Entanglements, Defects, and Inhomogeneities in Nitrile Butadiene Rubbers: Macroscopic versus Microscopic Properties

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ABSTRACT: Combined mechanical and NMR experiments were performed on bulk as well as swollen elastomers. Uniaxial stress–strain experiments in combination with current models of entangled rubber elasticity were used to disentangle the contributions from entanglements and chemical cross-links (including trapped entanglements) in a series of peroxide-cross-linked nitrile butadiene rubber (NBR) and its hydrogenated analogue (HNBR). The role of network defects was assessed by ultraslow stress–strain experiments and dynamic mechanical analysis. These macroscopic properties were compared with molecular-scale information obtained by advanced proton NMR spectroscopy techniques applied to bulk and swollen samples, which provide information on average cross-link density, its spatial heterogeneity, entanglement contributions, and the amount of inelastic defects. The emerging picture is that both NBR and HNBR elastomers feature significant cross-linking inhomogeneities, but the latter, related to on average much lower cross-linking efficiency and modified peroxide reactivity, contains significant (>20%) amounts of slowly relaxing, complex defect structures. For NBR, mechanical and NMR analyses are mutually consistent and allow for an absolute-value calibration of inter-cross-link and entanglement molecular weights and for a quantitative analysis of swelling experiments in a typical plasticizer (DBP), which turns out to be a good solvent. Data for HNBR suggest dominant entanglement effects, but likely due to the large defect content, mechanical and NMR results are not fully consistent. Highly inhomogeneous rubbers with significant defect contents remain to be a challenge for truly quantitative evaluation of different experimental results.

I. INTRODUCTION

The elasticity of rubber, and more specifically the rheological behavior at variable time (or frequency) scales and temperature, including dissipative properties, is primarily governed by the microscopic structure of the network.1,2 This concerns first the effect of nominally elastically inactive defects such as dangling chains, loops, or sol, linear or branched, with variable molecular weight. These defects are hard to quantify and have a complex influence on the mechanical properties, potentially leading to slow relaxations and transient phenomena. The effect of well-defined linear-chain defects has been the subject of previous investigations of model systems with controlled defects,3–5 yet their role in technologically relevant elastomers is yet to be elucidated.

A second point of concern is spatial variations (inhomogeneities) in the cross-linked matrix itself, which have also in recent years become directly accessible by suitable nuclear magnetic resonance (NMR) techniques.6,7 So far, their effect on macroscopic properties of bulk rubbers such as their stress–strain or the swelling response is experimentally not clearly established.8 Recent studies on model hydrogels based upon mixed microgel packings indicate that the macroscopic storage modulus of a bimodal system is close to that of a homogeneous system with the same average cross-link density,9 which is in agreement with earlier theoretical work on bulk rubbers.10 In contrast, the equilibrium degree of swelling11 may be much higher than expected (suggesting a too low cross-link density) if the degree of inhomogeneity is large.12

To address these aspects, we here compare a series of peroxide-cross-linked nitrile butadiene rubber (NBR) samples with its hydrogenated analogue (HNBR) of variable cross-link density, with identical acrylonitrile content of 39% and thus similar glass transition temperatures ranging from −23 to −18 °C (HNBR) and from −14 to −7 °C (NBR), increasing slightly with cross-link density.

Along the lines of an early study of NBR combining mechanical and swelling experiments,13 we use uniaxial stress–strain measurements to extract information on entanglement contributions, yet we focus on an analysis with more recent theoretical models of entangled rubber elasticity. In particular, we assess the "nonaffine"14 and "slip tube" models,15,16 whereby the influence of entanglement contributions on the fitted topological constraint modulus and cross-link modulus is considered. The potential influence of defects on the mechanical properties is assessed via dynamic-mechanical analysis (DMA) and long-time relaxing stress–strain measurements carried out at very slow strain rate.

Received: August 18, 2016  
Revised: November 4, 2016  
Published: November 23, 2016
Conclusions on the validity of a specific tube theory cannot be drawn without careful consideration of the network microstructure, which determines the entanglement density. Therefore, we use advanced $^1$H low-field NMR techniques to quantitatively assess the microscopic degree of cross-linking, its inhomogeneity, and the amount of network defects, seeking potential correlations with the macroscopic properties. Our study is complemented by the NMR study of samples swollen in a typical plasticizer, dibutyl phthalate (DBP), which enables an assessment of the entanglement contribution to the microscopic effective cross-link density.$^{6,17}$ We also assess the thermodynamic properties of DBP by analyzing data taken at swelling equilibrium.

NBR is an important, resilient, and chemically resistant performance elastomer that is widely used for protective gloves, seals, and hoses, specifically for applications where its low affinity to aliphatic hydrocarbons such as oils is of advantage. Hydrogenation, yielding HNBR, further improves its chemical resistance and the mechanical properties, in particular the low-temperature properties and ultimate behavior, and thus its service life under challenging conditions.$^{18}$ Hydrogenation of the unsaturated poly(butadiene) parts has two important consequences. First, it yields a more "poly(ethylene)-like" backbone with possibly modified stiffness and entanglement spacing.$^{19}$ Second, the removal of double bonds affects the efficiency of peroxide-based vulcanization systems. Both effects have an important impact on the mechanical properties of the rubber, which are at the focus of this contribution.

NMR studies of NBR have so far been rare.$^{20−23}$ High-resolution solid-state NMR as well as electron paramagnetic resonance spectroscopy techniques have been used to elucidate the complexity of radiation-induced radical reactions in NBR.$^{20}$ Its chain-level structural inhomogeneity related to comonomer blocks was revealed by site-resolved $^{13}$C longitudinal ($T_1$) relaxation time studies.$^{21}$ Later, the use of traditional transverse ($T_2$) relaxation time measurements as a probe of the level of cross-linking was also demonstrated for NBR.$^{22}$ More recent work noted the multieponential nature of the $T_2$ decays and ascribed it also to the block sequence distribution.$^{23}$ Such results are now complemented by our more quantitative NMR results.

