the Taylor expansions of Eqs. (10) or (15), corrected by 3/2 exponential, while Fig. 13 clearly shows a non-exponential behavior. The cross-link density, and the geometry and timescales of chain dynamics of common elastomers.

$3.1. \text{Chain order distributions and heterogeneities}$

Bimodal end-linked poly(dimethylsiloxane) networks were investigated as a test case for the quantitative assessment of heterogeneity in the local cross-link density [37]. Bimodal networks with a large difference in constituent chain length are known to be phase-separated on the nanometer scale [67,68]. This is basically a statistical consequence of the fact that the short chains provide the vast majority of reactive chain ends and thus mainly undergo cross-linking with themselves, even at rather low concentration.

The increasingly steep build-up curves in Fig. 15 give a direct indication of the growing average cross-link density upon increasing the short-chain content. Notably, the build-up curves of the mixed systems show distinct differences in their shape. In order to provide unambiguous proof that the shape of the curves reflect microscopic heterogeneity, one can simply compare these curves with linear combinations of the pure-component responses using the correct stoichiometry. The success of this approach speaks for itself; the results thus indicate that normalized DQ build-up curves obtained using the Baum/Pines sequence can with good confidence be analyzed in terms of distributions of residual couplings. Generally, it should be pointed out that this applies only to permanent networks, for which the point-by-point normalization is successful in rendering the results temperature-independent.

Fig. 14. Fits to proton DQ build-up data of protons at 20 MHz for cis-butadiene rubber at two different temperatures. In agreement with common practice in the respective literature, normalized $I_{DQ}(\tau_{DQ})$ data using the Baum/Pines sequence were fitted to Eq. (15), while the fits to non-normalized $I_{DQ}(\tau_{DQ})$ excited by the two-pulse segment contain an additional exponential damping term, Eq. (21). Note that the latter data was divided by (1-%sol) to take into account that DQ intensities arise only from the network fraction. The fitting limits are indicated by vertical bars and are based on the validity limit of the spin-pair approximation.

3. Applications to elastomers

This section summarizes results that were mostly obtained using the Baum/Pines version of the proton MQ experiment, and many of them were measured on simple low-field spectrometers. MQ NMR is shown to provide information on heterogeneous microstructure and swelling behavior, the cross-link density, and the geometry and timescales of chain dynamics of common elastomers.
Apart from fitting build-up curves to the quasi-static approximation formula, Eq. (15), or multi-component superpositions thereof, one can assume the coupling distribution to be Gaussian (see Fig. 2a), and use Eq. (17) to obtain an averaged value of $D_G$ and the standard deviation $\sigma_G$. The most general approach is to use Eq. (15) as the Kernel function in a regularized inversion procedure to obtain an estimate of the actual distribution function [37].

It must be mentioned that systematic errors on the 20% level cannot be avoided, as Eq. (15) does not describe the slight intensity maximum observed experimentally, whereby the more strongly coupled components are always slightly overestimated. Another limitation arises for very wide distributions with components that have very different $\ell_{EMO(TDQ)}$ decay times. Then, the more weakly coupled components are progressively overestimated, as the full $\ell_{EMO(TDQ)}$ used for point-by-point normalization lacks the more strongly coupled contributions and changes the relative scale of $I_{DQ(TDQ)}$. Generally, the distribution assessment is reliable in this respect as long as $\ell_{EMO}$ does not decay substantially until $I_{DQ(TDQ)}$ has reached 0.45. Raising the temperature, it is usually possible to reach the safe regime in which the result is temperature independent.

A comparison of $D_{res}$ distributions measured on different types of elastomers is presented in Fig. 16. The bimodal networks yield nicely bimodal distribution functions (Fig. 16a). Notably, the maximum associated with the more weakly coupled longer chains does not shift appreciably, indicating that the long-chain dynamics is not substantially influenced by the presence of the short-chain clusters.

For the case of styrene–butadiene rubber (Fig. 16b), rather wide distributions are obtained, which, in view of the much narrower distributions obtained for chemically uniform systems, is interpreted in terms of different RDCs associated with the different monomeric units. As it is also apparent from this set of data, the presence of filler particles, carbon black as well as silanized silica, does not appreciably change the cross-link density of the rubber matrix. This finding is in stark contrast to results from $T_2$ relaxometry, and the results shown here lead the way to the identification of the serious fitting artifacts associated with the latter approach, as discussed in Section 2.3.
The most important results from the point of view of polymer physics are the distributions of $D_{\text{res}}$ measured for natural rubber (Fig. 16c). Apart from weak contributions of more strongly coupled chains, associated with preparation-specific heterogeneities, these distributions are extremely narrow over the whole range of cross-link densities investigated, and a number of important conclusions can be drawn.

The virtual single-component nature of the result is in decisive contrast to what is expected from (i) the Gaussian distribution of end-to-end distances of network chains, which should lead to a gamma distribution of couplings, Eq. (6), and (ii) the polydispersity of network chain lengths, which should be described by an exponential distribution [69]. The non-observation of any type of distribution effect means that chain order, as perceived by NMR, is measured as an average over a region in space spanning several network chain dimensions. Even more consequentially, this means that network chain entropy, as determined by the number of accessible conformational microstates, cannot be described in terms of single-chain concepts; it is dominated by cooperativity.

In this regard, it is interesting to consider the result of a recent transverse relaxation study of Cohen-Addad [70], in which the influence of chain ends on orientation correlations in entangled melts was studied by means of comparing fully hydrogenous chains with selectively end-deuterated ones. The central result was that the long tail of the relaxation curves, that is commonly attributed to the isotropically mobile unentangled end parts, is still observed when extended end sections are deuterated. This was interpreted in terms of mobilization of the inner parts of chains that are in proximity to the ends of other chains, confirming a picture where the detected chain order is averaged over a certain region in space. This interpretation now provides a rationale for the non-observation of substantial distribution effects on the distribution of residual couplings between protons measured by MQ spectroscopy, and such observations may provide a crucial test criterion for refined theories of chain dynamics and rubber elasticity.

These findings challenge many (NMR-) works that, directly or indirectly, rest upon the assumption of Gaussian chain statistics. Proton relaxation functions [17,22,23] as well as $^2$H lineshapes [41–43] have been described in terms of such statistics. A question to be addressed is of course why experimental $^2$H lineshapes [41,44,45] sometimes do resemble the “super-Lorentzian” calculated on the basis of the gamma distribution (Fig. 2c). We explain this first by the presence of sol- and dangling-chain contributions, which always lead to a sharp spectral center, and by the additional effect of intermediate motions, that do affect $^2$H lineshapes, but can be normalized away in an MQ experiment.

The importance of cooperativity is also supported by the observation of a splitting in $^2$H spectra of strained elastomers [41,71,72], which is unexplainable in terms of the common single-chain model [42,43]. An orientational mean field has been invoked as an explanation [42,73], and our results indicate that the associated cooperative packing effect, potentially attributable to entanglement effects and describable in terms of tube models [1,74,75], might also be active in unstrained elastomers. Note also that deuteron signals from probe molecules or oligomers that perform a (restricted) diffusive average over a certain region in space always exhibit a well-defined splitting in strained elastomers [76–78], and sol and dangling chains fall in the same category. Therefore, the observation of a splitting in the sharp spectral center is always expected.

This section is concluded with an actual application of distribution analysis in γ-irradiated, silicone elastomers by Maxwell and coworkers [79,80]. The subject of this study was a commercially available silica-filled peroxide-cured system that consists mainly of poly(dimethylsiloxane), and the aim was to investigate the resistance of this highly robust material to radiation-induced damage. Typical proton nDQ build-up curves are shown in Fig. 17. Their shape is similar to those of the bimodal networks of Fig. 15, and indeed, it was possible to reliably fit the data to a bimodal model based on Eq. (15), yielding two residual couplings and a relative weight.

The bimodality was attributed to the highly abundant (~30 wt%) silica filler, with more highly cross-linked domains in the vicinity of the particle surfaces, that might either contribute additional chemical or physical links, or affect the cross-linking reaction. The results shown in Fig. 18 indicate a slight increase of the cross-link density in both domains upon γ-irradiation. Notably, the amount of more highly cross-linked material is also increased substantially, which means that the irradiation effect is not homogeneous over different domains.