In the following, a brief summary of the theory of rubber elasticity is given, focusing on the extended "nonaffine tube" and "slip tube" models. These models are fitted to quasi-static stress–strain measurements showing excellent agreement in both cases. The variation of the fitting parameters at small and ultrasmall strain rates is discussed based on dynamic-mechanical loss spectra in the low frequency range. The mechanical results are correlated with results of NMR investigations delivering microscopic network parameters such as defect content, average microscopic cross-link density, and the width of the inhomogeneous cross-link distribution in order to delineate their relevance. Finally, a network chain calibration is performed, also based upon results of swollen samples.

II. THEORETICAL BACKGROUND

Extended Nonaffine Tube Model. The nonlinear elastic response of stretched polymer networks is most basically described by a tube model of rubber elasticity. It takes into account that the network chain fluctuations in a highly entangled polymer network are restricted due to packing effects, which are described by virtual tubes around the network chains. When the network elongates, Heinrich et al.$^{14}$ have assumed that the tubes deform less than affinely with a deformation exponent $\nu = 1/2$ (see Figure 1a). This arises from a partial relaxation of the entanglements related to the first relaxation process in the Doi–Edwards terminology and implies that the tube diameter $d_\mu$ in spatial direction $\mu$ of the main axis system depends on the deformation ratio $\lambda_\mu$ as follows:

$$d_\mu = d_0 \lambda_\mu^{\nu}$$

(1)

Here, $d_0$ is the tube diameter in the undeformed state. Experimental evidence of nonaffine tube deformations according to eq 1 was provided by neutron scattering of strained rubbers,$^{24}$ stress–strain measurements on swollen polymer networks,$^{25}$ and more recently by NMR spectroscopy.$^{26}$

The nonaffine tube model was originally derived for the case of Gaussian chain statistics.$^{14}$ For applications up to large strains, we take into account that the network chains have a finite length. Then, in the case of uniaxial deformation, the engineering stress in stretching direction of the extended, non-Gaussian tube model with nonaffine tube deformation is obtained as$^{27−52}$

$$\sigma = \sigma_c + \sigma_e$$

(2)

$$\sigma_e = (\lambda - \lambda^{-2}) G_c \left[ \frac{1 - \frac{\lambda}{\Lambda}}{\left(1 - \frac{\lambda}{\Lambda}\right)^2} \right] = \frac{T_c}{\Lambda} \left[ 1 - \frac{\lambda}{\Lambda} \right]$$

(3)

$$\sigma_c = 2 G_0 (\lambda^{-1/2} - \lambda^{-2})$$

(4)

where $\Lambda = \lambda^2 + 2/\lambda - 3$, $n_s$ is the number of statistical chain segments between two subsequent entanglements, and $T_c$ is the trapping factor ($0 < T_c < 1$) which characterizes the portion of elastically active entanglements. Equation 3 refers to the constraints due to elastically active interchain junctions and takes into account the finite chain extensibility.$^{33,34}$ For the limiting case $T_c/n_s = 1/A_c$, $\sigma_c$ thus diverges, corresponding to full stretching of the chains between successive permanent links or trapped entanglements.

We point out that $T_c/n_s$ is used in eq 3 because in almost all technical applications of rubber the number of trapped entanglements is much larger than the number of chemical cross-links, ensuring good ultimate properties. For highly cross-linked networks $T_c/n_s$ has to be replaced by the sum $T_c/n_s + T_c/n_s$.
$1/n_c n_e$ being the number of segments between subsequent chemical cross-links (below we stick to using $T_v/n_e$ as single fitting parameter and take the $1/n_c$ contribution as implicated). Note that just above the gel point the first term increases much faster than the second term since, depending on the molar mass of the rubber melt, several entanglements can be trapped by the addition of a single cross-link. This ensures that the networks are entanglement-dominated at moderate cross-link concentrations. At higher cross-linking, $T_v$ approaches a constant value of 1 if no chain scission occurs during cross-linking. 29–32

For the moduli $G_e$ and $G_m$ the following relations to molecular material parameters hold:

$$G_e = (A_e \nu_e + A_p \nu_p T_v)RT$$  \hspace{1cm} (5)

$$G_m = \frac{\rho l^2 RT}{\sqrt{6 M_c d_0}} = \frac{1}{\sqrt{6}} \nu_e RT$$  \hspace{1cm} (6)

In eq 5, $\nu_e = \rho/M_c$ and $\nu_p = \rho/M_e$ ($\rho$: density; $M_c$ and $M_e$: inter-cross-link and entanglement molecular weights, respectively; see e.g. ref 31), $R$ is the gas constant, $T$ is the absolute temperature, and $A_e$ is a macrostructural factor that describes the fluctuations of network junctions. It equals $A_e = 1$ if the cross-link fluctuations are totally suppressed (affine model) and $A_e = 1 - 2/f = 1/2$ for freely fluctuating cross-links (phantom network with functionality $f = 4$). In the present case of tetrafunctional cross-links with fluctuation constraints due to adjacent cross-links and trapped entanglements it equals $A_e = 0.67$. 35 The fluctuations of trapped entanglements are described by the prefactor $A_f$, which is smaller than $A_e$ due to the sliding ability. In previous experimental studies it was estimated to $A_f = 0.2$.35

Equation 6 considers the topological tube constraints, with $G_m$ being proportional to the entangled chain density $\nu_e = \rho/M_c$ of the rubber. Here, $M_c$ and $l_0$ are the molar mass and length of the statistical segment, respectively.

**Nonaffine Slip Tube Model.** The slip tube model of Rubinstein and Panyukov is based on the assumption that chain fluctuations are suppressed by mobile slip links, which are able to move along the polymer chains (see Figure 1b). The constraining potential arises from fluctuating “slip links” at the end of the virtual chains. The resulting sliding motion hinders the segmental fluctuations and thus provides an expression of the stored length along the confining tube. On the molecular scale, a chemical bond due to a cross-linking event leads to a cross-link on each of it. The effective network chain density $\nu_e = \rho/M_c$ of the rubber. Here, $M_c$ and $l_0$ are the molar mass and length of the statistical segment, respectively.

Following eq 2, this is finally combined with the cross-link contribution $\sigma_e$ carrying the finite-extensibility effect as discussed above (see eq 3).

**NMR Observables of Network Structure and Relation to Swelling Behavior.** Proton NMR of elastomeric systems is dominated by dipole–dipole interactions between $^1H$ nuclei attached to the polymer chains. Given largely fixed distances and a well-defined static-limit coupling constant $D_{stat}$ the primary source of information is the orientation dependence of the interaction frequency $\omega_D = D_{stat}^\beta (3 \cos^2 \beta - 1)/4$ (units: rad/s). Fluctuations of the chains impart a time dependence on $\beta(t)$, which cause an averaging of the interaction to zero in the case of fast isotropic reorientations on the time scale of the NMR experiment ($\sim$100 µs). For monomers in network chains with two fixed ends (cross-links or other topological constraints), however, the fluctuations are anisotropic, and a finite and well-defined average residual coupling constant $D_{res}$ remains. 36,37 Note that this is an effective value that is characteristic for all protons in a given monomer. 38 It is proportional to a dynamic chain order parameter, $S$: 39–41

$$D_{res} \propto S = \frac{1}{2} \left[ (3 \cos^2 (\theta) - 1) \right] = \frac{3}{5} \left( \frac{R}{R_0} \right)^2$$  \hspace{1cm} (8)

Here, $l$ is the segmental length, $\theta$ is the segmental orientation with respect to the end-to-end distance, and $\langle ... \rangle$ indicates thermal conformational and structural (segmental) ensemble averages, respectively. Effects of macroscopic strain and also swelling enter through the dependence on the end-to-end vector $R^2/R_0^2$, $R_0$ being the unperturbed dimension. 40,41

For bulk samples, we have $R^2/R_0^2 = N_s$, leading to $D_{res} \propto 1/N$. Thus, $D_{res}$ measures the number of statistical segments $N$ of the constrained chain, including the effect of entanglements.

The direct relationship with the effective network chain density $(1/M_{eff} \approx 1/M_c + 1/M_e)$

$$\frac{1}{M_{eff}} = \frac{D_{res}/2\pi}{d_{ref}} f$$  \hspace{1cm} (9)

depends on a proportionality factor $d_{ref}$ that can be derived on the basis of model considerations involving assumptions concerning fast subsegmental motions and arguments related to chain stiffness. 38 It takes a value of about $740$ Hz kg/mol for cis-poly(butadiene), $620$ Hz kg/mol for natural rubber (NR), and $1270$ Hz kg/mol for PDMS. 38 Following the same arguments as in ref 38, we can estimate a value of $950$ Hz kg/mol for poly(ethylene). The functionality of the cross-links $f$ enters through application of the phantom model, which was recently shown to provide an improved correlation even in the bulk. 42 A measure of $D_{res}$ was historically estimated from transverse relaxation experiments 6,37 but is nowadays best measured directly by multiple-quantum (MQ) NMR. 6 This has the advantage that not only a reliable average $D_{res}$ value but also its distribution width and shape in the case of spatially inhomogeneous samples are accessible.

For swollen samples, neglecting subtle effects of solvent quality on $R_0^2$ that require a treatment by scaling approaches, 40,41 one can expect from eq 8 a direct dependence on the volumetric swelling degree $Q$ or its inverse, the polymer volume fraction $\phi_p = 1/Q$. Since $R^2 \sim Q^{2/3}$, we expect $D_{res,sw} \sim Q^{-2/3}$ in the affine limit. Our previous work on partially swollen networks 17 has demonstrated that this is the case after an initial desinterspersion regime, during which entanglement constraints
are removed (see also Figure 8a). This has led to the definition of a “phantom reference network” value

\[ D_{\text{res,PRN}} = D_{\text{res,eq}} Q^{-2/3} \]

which characterizes a virtual state free of entanglement-related packing effects, subject only to fixed chemical constraints and topologically trapped entanglements. The NMR quantities \( D_{\text{res}} \) and \( D_{\text{res,PRN}} \) should obviously be proportional to the mechanical observables \( G_{\text{tot}} = G_e + G_c \) and \( G_{\text{tot}} \), respectively, as demonstrated previously for NR. This will be tested for the (H)NBR samples below.

Equilibrium swelling experiments provide an alternative means to assess 1/\( M_c \). The phantom model predicts the following relation

\[ 1/M_c = \frac{\ln(1 - \phi_{\text{eq}}) + \phi_{\text{eq}} + \chi \phi_{\text{eq}}^2}{f} \]

where \( V_s \) is the solvent molar volume, \( \chi \) the Flory–Huggins interaction parameter, and \( \phi_{\text{eq}} \) the polymer volume fraction at swelling equilibrium. Note the correction due to the fraction of elastically inactive network defects \( \phi_{\text{def,n}} \) (see the correction to ref 42), which is only accessible by NMR experiments in the swollen state.\(^{14,24}\) In this context, the influence of \( \phi_{\text{def,n}} \) on the mechanical observables is also of concern, as discussed below.