![Fig. 17. Normalized 400 MHz proton DQ build-up curves for filled silicone elastomers exposed to different doses of γ-irradiation given in kGray.](image)
3.2. Quantitative interpretation of residual couplings

In order to convert the NMR-determined RDCs into a cross-link density (or the average molecular weight of a network chain, \(M_c\)), a model needs to be adopted [60]. This comprises two major steps. Following Eq. (2), a properly defined "rigid-limit" coupling \(D_{\text{stat}}/k\) is first to be determined in order to obtain a backbone order parameter \(S_b\). This reference value should comprise an average over all fast conformational fluctuations that occur within a single statistical (Kuhn) segment.

Second, under the assumption of Gaussian statistics, \(S_b\) yields the number of statistical segments \(N\), which in turn can be converted into \(M_c\) using the known characteristic ratio \(C_{\text{wc}}\) [81]. As is obvious from the preceding section, the assumption of Gaussian statistics, and therefore the prefactor 3/5 in Eq. (2), is critical. Our computer simulations [82] show that the value of the prefactor in fact depends on details of the fluctuation statistics (as a consequence of the tensorial nature of the averaged quantity), and that particularly serious deviations from the value of 3/5 can occur in the swollen state, where solvent quality (size of the excluded volume interaction) plays a significant role (see Section 3.4 for details). In the following, these complications are neglected, and a comparison of results for different network systems will show that this is not the only source of ambiguity.

Coming back to the first step, our approach to define a reference \(D_{\text{stat}}/k\) is based on spin dynamics simulations of a small segment of the polymer backbone comprising each of the different types of protons and its most strongly coupled neighbors (4–7 ones need to be taken into account to obtain build-up curves whose initial parts are almost independent of the spin system size). The chain within the Kuhn segment is supposed to be extended (a common but not unquestioned assumption [83]) and best approximated by the lowest-energy conformation adopted in the crystal structure. Intra-segmental motions are mimicked by a simple rotation, where the only free parameter of the model is the orientation of the local rotation axis with respect to the backbone orientation.

The orientation of the rotation axis is optimized by comparing the results of numerous simulations to experimental constraints, namely (i) group-specific build-up curves detected for the different types of protons that are resolved at high field, and (ii) the ratio of intra-group DQ coherence intensities to coherences involving two different types of protons. The latter information can be obtained from 2D DQ correlation spectra such as the one shown in Fig. 19, where the former appear on the diagonal, and the latter as off-diagonal intensities. This general approach was first introduced by Graf et al. [33], who used highly resolved magic-angle spinning (MAS) spectra and a DQ recoupling sequence to detect the site/pair-specific build-up in linear poly(butadiene) (see also Fig. 32a). Their conclusions, based on spin-pair considerations, may be somewhat challenged by the complication that the intensity scale for each of the build-up curves is not easy to define. It must comprise

![Fig. 18. Relative population of the weakly cross-linked contribution (a) and average residual couplings (b) derived from two-component fits to 400 MHz proton nDQ build-up curves of filled silicone elastomers as a function of \(\gamma\) irradiation dose. \(D_{\text{res}}\) is equivalent to \(D_{\text{res}}\). Figure reprinted with permission from Ref. [79].](image1)

**Fig. 19.** Two-dimensional proton DQ correlation spectrum of cis-butadiene rubber (1 phr sulfur) acquired at 500 MHz with \(r_{\text{DQ}} = 1.3\) ms. Such a spectrum is easily obtained by introduction of an incremented \(t_1\) evolution period between DQ excitation and reconversion in a DQ-filtered MQ experiment (see Fig. 3b). The projections are taken over the shaded areas. Spectrum replotted from Ref. [60].
information on the number of couplings partners, and the fitting result depends on this choice. Our approach was therefore to always represent intensities relative to the full sum magnetization detected at a specific spectral position.

Natural rubber and cis-butadiene rubber share almost the same conformations in their crystal structures, such that the same set of simulation geometries can be used to obtain a calibration for both systems, just replacing one of the olefinic protons by a methyl group. Fig. 20a shows results for BR, where an inclination of the local rotation axis with respect to the backbone by 12° was found to match the experimental constraints best. Note that this “best-fit” orientation should not be given too much physical significance. It merely parameterizes the intra-segmental dynamics in a way that is consistent with the observations, under the assumption that the actual degree of averaging afforded by the true local conformational jumps is similar to that of the simplified rotation. A surprising result from our simulations that also highlights the dangers inherent to simplified models was that the dominant coupling for the CH2 protons is not the intra-group coupling but the coupling to one of the CH2 protons located on the other side of the central cis double bond (protons 3 and 5 in Fig. 20a). The reason is the geometry of local motion (“rotation” around the backbone) as well as the close spatial proximity afforded by the favored skew conformations of the H2C–CH bonds.

A weighted average of the simulated site-specific build-up curves can finally be fitted to Eq. (15) to obtain the reference couplings,

\[
D_{\text{stat}}^{\text{cis-BR}}/k = 2\pi \times 8.1 \text{ kHz},
\]

\[
D_{\text{stat}}^{\text{NR}}/k = 2\pi \times 6.3 \text{ kHz}.
\]

The results of Graf et al. [33] indicate that the residual coupling associated with trans-BR should be about twice as large as for cis-BR, which means that either the associated dynamic order parameter is higher or that the intra-segmental averaging is less efficient (higher \(D_{\text{stat}}/k\)). It is worth mentioning that the variation of the final \(D_{\text{stat}}/k\) for both NR and BR was never more than 25% over the whole range of orientations studied.

When the model cannot be constrained appropriately, as is the case for PDMS with its single type of protons, one needs to adopt an assumption of the local orientation of the rotation axis. For PDMS, we simply used an extended all-trans segment, with an angle of 90° between the Si–C bond and the backbone (Fig. 20b). The reference coupling is then [60]

\[
D_{\text{stat}}^{\text{PDMS}}/k = 2\pi \times 7.58 \text{ kHz}.
\]

Note that in our first paper on PDMS rubber [37], a methyl-group specific build-up function was used, fits to which yield different values for \(D_{\text{res}}\) than Eq. (15). Since

![Fig. 20. Multi-spin simulations of proton DQ build-up in rigidly rotating chain segments. (a) Individual and averaged build-up curves for the different protons in cis-butadiene rubber, based on 8-spin simulations using the indicated protons (\(S_\text{b} = 0.01\)), and fits to the averaged simulation result [60]. (b) Simulated build-up curves for a single CH1 and a poly(dimethylsiloxane) monomer unit (\(S_\text{b} = 0.02\), dotted and dashed lines, respectively), compared to a fit to Eq. (15) and actual experimental data [37].](image-url)
the lower $I_{\text{DQ}}(\tau_{\text{DQ}})$ plateau of 0.33 that is specific for the peculiarities of MQ dynamics in isolated methyl groups \[84,85\] is never observed due to multiple extra-group couplings (see Fig. 20b). I recommend to always use Eq. (15), which yields an apparent $D_{\text{res}}$ that is properly defined by its relationship to the dipolar second moment, Eq. (3).

Finally, using the definitions of Flory’s characteristic ratio and the Kuhn segment length (and assuming an extended chain conformation within the Kuhn segment), one obtains relationships between experimental RDCs and $M_C$:

\[ M_{\text{e}}^{(\text{NR})} = \frac{617 \text{ Hz}}{D_{\text{res}}/2\pi} \text{ kg/mol}, \]  
\[ M_{\text{e}}^{(\text{PDMS})} = \frac{1266 \text{ Hz}}{D_{\text{res}}/2\pi} \text{ kg/mol}. \]

Results for NR and PDMS for various cross-link densities are collected in Fig. 21, where they are compared with results from established Flory–Rehner swelling experiments. The most prominent feature is the nice linear relationship between the NMR observable and the macroscopic measure of network structure, and such linear relationships have been reported for a large number of different elastomer systems [17,27,49,86-92]. There are, however, a few exceptions in the literature [31,32,48,93], where specific deviations from Gaussian chain statistics are discussed as possible causes. These works have in common that the data analysis is based on a slow-motion model, the inapplicability of which is discussed in Section 3.3. Judging from the overwhelming evidence for a linear relationship, it appears that the latter results are model-specific artifacts.

Using the model described above, we can now attempt a more quantitative assessment of the linear relationship. There are several implications that follow from our comparison in Fig. 21, and details can be found in Ref. [60].

The salient points are: (i) NMR and swelling results disagree by a factor of 2, which is fully acceptable considering the many model assumptions. It is, however, unclear why NR and PDMS show deviations in different directions. (ii) The intercept with the y-axis depends on both the entanglement density ($\sim 1/M_c$), that contributes to the NMR observable but not necessarily to the swelling result, and on the density of trapped entanglements ($1/M_w$) that do affect the swelling. The results for NR are roughly consistent with what is known from the literature after a correction factor of 2 is considered, while the entanglement density (or contribution from "local chain packing") for PDMS is largely overestimated. This is specifically surprising because the slope is underestimated, thus agreement cannot be reached by introducing a correction factor.

At this point, we conclude that a consistent quantitative interpretation of residual couplings in terms of an average order parameter of the polymer backbone is not possible in the framework of the simple Kuhn chain model. While at least some papers in the literature do report good agreement between NMR-derived cross-link densities and values obtained from other techniques, it would appear that it results from a cancellation of errors arising at various stages of the modelling. This certainly does not invalidate such approaches; it merely shows that the final conversion factor of an RDC to $1/M_c$ should be considered a material-dependent calibration quantity. Most importantly, coming back to our observation of narrow RDC distributions, the role of end-to-end distance distributions and the network chain polydispersity is fully unresolved.

### 3.3. Chain dynamics in elastomers: failure of the slow-motion model

As opposed to the special case of $I_{\text{DQ}}(\tau_{\text{DQ}})$ curves measured for protons in permanent elastomers, the directly obtained build-up and decay functions of the MQ experiment, Eqs. (10) and (13), always exhibit a marked temperature dependence. This is demonstrated in Fig. 22. In Ref. [94], it is shown that instrumental factors (duty cycle, pulse imperfections) play a minor role, such that $I_{\text{DQ}}(\tau_{\text{DQ}})$ and $I_{\Sigma\text{MO}}(\tau_{\text{DQ}})$ can be analyzed in terms of chain dynamics.

Using the Andersen–Weiss (AW) approximation [55] in combination with a suitable model for the loss of orientation correlation as sketched in Fig. 1, analytical fitting functions can be obtained for different scenarios [94]. In short, the first step comprises the rearrangement of, e.g., Eq. (10) under the assumption of a Gaussian distribution of interaction frequencies:

\[ I_{\text{DQ}}(\tau_{\text{DQ}}) = \sinh(\langle \phi_{\text{DQ}} \rangle) \exp(-\langle \phi_{\text{DQ}}^2 \rangle). \]

The second step consists in evaluating the time and ensemble averages of the phase factors in this equation in terms of the orientation autocorrelation function, $C(t)$, of the effective dipolar tensor, Eq. (1). For example, for the mixed product of DQ phases, the average becomes

\[ I_{\text{DQ}}(\tau_{\text{DQ}}) = \sinh(\langle \phi_{\text{DQ}} \rangle) \exp(-\langle \phi_{\text{DQ}}^2 \rangle). \]
\[ \langle \phi_{DQ} \phi_{DQ} \rangle = \frac{4}{9} M_{2\text{eff}} \int_{0}^{T_{DQ}} \int_{0}^{T_{DQ}} C(t_a - t_b) dt_a dt_b, \]  
\[ \langle 2 \rangle \]

where the powder average simply leads to a factor of $1/5$ that is absorbed into the definition of $M_{2\text{eff}}$, Eq. (4). Starting from here, and using some rules for the evaluation of the double integral [3], specific scenarios for $C(t)$ can be implemented.

The detailed account of the theory presented in Ref. [94] builds upon and extends the treatment of the $\beta$ function published by Ball, Callaghan and Samulski [30], which is a direct analogue of $I_{DQ}(T_{DQ})$ constructed by a clever combination of Hahn- and solid echoes [28]. Demco and coworkers presented how the Andersen-Weiss model can be generalized for the evaluation under an actual pulse sequence that consist of a succession of evolution intervals rather than a single dipolar phase [48], and using these concepts, it turns out that relaxation under an MQ experiment can be treated in terms of evolution under an average Hamiltonian, Eq. (9), with only minor effects of finite pulses and the finite cycle time [36,94].

Up until now, the majority of models dealing with transverse relaxation phenomena in mobile polymer systems rest upon the assumption that the segmental modes that afford the primary averaging down to $D_{\omega a}$ do not exert a dominant influence on the decay [28–32,48]. The slow-motion model, in particular the one that assumes an exponential loss of correlation,

\[ C(t) = S_0^2 \exp\{-t/\tau_s\}, \]  
\[ \tau_s \]

goes back to Fedotov and coworkers, who applied it to proton transverse relaxation experiments of elastomers [11]. The dangers inherent to using the resulting signal function, Eq. (20), for fitting were highlighted in Section 2.3.

Fits of analogous analytical expressions [36] for $I_{DQ}(T_{DQ})$ and $I_{2\text{MOQ}}(T_{DQ})$ to proton MQ experiments on vulcanized NR are shown in Fig. 22. The backbone order parameters calculated from the fitted RDCs are plotted in Fig. 23. These results, along with the correlation times $\tau_s$ discussed below, show that the slow-motion model is indeed not applicable to elastomers. Strikingly, fits to $I_{DQ}(T_{DQ})$ and $I_{2\text{MOQ}}(T_{DQ})$ yield very different $S_0$ values, and results from the latter show large changes with temperature. It is also not possible to perform a simultaneous fit to both functions using shared parameters, which should be possible if the model is correct.

Other ACFs considered are a single exponential that models only the fast segmental process,

\[ C(t) = (1 - S_0^2) \exp\{-t/\tau_i\} + S_0^2, \]  
\[ \tau_i \]

a (seemingly more realistic) model that combines two exponential processes,

\[ C(t) = (1 - S_0^2) \exp\{-t/\tau_i\} + S_0^2 \exp\{-t/\tau_s\}, \]  
\[ \tau_i, \tau_s \]

where $\tau_i$ and $\tau_s$ are the fast and slow correlation times, respectively, and finally a power-law ACF for the fast initial decay,

\[ C(t) = \begin{cases} 1 & \text{for } |t| < \tau_0 \\ (1 - S_0^2)(\tau_0/|t|)^\kappa & \text{for } |t| \geq \tau_0. \end{cases} \]  
\[ \tau_0, \kappa \]

with $\tau_0$ as the onset time and $\kappa$ as the characteristic exponent. Kimmich and coworkers have proposed the use of Eq. (33) for a more realistic account of polymer dynamics mainly in the context of $T_1$ relaxometry [5]. It is probably the most realistic model, as superpositions of processes on different timescales (e.g., Rouse modes) must be expected. Note that in their work on the dipolar correlation effect in rubbers [31], they have used such a function to model the alleged slow process, and our corresponding tests showed that this leads to the same unphysical temperature dependence that we have observed for the exponential slow-motion ACF.

As an example, only the explicit signal functions derived for the combined model, Eq. (32), are given:
The slow- and the fast-motion-only expressions are published in Ref. [36]. They are easily obtained as limiting cases letting the correlation times $s$ tend to $0$ and $\infty$, respectively.

Fits of the temperature-dependent $I_{DQ}(\tau_DQ)$ and $I_{SMQ}(\tau_DQ)$ to expressions based upon these models are compared in Fig. 24. In all cases, simultaneous fitting with shared parameters was possible, and the quality of all fits in the validity region given by Eq. (16) is similar. Best agreement is found for the power-law model, that also gives the best long-time prediction. Note that experimental data are always expected to fall below the model predictions at longer times, as multi-spin correlations that lead to more effective relaxation are not included in the theory.

The fast correlation time $\tau_f$ obtained from fits to the fast-motion and the combined model are very similar, and are in Fig. 25 compared to $\tau_s$ obtained from the (necessarily independent) slow-motion fits to $I_{DQ}(\tau_DQ)$ and $I_{SMQ}(\tau_DQ)$. Strikingly, $\tau_s$ derived from the latter two signal functions not only differ by up to two orders of magnitude, but they also exhibit a completely unphysical temperature dependence. The same is true for the $\tau_c$ derived from the combined model (for data see Ref. [36]). From this we conclude that there is no sustainable evidence for a detectable influence of a slow cooperative process in networks. The same conclusion was drawn earlier from $^2$H spin-alignment experiments on PDMS networks [95].

The $\tau_f$, however, do exhibit a reasonable temperature dependence, and a fit to a Williams–Landel–Ferry function yields an extrapolated glass transition that matches the DSC value within 1 K. This provides an unambiguous proof that the overall intensity decay is indeed dominated by fast segmental modes that are coupled to the segmental $\pi$ relaxation. The results from the power-law model are qualitatively similar, yet at the moment we lack the theoretical understanding to attach physical significance to the onset time $\tau_0$ and the exponent $\kappa$. The work of Kimmich and Fatkullin suggests that the true ACF might in fact follow different power laws over different time regimes [5], and we hope that future theoretical work will reveal the true shape of network chain autocorrelation functions.