### III. EXPERIMENTAL SECTION

#### Samples

The NBR grade of choice for the present study was Perbunan 3945 from Arlanxeo with an acrylonitrile (AN) content of 39% and a density of 0.99 g/cm\(^3\), to be compared with the saturated HNBR Therban AT 3904 from Arlanxeo with the same AN content and a density of 0.95 g/cm\(^3\). Mooney viscosities were measured with a Mooney viscometer MV 2000 E from Alpha Technologies as ML(1 + 4) = 52 MU and ML(1 + 4) = 40 MU at 100 °C. Gel permeation chromatography (GPC) with THF as solvent vs PS standard provided \( M_n \) of 190 and 150 kg/mol and as well as polydispersities of 3.2 and 2.4 for NBR and HNBR, respectively. These findings are consistent with the fact that HNBR, which is industrially produced from an NBR precursor polymer, is subjected to a degradation process before hydrogenation in order to retain a low melt viscosity, which would otherwise be strongly increased due to the lowering of the entanglement molecular weight \( M_e \) after hydration (see below for a discussion of actual values). Note that for reticulating entangled chains the viscosity scales inversely with \( M_e \).

At the given AN content, NBR and the derived HNBR are statistical and therefore amorphous copolymers with less than 30% AN diads.\(^{20,25}\) The supplier determined the order of 20% 1,2-vinyl units in the BR part. Therefore, homogeneous network structures could in principle be expected on the basis of the precursor polymers. Note that HNBR at both lower or higher AN content can be semicrystalline due to extended methylene or highly alternating sequences, respectively.\(^{19,24}\) We applied suitable NMR techniques to safely exclude crystallinity in our sample.\(^{45}\) The samples were cured with the peroxide Luperox 101XL45 from Sigma-Aldrich consisting of 50 wt % bis(tert-butylperoxy)-2,5-dimethylhexane, 25 wt % calcium carbonate, and 25 wt % silica. Different degrees of cross-linking were realized by different amounts of Luperox cross-linker specified in terms of phr (per hundred rubber): 2, 3, 4, 6, 8 and 4, 6, 8, 10, 12, 15 phr for NBR and HNBR, respectively. The sample names used below, (H)NBRx, indicate the Luperox content. The curing time was chosen as the time at which 90% of the torque increase is reached, as obtained from vulcanometer measurements, plus 1 min per mm sample thickness.

#### Swelling Experiments

Dibutyl phthalate (DBP) as purchased from Sigma-Aldrich (density 1.05 g/cm\(^3\)), a typical plasticizer, was used for swelling studies, taking advantage of its low volatility. For swelling equilibrium kinetics measurements, sample specimens (five discs of 5 mm diameter for each sample) were placed in the solvent, taken out at regular intervals, wiped, and weighed. The swelling process was rather sluggish, with equilibration times of the order of 25 and 40 days for HNBR and NBR, respectively. NMR measurements of the equilibrium-swollen samples using a small excess of DBP in sealed tubes were performed after 2 months. The volumetric degree of swelling \( Q \) was calculated on the basis of the known densities. For one sample (HNBRR) we also performed NMR experiments on a series of pieces swollen to a defined degree below equilibrium (controlled solvent content).

#### Stress–Strain Measurements

The uniaxial stress strain behavior was studied with universal testing machines Zwick 1445 and Zwick Z010, using strip samples (according to S3A norm) with reflection points for optical strain measurements. The samples (three of each species) were stretched up to break at two different cross-head speeds: 200 and 0.2 mm/min. With an effective sample length of 12 mm, this delivers strain rates \( \dot{\epsilon} \) of 0.28 and 0.00028 1/s, respectively.

#### DMA

The dynamic-mechanical measurements were performed with cylindrical strip samples (350 × 7 × 2 mm\(^3\)) in torsion mode with the system RDAII (Rheometric Scientific) in the linear range at 1.5% strain. The frequency range was 0.1–100 rad/s, and the temperature range was −20 to 140 °C. For the construction of master curves, first, \( \tan \delta \) was shifted horizontally to obtain overlapping branches (\( T_{\text{ref}} = 20 \) °C). For the construction of moduli master curves, also vertical shifts were done to account for the temperature dependences of mass density and entropy elasticity. Equal shift factors were applied for \( G' \) and \( G'' \), implying that \( \tan \delta \) is not shifted vertically.\(^2\)

#### NMR Spectroscopy

NMR experiments were performed on a Bruker minispec mq20 at a ‘H Larmor frequency of 20 MHz (\( B_0 = 0.47 \) T) according to previously published procedures.\(^{6,7,38,46}\) The 90° pulse length and the receiver dead time were 1.6 and 13 µs, respectively. All experiments were conducted at a sample temperature of 393 K in order to ensure sufficiently fast segmental dynamics, needed to have sufficient dynamic contrast between network and defect chains, and to faithfully probe cross-link constraints. In fact obtained nearly temperature-independent results in a range between 363 and 473 K, but weak and slow degradation effects became apparent in some samples above 413 K. Specifically, we used multiple-quantum (MQ) NMR\(^{7}\) to obtain quantitative results for the average residual coupling constant \( D_m \) (eq 8) and its distribution in the inhomogeneous samples. The advantage of MQ (sometimes also referred to as double-quantum, DQ) NMR over the more traditional Hahn echo experiment to study the transverse relaxation is the possibility to separate the effects of the chain dynamics time scale, which is not of concern, and the quasi-static (fast-limit) structural constraints dominating \( D_m \). Details on the measured signal functions and their processing are discussed below on a specific example from the present study.

### IV. RESULTS AND DISCUSSION

#### A. Mechanical Characterization: Uniaxial Stress–Strain Measurements

A basic sample characterization in terms of microstructural parameters obtained by direct nonlinear least-squares fitting of the data to eq 2 in combination with either eq 4 or 7 has been performed, providing the cross-link modulus \( G_e \) the entanglement modulus \( G_c \) and the average number of statistical segments between two trapped trapped entanglements, \( n_e/T_e \). The stress–strain curves of all samples alongside with their fits are shown in Figure 2a. The fits are obviously very good, with the only noticeable exception being the slip-tube model fit to the lowest cross-linked HNBR sample. The plots for NBR (left) and HNBR (right) are on the same x- and y-axes scales, so their comparison directly reveals the lower average modulus of the latter, along with more pronounced strain softening (related to entanglement effects) and correspondingly large ultimate drawability.
The derived moduli $G_c$ and $G_e$ are plotted in Figure 2b in dependence of the cross-linker content. Consistent results are obtained for both the extended tube and slip-tube models. The trends for $G_c$ are fairly linear, with a much larger slope for NBR, demonstrating the low cross-linking efficiency of the saturated HNBR. Notably, apart from some fitting ambiguity, $G_c$ is in both cases similar yet somewhat higher for HNBR and virtually constant for all samples. This is an expected result that superficially supports the validity of the fits. In the Appendix, we discuss the alternative estimation of $G_c$ and $G_e$ from Mooney–Rivlin (MR) plots, which is a rather popular approach. See ref 8 for a recent critical discussion. Also, those results are largely consistent with the tube model fits.

The values of $G_c$ can be compared with the corresponding values of the plateau modulus found from dynamic mechanical master curves for the non-cross-linked NBR and HNBR melts as shown in Figure 3, where $G'$ and $G''$ are plotted vs reduced frequency $\omega/\omega_o$ ($\omega_o$ being the shift factor). The plateau moduli $G_N$ are estimated as $0.79 \pm 0.02$ and $1.38 \pm 0.02$ MPa, respectively. A comparison with the $G_c$ values shows that for both rubbers the relation $G_N \approx 2G_c$ roughly holds. This is in agreement with theoretical estimates, since the prefactor in eq 6, $1/\sqrt{6}$, is almost half the prefactor $4/5$ for $G_N$ ($G_N = (4/5)e^{1/RT}$). Accordingly, the entanglement spacing $d_e$ obtained from eq 6 is the comparable to that found from the plateau modulus for both rubbers. The master curves of the moduli confirm that the molecular weights are comparably small, since the plateaus are not well developed for both systems. In addition, we see that the crossover frequency of NBR lies about 1 order of magnitude lower than that of HNBR, confirming that NBR has a higher molar mass. Finally, from the shape of the crossover range it can be concluded that the molar mass distribution of HNBR is narrower than that of NBR, in agreement with the polydispersities of 2.4 and 3.2, respectively, as found by GPC.

In Figure 4, we provide a consistency check of the notion that the quantity $T_e/n_e$ from the finite-extensibility term in eq 3, common to both models, should also reflect the cross-link density that is expected to dominate $G_e$. We remind that $T_e/n_e$ must be replaced by $T_e/n_e + 1/n_c$ when cross-links cannot be neglected in comparison to trapped entanglements, which is the case for the highly cross-linked NBR samples. We also have to keep in mind that according to eq 5 an additional trapped entanglement contribution is affecting $G_e$, but due to the small value of the prefactor $A_e$, this is expected to be small. Since $n_e$ is a constant for each rubber, the analysis of Figure 4 delivers information about the increasing $1/n_e$ and the potentially nonconstant (increasing) trapping factor $0 < T_e < 1$. For both samples and both fitting approaches, the plotted $G_e$ vs $T_e/n_e$ correlations are consistent with near-linear dependencies.

On first view, the data in Figure 4 suggest a much different trapping behavior for the two rubbers, since the slope of HNBR is lower by a factor of 3. However, for a discussion of the rubber-specific and cross-link-dependent entanglement trapping behavior, we have to take into account that $n_e$ is significantly lower for HNBR. This is expected on the basis of its potentially lower $M_c$ (thus lower $n_e$), leading to a larger $T_e/n_e$. From the plateau modulus evaluated in Figure 3, the entanglement molecular weight $M_e = 4/k_BT/G_N$ can be estimated to $M_e = 1440 \pm 100$ and $2400 \pm 100$ g/mol for HNBR and NBR, respectively. This indicates that also $n_e$ differs by almost a factor of 2, implying that the $x$-axis for HNBR is
stretched by this factor. Nevertheless, the slope of HNBR still remains lower by about 50%, which may be related to a higher trapping efficiency of this system, i.e., larger \( T_\alpha \) values at the same cross-linking level. However, as will be shown below, the HNBR samples feature a significant content of long-chain defects, which could affect the behavior at high strains and thus challenge the applicability of the fitting model and affect the apparent \( T_\alpha/n_\alpha \) values. We do not expect that this would impose a large systematic error on the \( G_\alpha \) values, as these are mostly reflected in the low-strain part of the stress–strain curves. This is corroborated by our MR analyses (see the Appendix), which neglect finite extensibility by focusing on the low-strain region.

Defect Relaxation. Defect-rich rubbers are well-known to exhibit a rather sluggish power-law type relaxation of the stress relaxation modulus after step strain. These will obviously have an influence on stress–strain curves taken at finite strain rate and also on results from DMA. In order to characterize slow relaxations, we turn to the DMA results in Figure 5a, where the loss tangent is plotted vs \( \log (\dot{\epsilon}) \) in double-log representation. For NBR, we observe significant low-frequency losses only for the lowest cross-link density, while all HNBR samples feature a broad, long-tailed relaxation spectrum toward low frequencies. These latter results are rather comparable to those measured on weakly peroxide-cured NR.