Brereton has repeatedly criticized the use of the AW approximation that is central to our and earlier approaches [23,24,34], and this potentially serious objection deserves a few comments. His treatment of transverse relaxation of mobile polymer chains is based on a scale-invariant “submolecule” model [21,22,24,34], and it is argued that the cartesian components of the submolecule end-to-end vectors are statistically independent and that Gaussian statistics should apply. This specifically implies a Gaussian distribution of end-to-end separations that is either sampled rapidly in time in the case of short melt chains, or leads to a quasi-static response function (“frozen-bond” limit) that then consists of a superposition of frequency contributions given by Eq. (6). In Section 3.1, it was however shown that Gaussian chain statistics and the resulting

$$I_{DQ}(\tau_DQ) = \exp \left\{ -\frac{8}{9} (1 - S_b^2) M_{2\text{eff}} \tau_f^2 \right\} \times \left\{ \left( e^{\frac{\tau_DQ}{\tau_f}} - \frac{\tau_DQ}{\tau_f} - 1 \right) - \frac{8}{9} S_b^2 M_{2\text{eff}} \tau_f^2 \right\} \times \left( e^{\frac{\tau_DQ}{\tau_s}} - \frac{\tau_DQ}{\tau_s} - 1 \right) \} \times \sinh \left( \frac{4}{3} (1 - S_b^2) M_{2\text{eff}} \tau_f^2 \right) \times \left( e^{\frac{\tau_DQ}{\tau_f}} - 2 e^{\frac{\tau_DQ}{\tau_f} + 1} + 4 S_b^2 M_{2\text{eff}} \tau_f^2 \right) \times \left( e^{\frac{\tau_DQ}{\tau_s}} - 2 e^{\frac{\tau_DQ}{\tau_s} + 1} \right) \right\},$$

$$I_{SMQ}(\tau_DQ) = \exp \left\{ -\frac{4}{9} (1 - S_b^2) M_{2\text{eff}} \tau_f^2 \right\} \times \left\{ \left( 4 e^{\frac{\tau_DQ}{\tau_f}} - e^{\frac{2 \tau_DQ}{\tau_f} + 1} + 2 \tau_DQ \right) - 3 \right\} \times \left( 4 e^{\frac{\tau_DQ}{\tau_s}} - e^{\frac{2 \tau_DQ}{\tau_s} + 1} + 2 \tau_DQ \right) - 3 \right\}. \tag{35}$$

Fig. 24. Simultaneous fits to the two MQ signal functions for different models of correlation loss. Data replotted from Ref. [36]. The grey bar indicates the fitting limit given by Eq. (16).
gamma distribution of RDCs do not describe the data well in this limit; a rather narrow distribution of couplings is found experimentally. Therefore, the AW approximation with its single residual second moment describes experimental data better, and Gaussian single-chain models will have to be improved by introduction of a degree of cooperativity of chain motion that screens such local distributions. In Ref. [36], we have also performed Monte-Carlo simulations of a rotational diffusion process, that is characterized by exponential loss of correlation and should model local conformational jumps, to show that the AW model represents a good approximation all the way from the slow to the fast limit. In addition, the second-moment approximation that is part of the AW model (i.e., that a Pake-like quasi-static dipolar coupling distribution is reasonably well approximated by a Gaussian) can be tested experimentally as it allows the derivation of a conversion formula of MQ to dipolar-dephasing data, which matches the experimental Hahn-echo decay very satisfactorily.

Finally, the shape of the $I_{2MQ}$ relaxation functions should be discussed. Close inspection of the fits in Fig. 24 shows that the decay of $I_{2MQ}^M(\tau_{DO})$ for the fast-limit model is mono-exponential, and for small $\tau_f$ and $\tau_s \to \infty$, an apparent $T_2$ can be derived from Eq. (35):

$$T_{2MQ} = \frac{8}{9} \left( 1 - S_b^2 \right) M_{2eff} \tau_f \approx 2.5 \left( \frac{D_{stat}}{k} \right)^2 \tau_f^{-1}.$$ (36)

A relaxation term of similar form was predicted by Breyeron for the case of transverse relaxation of Rouse chains in melts and networks [23,34]. In the latter case, $(1 - S_b^2)M_{2eff}$ is associated with the coupling within a sub-molecule, similar to when using a pre-averaged $M_{2eff} \approx (D_{stat}/k)^2$ for the Kuhn segment, and $\tau_f$ is associated with the fastest Rouse mode.

In contrast, experimental $I_{2MQ}^M(\tau_{DO})$ decays can be decisively non-exponential (see Fig. 22). Since a true slow-motion contribution that would introduce some convexity in the decay curve appears unlikely, one could of course attribute the convexity to a more complicated (e.g., power-law) ACF that extends into the experimental timescale. Yet, another effect that deserves careful discussion is the influence of isotropic $J$ couplings. Fig. 26 shows some unpublished simulation data featuring a realistic set of dipolar and $J$ couplings. Clearly, $I_{2MQ}^M(\tau_{DO})$ is significantly affected by $J$ couplings that are about an order of magnitude weaker than the average RDC. This somewhat counterintuitive behavior can be explained superficially by the fact that dipolar couplings to a third spin renders two otherwise equivalent spins magnetically inequivalent in the same way as a chemical shift difference; the formal derivation involves the non-zero commutator $[H_{DO}, H_J]$ [96]. Note that this must also be taken into account for rubbers with chemically equivalent protons such as PDMS.

Importantly, this higher-order effect causes a downward curvature of any $I_{2MQ}^M(\tau_{DO})$ decay. Even though it appears to be rather weak in relevant elastomer cases, the effect may become more pronounced in weakly coupled entangled polymers. More importantly, such deviations of true experimental behavior from what is provided by the fitting model may always lead to severe fitting instabilities once many parameters are involved, as exemplified already in Section 2.3. This stresses the importance of simultaneous fitting of $I_{2MQ}^M(\tau_{DO})$ and $I_{DO}^M(\tau_{DO})$, which stabilizes the result even when the experimental trend cannot be fully reproduced by the theoretical expression. A factor that also deserves closer attention in the future is the necessarily limited validity range of spin-pair based theories for any type of experiment; enforcing a fitting limit as given by Eq. (16) might help to stabilize fits and improve the results.

### 3.4. Network swelling

A subject area of pronounced current controversy is the microscopic picture of network swelling. In short, the affine theory of Flory and Rehner [35] that stipulates additivity of the entropy-elastic and osmotic free-energy contributions upon solvent take-up and volume increase has long been challenged by thermodynamic investigations that suggest an increase in chain entropy rather than a decrease at intermediate degrees of swelling [97]. The role of complex topological rearrangements has been stressed more recently; these ultimately lead to the appearance of pronounced heterogeneities that can be detected by a variety of experimental methods, and are also found in computer simulations, see Ref. [52] and references therein.

The first systematic NMR investigations on the swelling dependence of orientation correlations in permanent networks were made by Cohen-Addad et al. [27,98–101], who found that at least for systems cross-linked in solution, an NMR quantity that is related to the RDC first decreases and then increases upon swelling [98,99]. Such behavior has been interpreted in terms of a chain “desinterspersion”, whereby chains first increase their conformational space...
and their entropy as packing-induced orientation correlations are relieved, while a pronounced loss in conformational entropy is observable only at later stages. Even though the general idea was published almost 30 years ago [102], the attractively simple picture of a nematic-like orientational mean field contribution that can explain thermodynamic as well as NMR observations [103], has not yet found its way into current theories of rubber elasticity.

While the earlier NMR work of course discussed only a single averaged NMR observable, our contribution to this field has been focussed on the quantification of changes in the chain order parameter distribution, that may of course be related to the heterogeneities found in many scattering studies [52,82]. Before discussing the experimental findings, it is instructive to first consider the behavior that is expected from the simple Flory–Rehner model. A homogeneous affine and isotropic volume increase of a network will lead to an affine stretching of each network chain, which means that any chain order distribution function (see Fig. 16) will just be stretched (scaled) along the x-axis, according the change of $r^2 = r_0^2$ in Eq. (2).