For comparison, the vertical dashed lines indicate inverse strain measurements with a very low strain rate (\( \dot{\epsilon} = 2.8 \times 10^{-4} \) s\(^{-1}\), i.e., 1000 times slower than normal, being at the limit of practical feasibility). Changes in \( G_\rho \) are particularly relevant, as this quantity is less affected by the differences among the fitting models. From Figure 5a we infer that even under ultraslow stretching, the defect contribution to the apparent \( G_\alpha \) is expected to be only partially relaxed. The measured data were again analyzed by both tube models, with a fitting quality that was as good as for the data shown in Figure 2. Figure 5b shows a comparison of the fitting results with those reported in Figure 2b (but now comparing \( G_\alpha \) rather than \( G_\rho \)).

For NBR, the \( G_\alpha \) (as well as not shown \( G_\rho \)) results from the two fitting models are not as consistent as for normal-speed stretching, but the \( G_\alpha \) values are in good mutual agreement, indicating a rather weak (~10%) reduction due to defect relaxation for all samples irrespective of cross-link density. For HNBR samples and both models consistently, \( G_\alpha \) from slow stretching is progressively reduced upon increasing the cross-link density. However, \( G_\alpha \) is significantly decreased only for the more lowly cross-linked samples, which means that the entanglement contribution \( G_e \) is now increasing significantly with cross-link density, leading to a balancing effect for the highest cross-linked samples. Obviously, the defects in the highly cross-linked samples have not relaxed to an appreciable extent. It is thus demonstrated that the HNBR results measured at the standard strain rate contain a significant contribution from unrelaxed defects, with qualitative differences as compared to NBR. We now turn to characterizing the cross-link density as well as the defect content of the samples on a microscopic level.

B. NMR Results. Data Analysis. Figure 6 shows the different steps of NMR data analysis and the corresponding results for one sample (HNBR4). The MQ NMR experiment provides two signal functions, the DQ build-up function \( I_{DQ}(\tau_{DQ}) \) and the reference decay curve \( I_{ref}(\tau_{DQ}) \), both measured as a function of pulse sequence duration. The rising part of the former reflects the target quantity \( D_{res} \) and its distribution, while the latter provides a means to correct for relaxation effects (long-time decay) due to the time scale of chain motions. Their sum, \( I_{MQ}(\tau_{DQ}) \), is the desired relaxation-only function used to correct for the relaxation effect in \( I_{DQ}(\tau_{DQ}) \). However, it contains non-network, i.e., isotropically mobile defect contributions, which need to be quantified and subtracted before normalization. The fit is best done on the intensity difference \( I_{res} - I_{DQ} \) as shown in Figure 5a, which exhibits a well-separated tail that was in our case best fitted by a biexponential decay (suggesting a distribution of defect types with different mobility). The resulting overall defect contents will be discussed below.

Now, the normalized DQ build-up function, \( I_{DQ}(\tau_{DQ}) \), is constructed (see Figure 5b). The overall shape of the nDQ build-up curve shows clear indications for pronounced inhomogeneity, i.e., a significant distribution of \( D_{res} \) values, as it deviates significantly from an
inverted Gaussian expected for a homogeneous network. Using previously established fitting approaches, we compared different ways of modeling the distribution (see Figure 6b). We compare the direct determination of the distribution by regularization analysis with fits to analytical formulas. In this regard, a \( \Gamma \) distribution provided a good fit. Such a distribution was found to describe the typical inhomogeneities in swollen gels rather well. It has a width (standard deviation \( \sigma \)) that is related to its average; i.e., it features no additional width parameter. It is a rather broad distribution, significantly wider than what is typically found for pure diene elastomers. For most of our networks, a bimodal fit based upon a \( \Gamma \) distribution function and an additional Gaussian distribution (or two \( \Gamma \) distributions) was stable and provided a good fit of the data. Importantly, the summed distribution matched well with the numerical results (see Figure 6c). On the basis of such fits, we extracted two quantities: a distribution-averaged \( \langle D_{\text{res}} \rangle \) and the overall relative distribution width \( r = \sigma / \langle D_{\text{res}} \rangle \).

Network Defects. In Figure 7 we collect the fitting results concerning defects and inhomogeneities. In addition to bulk samples, we have also studied equilibrium-swollen samples. As our swelling solvent, DBP, is fully protonated, its contribution to the NMR signal was carefully considered. Its contribution to the experimental intensity can be minimized by choosing a short repetition delay, taking advantage of its much longer longitudinal \( \langle T_1 \rangle \) relaxation time of about 600 ms, as compared to about 60 ms for the polymer components. On the basis of measured \( T_1 \) values for every sample (using a saturation-recovery pulse sequence), we quantified and subtracted the solvent contribution to the apparent defect content.

Figure 7. NMR characterization of sample inhomogeneity: (a) defect content determined in the bulk \( \langle \omega_{\text{def,bulk}} \rangle \) and equilibrium-swollen \( \langle \omega_{\text{def,sw}} \rangle \) states and (b) relative width of the cross-link density distributions (corresponding to \( D_{\text{res}} \) distributions; see eq 9), both plotted vs the distribution average \( \langle D_{\text{res}} \rangle \) in the respective states.

In contrast, the defect fraction in HNBR is not only about twice as high as in NBR in the bulk, it also increases further on swelling to a nearly sample-independent value of around 35%. Obviously, the microstructure of the defects is qualitatively different in this case. While lowly cross-linked samples feature mainly short-chain defects that are quantitatively visible in the bulk, a higher peroxide loading leads to more complex and possibly branched defect structures that relax very slowly in the bulk. Peroxide cross-linking was in fact shown to lead to chain scission and high defect contents in NR, and the situation is apparently similar here. This finding provides a nice molecular-scale rationale of the complex long-time relaxation in these samples (see Figure 5a). Summarizing, while the true defect contents in most NBR samples is of the order of 20% or lower, imposing moderate uncertainties for the mechanical and NMR properties measured in bulk, defects in HNBR must probably be considered in trying to understand its properties. Specifically, the relation of the mechanical observables to the microstructure must be modified.

Generalizing eqs 5 and 6, we have

\[
G_i = \left( 1 - \alpha_{\text{def,sw}} \right) \nu_{\text{app}} RT
\]

where the apparent chain densities \( \nu_{\text{app}} \) equal \( \rho (A_i / M_i + A_s T_s / M_s) \) or \( \rho / (6 M_s) \) for \( G_c \) or \( G_s \), respectively, or approximately \( A s \rho / M_{\text{eff}} = A_s \rho (1 / M_s + 1 / M_i) \) when \( G_{\text{tot}} \) is
analyzed. It is a matter of ambiguity and a question of the defect relaxation time scale which NMR-based measure, \( \omega_{\mathrm{def}} \) or \( \omega_{\mathrm{def,lin}} \), is to be used.

**Rubber Matrix Inhomogeneity.** The relative distribution width \( r \) characterizing the (inh)omogeneity of the rubber matrix is plotted in Figure 7b. It is typically 0.2 or even lower for homogeneous, sulfur-vulcanized diene rubbers. Peroxide cross-linking, though, leads to pronounced spatial inhomogeneities, with \( r \) values of 0.4 or even higher. The even higher value of around 0.9 found for our samples is nearly constant for all samples irrespective of the state of cross-linking or swelling. It is rather typical for any kind of swollen rubber or gel,\(^{17,49} \) where it reflects the topological complexity and the resulting inhomogeneity of the unfolded swollen state.

For the bulk state, however, \( r \approx 0.9 \) indicates substantial spatial variations in cross-linking, at a level much higher than what we have previously observed for peroxide-cured diene elastomers.\(^ {7} \) It is however rather comparable to EPDM,\(^ {46,50} \) which is also a complex copolymer. For NBR, our results nicely complement earlier conclusions on its dynamic inhomogeneity on the comonomer level by high-resolution \(^ {13} \)C NMR\(^ {2} \) and the multieponential nature of \( T_2 \) decays,\(^ {23} \) the latter having the very same origin as our result, yet only probed with a less quantitative technique. The latter finding was ascribed to variations in block sequence distribution, which we consider not realistic from the point of view of the statistical nature of the copolymers at the given high AN content\(^ {20,23} \) and the similar proton spin configurations in the AN and butadiene units,\(^ {38} \) i.e., CH and CH\(_2\) groups forming the main chain. Note that even styrene–butadiene rubbers (SBR) feature reasonably narrow distributions (\( r \approx 0.35 \)) despite the rather different monomeric units.\(^ {31} \) We thus favor an interpretation in terms of larger-scale cross-linking inhomogeneities, which may arise from radical rearrangement and chain reactions specific for NBR.\(^ {20} \) The observed level of inhomogeneity is actually comparable to what we have found previously for EPDM,\(^ {46} \) so a comparison of the two cases is of interest and will be taken up below.

**Phantom Reference Network.** We conclude this section by taking a closer look at the \( D_{\mathrm{res}} \) values determined in the bulk vs the swollen state; see the x-axes in Figure 7 (note that for simplicity we henceforth use just \( D_{\mathrm{res}} \) to denote the distribution-averaged residual coupling). As explained in the Theoretical Background section and shown schematically in Figure 8a, its change on swelling reflects a two-stage process of (i) desinterspersion of entanglement-related packing constraints and (ii) affine deformation at larger \( Q \).\(^ {17} \) Figure 8b shows for one HNBR sample also results from partially swollen samples (only one sample per \( Q \) value, thus the inferior statistics). The thick dotted trend line highlights the two-stage process, approaching affinity at higher \( Q \) as observed previously for other rubber types.\(^ {17} \) The dashed lines highlight the extrapolations according to eq 10 used to extract the phantom reference state value \( D_{\mathrm{res,PRN}} \) characterizing the cross-linked structure (including topologically trapped entanglements active in the swollen state), yet free from entanglement-related packing effects. The latter are quantified by the difference quantity, \( \Delta D_{\mathrm{res}} \).

Our earlier work suggests that \( D_{\mathrm{res}} \) measured at swelling equilibrium should scale with the corresponding swelling ratio \( Q_{\mathrm{eq}} \) with a power-law exponent of \(-1.5 \) for good solvents\(^ {30} \) and more strongly for poorer solvents.\(^ {47} \) The fitted exponent of \(-1.1 \) lies outside of the physical range, which would only be significant when DBP were not a good solvent (which it turns out to be; see below). We attribute the only moderate deviation to the complexity (inhomogeneity) of the samples already in the bulk, and the particularly high defect contents of the most poorly cross-linked samples, which impart some systematic error on the fitted apparent scaling exponent.