This is not what is observed experimentally [52,82], as well as in large-scale computer simulations [82]. Fig. 27 shows that the majority of chains, even at swelling equilibrium, remain unstretched or even relaxed, while only a smaller fraction experience a pronounced increase of $S_b$, thus contributing to balancing the osmotic driving force. Most notably, the maximum indicating the most probable order parameter does not shift towards higher values, and in all cases, the width of the distribution increases upon swelling. The almost semi-quantitative agreement of experiments and simulations is encouraging in that additional insight into, e.g., the internal structure of the swollen networks can now be extracted from the computer simulations, that are thus shown to model essential features of reality rather well.

An example of such an approach is provided in Fig. 28, where large concentration fluctuations are apparent. The phenomenon is not surprising as such, as they also appear in polymer solutions (and are responsible for light, neutron, and X-ray scattering phenomena). The important finding is that the regions are perfectly stable in time, i.e., the concentration fluctuations are static. The regions of high and low swelling have a length scale of a few radii of gyration of single network chains, which is thus in agreement with what is known from many scattering studies [104].

An important result of our extensive computer simulations concerning the quantitative interpretation of $S_b$ in terms of network chain length is summarized in Fig. 29. It concerns the validity of Eq. (2), the variation of $S_b$ along the chain, and the changes observed upon swelling. In a dry network, the distribution of $S_b$ along the chain is not very pronounced (±20%), and probably even less significant for longer chains. From our data, we concluded that the non-observation of large distribution effects, in particular of different end-to-end separations, is simply because chains that have rather short end-to-end separations are very likely to

Fig. 27. Chain order parameter distributions of swollen end-linked model networks at different degrees of volume swelling $Q = V/V_0$. The experimental data in (a) is from PDMS swollen in octane as a good solvent, and the simulated data in (b) is from large-scale bond-fluctuation Monte-Carlo simulations. Data replotted from Ref. [52,82].

Fig. 28. Time-averaged 3D density fluctuations of a swollen end-linked model network. Color (green to red) codes polymer chain concentration that varies by as much as 50% over the different regions. The picture is based on the simulations described in Ref. [82], and was kindly provided by Jens-Uwe Sommer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this paper.)
participate in topological links ("trapped entanglements") and thus cannot reorient freely as required by the model. One could of course also invoke nematic-like orientation correlations or a "tube" model to describe the phenomena [74,75]. Importantly, the NMR results are not in disagreement with neutron scattering studies that indicate that random networks indeed exhibit static Gaussian statistics over whole, long network strands.

Most significant is the deviation between vector and tensor orientation correlation, which should just differ by a factor of 3/5 (see Eq. (2)). For the dry network, the deviation is of course expected, since we have already seen that the Gaussian end-to-end separation distribution is screened, which changes the average. For the swollen network, however, the difference is much increased, which is a consequence of a change in the fluctuation statistics and the tensorial nature of $S_0$ ($=(3/5)\bar{G}$ from the simulations). It was further found that the plateau value of $S_G$ depends strongly on solvent quality. With excluded volume (good solvent), the average $S_G$ is lower, which is rather counterintuitive. Detailed studies along these lines are currently underway, and a closer understanding of the role of the fluctuation statistics is indispensable for a quantitative interpretation of the relationship between NMR-detected chain order, chain entropy, and the actual length of network chains.

### 3.5. Strained and oriented networks

The effects of macroscopic strain on the observables has been an important aspect from the earliest days of NMR investigations of elastomers. $^2$H NMR was the method of choice, and the importance of induced nematic-like orientation effects was first recognized by observation of well-defined splittings in $^2$H spectra of deuterated probe molecules dissolved in stretched elastomers [76]. Later work on lineshapes of stretched elastomers with deuterated chains stressed the importance of non-affine local stretching and distribution effects [72], and the use of deuterated oligomers or free probe chains allowed the quantification of the degree of orientational coupling between chains in a dense system [73,78,105]. Theoretical models employing an orientational mean field, as caused by excluded-volume interactions, have been successfully used to describe the phenomena [41,42,45], and the preparation conditions, i.e., the presence of trapped entanglements, have been shown to exert an appreciable influence on induced orientation [106]. More recently, biaxial deformations have been used to show that the orientational mean field follows the predictions of the phantom model [107].

Proton NMR investigations are less frequent and were initially restricted to conventional transverse relaxation studies [108–110]. Recently however, the Aachen group has demonstrated the use of proton DQ NMR using the two-pulse segment to directly detect the apparent RDC changes upon elongation as well as employing RDCs as a contrast mechanism in DQ-filtered NMR images [111]. As a proof of principle, Fechete et al. showed that angle-dependent DQ build-up (Fig. 30a) and dipolar-encoded longitudinal magnetization (DELM) decay curves can be used to study the degree of chain orientation and stretching [112]. The change in the maxima positions already gives a qualitative impression of the phenomenology, and more quantitatively, apparent values for $D_{res}$ can be extracted from the initial slopes. As expected, the angular variation of the apparent, normalized RDCs shown in Fig. 30b follows the second Legendre polynomial $|P_2(\cos \theta)|$, and the analysis of the absolute values could be the basis of a quantitative assessment.

It should be noted that the fitted values of $D_{res}$ are approximate because the fitting function is based on an isotropic distribution of residual tensor orientations, but this should be replaced by a uniaxially biased distribution in a stretched sample. An appropriate analysis was presented for the case of RDCs detected for water molecules that exhibit strongly anisotropic mobility in tendon [113,114], where the angular distribution function of collagen fibrils was determined. Consistent results were obtained from the analysis of orientation-dependent DQ build-up, DELM decay, and splittings in DQ-filtered spectra [114]. The application of proton and deuteron MQ NMR to the characterization of order in biological tissues was pioneered by Eliav and Navon [115,116], and it should be pointed out that this is a particularly favorable application, where relaxation effects due to polymer chain dynamics are largely absent, as rapidly exchanging/diffusing $H_2O$ is detected. In addition, well-resolved $T_{DQ}$-independent splittings are observed in DQ-filtered spectra as a result of the strong uniaxiality in such tissues.

For direct detection of elastomer chain signal, it is expected that the analysis of normalized DQ build-up curves using the Baum/Pines sequence offers an advantage with respect to an exact quantification. The data in Fig. 9b
shows that such build-up curves are rather sensitive to changes in the powder distribution, suggesting that it should ultimately be possible to extract similar detailed information as obtained from $^2$H NMR lineshapes. As a final remark, it should be stressed that the rich insights on induced orientation and lateral chain packing that were gained from experiments on stretched elastomers have not yet found their counterpart in the description of the undeformed state. The qualitatively new insights into actual RDC distributions presented in Section 3.1, which show that single-chain models are clearly insufficient to describe the narrow distributions found, may ultimately be explained by establishing direct correlations of the stretched and unstretched states. Work along these lines is in progress.

4. Entangled melt dynamics

The decisive difference between chain dynamics in networks and entangled melts is of course the possibility for large-scale chain motion on longer timescales in the latter, i.e., the occurrence of reptation [1]. Depending on the molecular weight of the chains and thus the number of entanglements per chain, the timescale of correlation loss associated with this process is more or less separated from the more localized Rouse modes (see Figs. 1 and 31). The timescale for reptation (between the longest constrained Rouse mode $\tau_R$ and the tube disengagement time $\tau_d$) in highly entangled melts ranges from about 0.1 ms up to the range of seconds [35]. This is outside the typical time window of inelastic neutron scattering and longitudinal NMR relaxation, yet NMR methods based on RDCs and transverse relaxation phenomena are ideally suited to directly probe this type of dynamics.

Conventional proton transverse relaxometry [14,20,24,25] as well as more advanced approaches such as the dipolar correlation effect (DCE) [117] and the $\beta$ echo [30,118] have been used to study reptation. Apart from conceptual details, they all differ in the type of orientation correlation function used to model this process. Brereton et al. [14,20,24,25] favor a description of transverse relaxation in terms of an exponential loss of correlation and successfully demonstrated the correct scaling law for the molecular-weight dependence of the reptation time derived [14]. Kimmich et al. achieved good agreement between the experimental DCE and theory using a power-law autocorrelation function [117], yet did not link their finding to established theories of polymer dynamics. Considerations based on the mean-square displacement predicted by the Doi–Edwards tube model (Fig. 31) and approximating $C(t)$, the orientation ACF, as a return-to-origin probability for reptation along the primitive path yields specific power laws for the important dynamic regimes of $C(t)$: $C(t) \sim t^{-1/4}$ for constrained Rouse modes up to $\tau_R$, and $C(t) \sim t^{-1/2}$ for reptation below $\tau_d$ [30]. Satisfactory agreement between this model and experimental $\beta$ echo data for long-chain poly(dimethylsiloxane) has been reported [118].
The first proton DQ NMR study of reptation effects was published by Graf et al. [33], who used high-resolution proton DQ MAS NMR to detect pair-specific DQ build-up curves in linear poly(butadiene) of different molecular weight. While MAS offers the possibility of high site resolution and thus the development of specific molecular models for chain order (see Section 3.2), DQ MAS recoupling pulse sequences are less flexible in the choice of the DQ evolution time due to the necessary rotor synchronization and/or longer finite pulses, leading to less points in the build-up curves. Another drawback can be their larger susceptibility to experimental timing imperfections, such that an equivalent function $I_{SMO}(\tau_{DQ})$ must be measured and used for intensity normalization [85].

Graf et al. extracted apparent RDCs by fitting normalized build-up curves, that are thus corrected for decay due to experimental imperfections and fast-motion induced relaxation (see below), to

$$I_{\text{nDQ}}(\tau_{DQ}) = AD_{\text{res}}^2\tau_{DQ}^2 \exp[-\tau_{DQ}/T_2^*] \tag{37}$$

at $T = T_g + 50$ K (see Fig. 32a). At this temperature, it was expected that the semi-local segmental averaging is essentially complete on the timescale of the experiment, such that the associated value of $S_b$ should reflect segmental order between entanglement constraints. Varying the temperature, time-temperature superposition was used to record data over several orders of magnitude in time. For this, a fixed $\tau_{DQ}^* (=0.5 \text{ ms})$ was chosen according to $D_{\text{res}}^2$ at $T = T_g + 50$ K, such that the parabolic short-time limiting behavior applies. Then, the exponential loss term can be neglected and the measured DQ intensity is proportional to the squared apparent RDC, with $I_{\text{nDQ}}(\tau_{DQ}) \sim D_{\text{res}}^2\tau_{DQ}^2 \sim D_{\text{eff}}^2 S_b^2 C(t/\tau_e) \tau_{DQ}^2$. This relation follows from Eqs. (28) and (29), and a formal derivation can be found in Ref. [119]. Plotting $I_{\text{nDQ}}(\tau_{DQ}, T)/I_{\text{nDQ}}(\tau_{DQ}, T_g + 50 \text{ K})$ thus directly yields the autocorrelation function $C(t/\tau_e)$ that describes correlation loss on the lengthscale of entanglements and beyond. Fig. 32b demonstrates that scaling regimes can be observed that are in agreement with the Doi–Edwards model.

A matter of some debate, however, is the rather high starting value of $S_b \approx 0.2$ at $T_g + 50$ K. An order parameter of about 0.03 would be expected for a chain comprising about 20 statistical segments that probes all conformational space between entanglements. Graf et al. concluded that either local packing constraints or a weak local stretching between entanglements plays a role. A clarification of this issue was, however, obtained from our comparison of $T$-dependent order parameters in networks and melts [36].

Generally, networks are an attractive starting point for a better understanding of the NMR signals of polymer melts, as they feature the same type of fast local dynamics, while reptation is of course not possible. Fig. 33 shows MQ build-up and decay data for the long-chain linear precursor of the previously investigated natural rubber sample series. A direct comparison of this data with Fig. 22 shows that the timescale of the $I_{S\text{MO}}(\tau_{DQ})$ decay is very similar for the network and the melt, indicating that the relaxation of this quantity mainly reflects fast segmental motions on the local scale. To the contrary, $I_{D\text{Q}}(\tau_{DQ})$ is much reduced in the melt and therefore carries the signature of reptation. We are currently extending the theoretical framework presented in Section 3.3 to reptation dynamics; it is expected that again, a simultaneous fitting of both sets of data will provide a basis for reliable fits and tests of different models for the autocorrelation function.

A first insight is provided by considering $I_{\text{nDQ}}(\tau_{DQ})$ for the linear NR (Fig. 33, right), which, as opposed to the almost temperature-independent network data, should mainly reflect reptation dynamics, since the fast-motion effect on $I_{S\text{MO}}(\tau_{DQ})$ and $I_{D\text{Q}}(\tau_{DQ})$ should be very similar.
and thus be cancelled out. Following the work of Graf et al., apparent residual couplings of the linear melt and two networks were determined from $I_{nDQ}(sDQ)$ (neglecting relaxation terms) and are compared in Fig. 34. It is seen that the segmental averaging process down to the entanglement level is far from complete at $T = T_g + 50$ K. Much higher temperatures are needed to actually observe the $T$-independent plateau even for rubbers with only low cross-linking. For the melt, the expected entanglement level is only reached at about $T = T_g + 140$ K.

This now explains the unusually high order parameter observed for PB melts. The $S_b$ values for NR are still lower, but considering the potential dependence on the model as well as the fact that trans units induce higher chain order, most of the discrepancy in the magnitude of $S_b$ is thus explained. Therefore, the value of $S_b$ does not simply reflect single-chain order at a given temperature, assuming the validity of averaging timescales derived from rheological models. The reason for this might in fact be local packing constraints that arise from overall cooperative motions, which could also be responsible for the screening of end-to-end distribution effects discussed in Section 3.2.

Another possible explanation is the retarded self-averaging behavior of fluctuating tensorial rather than vectorial interactions used to define an order parameter [82]. This phenomenon, which generally raises problems with respect to the proper interpretation of NMR data, is also responsible for the unexpected excluded-volume effects on chain order discussed in Section 3.4. Future developments will have to consider both possibilities, chain packing as well as peculiarities of tensorial self-averaging, in order to finally link up NMR observables with parameters that directly correspond to those derived from the macroscopic mechanical behavior as well as results from, e.g., neutron scattering.

5. Other applications

This section finally summarizes a few miscellaneous applications of proton MQ spectroscopy to other subject areas, namely grafted and confined chains as well as gelation phenomena.

5.1. Grafted chains

Block copolymers are an attractive model system for which to obtain insights into the reptation dynamics described in the previous section. In lamellar poly(styrene)-block-poly(butadiene) (PS-b-PB) diblocks or PS-b-PB-b-PS triblocks, PB chains are grafted at one or two ends, respectively, to a rigid glassy PS phase, and are confined to a domain of about 15 nm size, which spans many entanglement lengths. In the diblocks, only less efficient arm retraction processes can lead to correlation loss below the order parameter plateau dictated by entanglements, while for triblocks, the situation is reminiscent of a network, where essentially no correlation loss should be observed.

Experimental data published by Spiess and coworkers [120] nicely confirms this picture, as shown in Fig. 35a. In the diblock (one end fixed), the $r^{1/2}$ scaling regime characteristic for reptation is essentially suppressed on the time-scale of its typical occurrence in the melt, and in the triblock, hardly any decay of the order parameter is observed. Notably, strongly increased main-chain order is manifested in the block copolymers, indicating an influence of the confinement posed by the grafting to the lamellar structure.

An exciting result is the behavior of the order parameter observed for free, marginally entangled PB chains that are dissolved in the deuterated PB phase of a diblock (Fig. 35b). While their order parameter is almost the same as for the bulk polymer on a comparably reduced time-scale, the characteristic power law for its decay is changed considerably in the diblock structure and resembles that of the chains in the PB block. This can only mean that the matrix imposes it characteristic dynamics on the guest
chain, which again stresses the inadequacy of single-chain models. In other words, the time stability of the entanglements or the effective tube that constrain the free chain is dominated by the relaxation time of the matrix chains.

A model scenario developed to explain the above observations is reproduced in Fig. 36. In agreement with the cooperativity arguments brought forth repeatedly in the previous sections, nm-sized regions of uniform local order (describable by a nematic director) are postulated. These are statistically uncorrelated in free melts, and reptation leads to complete correlation loss at sufficiently long times. In the block copolymer, the local order of the domains is increased overall and retains some correlation with the wall confinement over the whole lamellar width, as a consequence of the tethering.

As a second, more application-oriented example, we turn to chain grafting as an important process for the physical modification of surfaces. It is often employed to stabilize multicomponent polymer systems and to achieve favorable wetting conditions or good dispersion. Of particular commercial relevance is the modification of inorganic filler particles for reinforcement or viscosity control of elastomers and polymer melts. Silica, either fumed or precipitated, is commercially available with a wide range of surface modifications. One example are poly(dimethylsiloxane) (PDMS) grafts, and the chain dynamics in such a system has previously been investigated in detail by Litvinov and coworkers using conventional transverse relaxometry at low field [121] (Fig. 37).

The systems were found to consist of up to three PDMS components with distinctly different dynamics (=apparent $T_2$). At low grafting density, only two majority components are observed. A series of such samples was subjected to a proton DQ NMR study by the Aachen group [122]. Fig. 38 shows DQ build-up curves for a low temperature (221K), where two distinct maxima are observed and can be attributed to a rather rigid surface layer and another more mobile domain.

It is important to note that this clear signature of pronounced heterogeneity arises only as a result of overall intensity relaxation. Without overall decay (or after a successful normalization), a stepwise or gradually increasing build-up function would be expected, as is for instance observed in our example of bimodal networks (see Fig. 15). This poses some limitations as to the quantitative evaluation of such multimodal build-up curves, where utmost care is needed when the intensity scale for each of the maxima is to be defined. For example, when the first
maximum in the DQ build-up curve is plotted on a scale of
the total magnetization, the fit must embody the contribu-
tion of the more weakly coupled components in its prefac-
tor (the more mobile components do not contribute yet to
the build-up, but are part of the intensity scale). Then, the
initial build-up intensity of the second component can be
affected because the intensity relaxation of the first compo-
nent occurs on a similar timescale.

As a consequence, in their initial report, Blu¨mich and
coworkers discussed only the positions of the maxima as
qualitative indicators of the actual RDCs. Both maxima
were found to shift to longer times with increasing tempera-
ture, pointing at a speeding-up of the dynamics and a
gradual increase in motional amplitude. In addition, the
maximum of the more mobile contributions was found to
broaden significantly, hinting at a significant distribution
of underlying couplings, thus considerable dynamic heterogeneity.

5.2. Confined chains

Purely geometric confinement of small molecules and
polymers on the nanometer scale has attracted much recent
attention, mainly because of the unusual and sometimes
counterintuitive changes which occur in the molecular con-
formation, the dynamics, and the glass transition. Under-
standing surface-induced phenomena is of paramount
importance for the proper design of new materials that
are structured on the nanometer level, such as for example
polymers filled with nano-sized fillers or thin films for sen-
sor applications.

Anapore® porous alumina membranes are a suitable
model system for studying surface-induced effects due to
their high inner surface and controlled cylindrical pore
sizes in the range of 10–200 nm in diameter and tens of
µm in length. A first study of polymer segment ordering
in such a system was due to Primak et al., who studied
poly(dimethylsiloxane) (PDMS) in 200 nm pores by 2H
NMR [123]. Up to three well-defined quadrupolar split-
tings were identified as a function or pore surface coverage,
indicative of discrete monolayer structures, each with its
individual dynamic properties.

The Aachen group has demonstrated that similar
results can easily be obtained without the need for isoto-
ic labeling using proton DQ NMR [124]. Fig. 39 shows
proton DQ build-up curves for PDMS in Anapore with
surface coverages spanning the first few monolayers.
The first monolayer is strongly absorbed, as indicated
by the sharp maximum at 37 µs. Increasing the coverage
first leads to the appearance of shoulder-like structures,
indicative of dynamic heterogeneity. At the highest con-
centrations, distinct dynamics evolves for the second,
third and forth monolayer, as indicated by the higher
maxima.

As in the previous example of grafted chains, the exact
quantification of the related dipolar couplings is not easy
due to the potentially ill-defined intensity scale via the
influence of relaxation and intermediate motions. Note
again that the distinct maxima structure is a result of com-
peting relaxation. Estimates of the RDC at least for the
most strongly coupled fraction can be obtained by either
analyzing the first initial rise or, alternatively, by analyzing
the width of DQ-filtered (“edited”) proton spectra [49]. In
the present example, short-τDQ-edited spectra even exhib-
ited a splitting, corroborating the well-defined dynamics in
the first layer. From the initial rise of the DQ build-
up, an estimate of the associated RDC of about 3.4 kHz
was obtained, indicating very restricted (probably uniaxial)
dynamics. At higher coverage, the first layer is somewhat
mobilized, characterized by a reduction of the coupling
by about 30%.

Similar studies along the same lines have also been per-
formed for lipid films, where effects of motional heteroge-
nity as a function surface coverage also became
particularly apparent [125]. Notably, the surface layers
with sub-monolayer coverage were found to exhibit
a systematically increased mobility as compared to the bulk surfactant.

5.3. Study of gelation

The applications of proton MQ spectroscopy to polymer melts and networks presented in the previous sections of course suggest that significant insight can also be gained for systems that undergo a transformation from one limit to the other, i.e., to linear polymers undergoing cross-linking and gelation. Such investigations were earlier performed using conventional transverse relaxation methods [126–128], and in a recent study [129], we have demonstrated the advantages of MQ spectroscopy in this context.

The subjects of our study were two conceptually different gelling systems, i.e., bulk cross-linking of short linear PDMS chains, and cross-linking of poly(styrene-co-aminomethylstyrene) [P(S-co-AMS)] in semidilute solution using deuterated toluene as solvent. For the first case, fully reacted systems were studied as a function of cross-linker concentration and were compared with rheological experiments, while for the latter, stoichiometric compositions were studied as a function of reaction time and are compared with dynamic light scattering (DLS) results [130].

In both cases, the chains are virtually unentangled so as to not exhibit any detectable DQ intensity in the initial state. It is then expected that significant RDCs become detectable only when the topological gel point is reached. At or above this point, the network structure becomes infinite and supports long-lived orientation correlations of the chain segments. It was indeed found that DQ intensity became detectable only in close vicinity to the mechanical gel point (that is defined as the state at which the loss tangent becomes independent of frequency).

Fig. 40 collects proton MQ data for the end-linking process of PDMS above the gel point. The analysis of the long-time tails of $\tilde{I}_{MQ}$ straightforwardly yields the sol content, that is seen to strongly decrease with increasing cross-linker concentration, as expected. Interestingly, $I_{DQ}(\tau_{DQ})$ shows two distinct maxima indicating a heterogeneous gel structure at the early stages just above the gel point. This behavior is very similar to the grafted and confined-chain applications discussed in the previous sections, yet here, the sol-corrected $\tilde{I}_{MQ}(\tau_{DQ})$ decays slowly enough so as to provide a reliable point-by-point normalization. The corresponding normalized DQ curves in Fig. 40b therefore show the expected two-step build-up and can easily be...
analyzed in terms of two distinct RDCs and a relative molecular weight. On the whole, these curves nicely reflect the gradual build-up of cross-link density.

From such build-up curves, and the fact that $I_{DQ}(t_{DQ}) > 0$ only above the gel point, it is easily inferred that the gelation process can also be monitored by a single-point measurement of the DQ intensity at a specific $t_{DQ}$. The value is best chosen such that the DQ intensity has its maximum at full conversion. The acquisition of a DQ and a reference intensity (when nDQ is to be monitored) with about a hundred scans each does not take more than about a minute or two, such that real-time experiments to investigate the gelation kinetics of systems in rather dilute solution are feasible even at low field.

An example is presented in Fig. 41a, where the cross-linking of poly(styrene-co-aminomethylstyrene) in solution of various concentrations with a dialdehyde as cross-linker, that readily occurs at room temperature, is monitored. The specific $I_{nDQ} = 4$ ms as well as the limiting value of $I_{nDQ}(4$ ms$)_{t \rightarrow \infty}$ were determined in separate long-time experiments. A fixed $I_{nDQ}(4$ ms$)_{t \rightarrow \infty}$ is needed to reliably fit the so-obtained growth curves, that were found to be exponential within experimental noise. As is obvious, growth only starts after a lag time that corresponds to the time at which the gel point is reached.

The gel point time as well as the gel formation time constant (that reflects the rate of formation of elastically active network chains) derived from the fits is plotted in Fig. 41b and compared with the gel point time obtained from dynamic light scattering. This latter method is based on the appearance of a speckle pattern arising from fixed concentration fluctuations when the system becomes non-ergodic above the gel point. Since the time and length scales intrinsic to this method are larger than for NMR, it was not surprising that it detects gelation somewhat earlier. It should, however, be noted that the investigations could not be performed on the very same samples; the deviation is well within the common range of reproducibility of such gelation reactions.

Important conclusions can be drawn from the independence of the network formation rate on concentration (Fig. 41b, right ordinate), as well as from the final analysis of the proton MQ data of the fully reacted gels. It was found that about 50% of the polymer contributes only to the formation of elastically inactive microgels, loops, or dangling chains. The remaining polymer is either highly mobile sol or is converted to 12–50% true network fraction depending on concentration. Surprisingly, the average RDC (thus the average network chain length) is also independent of concentration. All these observations are in good agreement with or complementary to those from detailed mechanical and DLS studies of this system [129,130]. The concentration-independence of the gel formation rate and the final cross-link density indicate that gelation is not diffusion-controlled and mainly occurs in heterogeneous clusters that in the end link up to form a macroscopic gel.

In summary, it is seen that a large spectrum of useful, partly unique insights can be gained from the application of MQ spectroscopy to gelling systems. Further work will have to show how the approach has to be adapted to the case of long, entangled pre-polymers that exhibit significant entanglement-induced residual dipolar couplings even when no crosslinks are present [33,36,126]. One might envisage the observation of a discontinuity in $I_{nDQ}(t_{DQ})$ at the gelpoint, yet, as entanglement-induced residual couplings are a strong function of temperature (see Section 3.3), an extended protocol might necessitate a study at different temperatures. Cohen-Addad has discussed other possible approaches along these lines based on proton transverse relaxation properties [126]; the application of MQ spectroscopy to this type of system is underway.

6. Summary and conclusions

This article was intended to deliver a broad survey over the many applications of proton MQ spectroscopy to mobile polymer systems. While the concept and the pulse sequence appear of course somewhat involved, its implementation is robust, the set-up is easy (only precise 90°
pulses and good on-resonance conditions are to be ensured), and it can be run in an automated fashion even on cost-efficient low-field equipment. The main advantage over more traditional NMR methods such as Hahn echo relaxometry or combinations of Hahn and solid echoes is the reliable separability of coherent dipolar effects and signal loss due to motion-induced relaxation by means of monitoring the DQ build-up as well as a reference intensity. The sum of DQ and reference intensities represents a fully dipolar-refocussed intensity function \( I_{\text{EMO}}(\tau_{\text{DQ}}) \), the decay of which is largely dominated by dipolar relaxation.

In permanently cross-linked networks, a point-by-point division of the DQ build-up by \( I_{\text{EMO}}(\tau_{\text{DQ}}) \) yields a normalised intensity that is temperature-independent and reflects elastomer microstructure only. It can be analyzed in terms of distributions of residual dipolar couplings, and a number of applications to different types of elastomers, bimodal PDMS networks, filled SBR, NR, and filled PDMS, has been presented. A particularly important finding is that all chemically uniform single-component rubbers are found to display surprisingly narrow, almost unimodal coupling distributions. This has significant consequences for the validity of single-chain models for the explanation of the NMR response as well as the mechanical and swelling behavior via the conformational entropy, where Gaussian statistics is assumed for the end-to-end separation of sub-chains. This distribution should lead to a broad gamma distribution of couplings, and this is not observed in our experiments. Additional cooperative contributions to local chain order, for instance describable in terms of an orientational mean field or a specific tube constraint, are possible explanations.

Using spin dynamics simulations, as well as site-resolved DQ build-up curves and 2D spectra, we have developed molecular models for the quantitative interpretation of the measured RDCs in terms of a polymer backbone order parameter for the cases of NR, cis-BR and PDMS. A comparison of the resulting NMR-determined cross-link densities with swelling results indicates satisfactory agreement within a factor of 2, yet many details concerning systematic deviations and the significance of temporary and trapped entanglements still remain unclear.

Experiments on swollen rubbers indicate a significant broadening of the RDC distribution that was attributed to swelling heterogeneities. The behavior is strongly subaffine, with only a small part of the chains being stretched significantly. It can be explained in terms of competing desinterspersion and stretching processes, where the former leads to a reduction of chain order via the relief of cooperative chain packing effects.

As to the chain dynamics in elastomers, the relaxation of overall intensity in the proton MQ experiment, thus also the incoherent contribution to the decay of transverse magnetization in Hahn-echo experiments, is shown to be solely governed by fast segmental processes, i.e., Rouse modes that afford the averaging of the effective static-limit reference coupling down to the plateau value given by the dynamic order parameter. An influence of slow processes that were often adopted in earlier work can be excluded on the basis of our data.

In linear entangled melts, reptation of course takes the role of the slow process that causes a further loss of residual orientation correlation. A comparison of networks and a long-chain melt showed that the overall intensity loss in the melt is still governed by the fast modes, while reptation has a decisive influence on the reduction of the apparent RDC derived from the DQ build-up. Importantly, temperatures that exceed \( T_g \) by at least 100 K are needed to detect an RDC that corresponds to the entanglement level. This explains earlier findings of unexpectedly high order parameters at lower temperatures, and exemplifies the non-trivial and as yet not well understood relationship between the true chain fluctuation statistics, the rheologically determined timescales of polymer dynamics, and the data determined by NMR. More theoretical work will have to be devoted to the development of a proper model for the orientation autocorrelation function for entangled chains, which should ultimately feature fitting parameters that can be related to classic theories of polymer dynamics.

Miscellaneous applications include the dynamic state of chains grafted at one or two ends in block copolymers and to silica surfaces. In the first case, the confinement is found to increase chain order and to effectively suppress reptation, confirming a picture that stresses the importance of local, cooperative order phenomena. In the latter case, the role of heterogeneity is apparent in build-up curves with two maxima reflecting strongly absorbed and more freely mobile chains in the outer layer. A decisive layering with increasing but well defined mobility was also found for molecularly thin PDMS layers in high-surface porous materials. Finally, proton MQ NMR has been demonstrated to provide unique insights into the gelation process of polymers in the bulk or in dilute solution. The results are in good agreement with or complementary to those from rheological and light-scattering studies, and indicate spatially inhomogeneous gelation processes in both solution and bulk.

In conclusion, MQ NMR will continue to improve our understanding of polymer chain dynamics, where the large variety of new opportunities ranges from industrial screening applications of elastomers to very basic questions concerning the theories of polymer dynamics and rubber elasticity. It should be stressed again that one salient advantage of MQ NMR, which is the reliable separation of coherent dipolar and relaxation effects by means of analyzing both a DQ build-up as well as an MQ sum intensity decay, also applies to deuterium, where the very same pulse sequence can be applied and where the excitation of DQ coherence is largely restricted to the dominating single-spin quadrupolar effect. It is expected that many arguments made herein can thus be refined, as ambiguities related to multiple coupled spins are absent. Complications may then of course arise due to the more limited validity of the second-moment approximation that is central to the presented theory, and improved approaches will have to be developed.
Possible extensions of the homonuclear MQ experiment are of course methods that measure heteronuclear RDCs, and make use of the improved site resolution of, for example, carbon-13 nuclei. This would ultimately allow for the development of yet more improved models for the geometry of local segmental motion, since better defined local tensor orientations may become accessible. The applicability of such methods for the study of elastomers [131,132] or chains in channel confinement [133] has already been exemplified. Specifically, methods based on SEDOR (spin–echo double resonance, for static samples [134]) and REDOR (rotational-echo double-resonance, under MAS [135]) hold much promise, as they also offer the possibility of intensity normalization [136]. It will have to test whether such data can also be analyzed in terms of correlation loss due to dynamics on various timescales. This is a particular challenge under MAS, where recoupling methods are to be used and where the timescale of sample rotation introduces additional complications [137].

Acknowledgments

This work has benefited invaluably from the fruitful work with many graduate students, PhD students, and collaborators, the names of which can be taken from the cited publications. I thank them all for their contributions. Very specific thanks are due to Jens-Uwe Sommer and Andreas Heuer, who were not only involved in starting my interest in the subject matter, but also provided the theoretical input without which our research in the area would still be in its infancy. Insightful and important discussions with Robert Graf, Hans-Wolfgang Spiess, and Jörn Schmidt auf der Günst are acknowledged. Much of the research work of my group was performed at the Institut für Makromolekulare Chemie at the University of Freiburg, where I am grateful to Heino Finkelman, Rolf Mühlaupt and Alfred Hasenhindl for their support. Funding over the years was provided by the Deutsche Forschungsgemeinschaft (SFBs 428 and 418), the Landesstiftung Baden-Württemberg, and the Fonds der Chemischen Industrie.

References


P. Sotta, Local order and induced orientation in PDMS model networks, studied by \(^1H \) NMR, Macromolecules 31 (1998) 3872–3879.


V.M. Litvinov, A.A. Dias, Analysis of network structure of UV-cured acrylics by $^1$H NMR relaxation, $^{13}$C NMR spectroscopy, and dynamic mechanical experiments, Macromolecules 34 (2001) 4051–4060.