**C. Comparison of Mechanical and NMR Results.** The central set of results of this work is collected in Figure 9, where the mechanical results (moduli) are compared with the microscopic NMR results characterizing the rubber matrix. As highlighted in the Theoretical Background section, it is expected that there are linear relations without intercept between \( G_{\mathrm{res}} = G_{\epsilon} + G_{c} \) and \( G_{\epsilon} \) with \( D_{\mathrm{res}} \) and \( D_{\mathrm{res,PRN}} \). Within the uncertainties to be expected from our limited data set, including significant inhomogeneity and defect contents, the results for NBR are in very good agreement with this expectation, in much the same way as our previously reported results for rather homogeneous NR.\(^ {8} \) Namely, the linear fits in Figure 9a (left) differ vertically by the value of \( G_{\epsilon} \) and horizontally by the experimental \( \Delta D_{\mathrm{res}} \). The intercept for \( G_{\epsilon} \) is reasonably close to the origin. Plotting the data vs \( D_{\mathrm{res,PRN}} \) (see Figure 9b, left) just shifts the data such that now \( G_{\epsilon} \) extrapolates roughly to the origin. Thus, mechanical studies and NMR are in good agreement concerning the separation of permanent cross-links and entanglement effects, further confirming the PRN concept.
Possibly, HNBR features a much increased tendency of entanglements to become trapped and active in the swollen state, while they can still slide and relax in the nonlinearly strained bulk sample. From the consistency check of the mechanical fit parameters $G_c$ vs $T_e/n_e$ in Figure 4 we indeed concluded an increased trapping efficiency of the HNBR compared to NBR. Note that nonlinear uniaxial stretching and isotropic dilation upon swelling must not necessarily be similarly effective in trapping entanglements. While Figure 4 may superficially suggest that the trapping efficiency increases over the HNBR series upon uniaxial elongation, the results in Figure 9 rather suggest an increased but constant trapped contribution for swollen samples. For our results on EPDM we have also discussed such an entanglement localization. 46 This could mean that the $D_{res,sw}$ and $D_{res,PRN}$ Values measured in the swollen state are comparably too large, explaining a too small $\Delta D_{res}$.

Finally, we need to consider the potentially large effect of defects in HNBR. As seen in Figure 7a, one-third of the mass of these samples is not elastically active, at least not in the swollen state. The qualitative difference to the apparent (partially relaxed) defect content in the bulk suggests that the defects relax on widely different time scales for the different cross-link densities. The $D_{res}$ measured in bulk is thus potentially biased toward low values arising from the contribution of defects that are not fully relaxed on the 100 $\mu$s time scale. The same ambiguity holds for the moduli, as is directly corroborated by the diverse results obtained for the different strain rates in Figure 9b. Note that slow relaxations reflected in the tan $\delta$ data in Figure 5a may well continue to even lower frequencies, as was found for NR a long time ago. 48 All of this adds some level of uncertainties to the correlations shown for HNBR in Figure 9.

D. Network Chain Density Calibration. We now turn to an absolute-value assessment of actual $1/M_{eff}$ Values for the different methods, using the mechanical data as a reference. Specifically, we aim at a determination of $\omega_{eff}$ in eq 9 for future NMR studies and an assessment of the $\chi$ interaction parameter for swelling in DBP. Considering the physically consistent behavior of our NBR samples in our multimethod assessment, and the significant peculiarities associated with HNBR, we restrict these analyses to NBR. A cross-link functionality of $f = 4$ will be assumed in all cases.

In Figure 10a, we plot $1/M_{eff}$ and $1/M_c$ values for NBR as calculated from $G_{tot}$ and $G_{o}$ respectively, using eq 12 and assuming in both cases $A_s = 0.67$ and further that $1/M_c = 1/M_c + (A_s T_e)/(A_s M_c)$. The latter is justified by the fact that also $1/M_c$ calculated from $D_{res,PRN}$ contains a (likely additive) contribution from trapped entanglements. In all cases we used $\omega_{eff}$ determined by NMR in bulk samples for the defect correction. This choice deserves a comment. On the basis of the time scale estimate for the normal-speed linear stress–strain experiments in Figure 5a (left), we take that the defects contributing to the tan $\delta$ shoulder have not relaxed during stretching. This is why the defect estimate from swollen-state NMR (Figure 5a) would likely be too large. On the other hand, short terminal chains that contribute to the bulk-detected defect estimate have certainly relaxed also in the normal-speed mechanical experiments.

Note that even if the NMR-detected defects (Figure 5a) were considered for Figure 9, the linear correlations between the NMR and the mechanical observables would improve over what was shown there, in a sense that the intercept came closer.
to the origin. This justifies the consideration of defects for Figure 10a. Importantly there, for both the effective and crosslink-only quantities we observe nearly the same dependency, reinforcing the high internal consistency of the data. From the fits in Figure 10a we derive an average reference coupling for NBR of $d_{\text{eq}} = 1540$ Hz kg/mol. This is larger than the values estimated for PB, NR, or PE (see the Theoretical Background section), but still within a reasonable range. Note that using a lower value for $A$ in eq 12, e.g., 0.5 (pure phantom behavior) instead of 0.67, would lead to an according decrease in the $d_{\text{eq}}$ fitted value. A potentially higher chain stiffness due to the AN counts could also contribute to the somewhat large value.

Using eq 9, we can now also estimate an entanglement molecular weight $M_c$ of about 2950 g/mol from the average value of $\Delta D_{\text{eq}} \approx 260$ Hz. This can be compared to a (bulk defect-corrected) value of $1800 \pm 500$ g/mol based upon eq 12 and $G_t$ as obtained by fits to the stress–strain curves (Figure 2). This can be further be compared with $M_e = (4/5)pRT/G_N$ estimated from the plateau modulus of the linear precursors (Figure 3), yielding $2400 \pm 100$ g/mol. Obviously, the NMR-based value is overestimated somewhat but still within a reasonable range of expected systematic error of the PRN concept.

For the calibration of swelling data, its important to consider that entanglement effects are largely removed in the swollen state, thus requiring a suitable measure of the actual effect of cross-links (plus trapped entanglements) in that state. In an early study of NBR swollen in various solvents (benzene, cyclohexane, n-heptane), the authors performed stress–strain experiments in the swollen state for that purpose. According to this study, benzene is a $\theta$ solvent ($\chi \approx 0.5$), and the other ones are poor ($\chi > 0.5$). Here, we rely on our reliable extraction of $G_t$ via our model fits, as further supported by the internal consistency arising in the comparison with NMR experiments performed in the swollen state.

Thus, we plot in Figure 10b a defect-normalized network chain density $(1 - \omega_{\text{def}})/M_e$ as a function of the polymer volume fraction at swelling equilibrium $\phi_{\text{eq}} = 1/Q_{\text{eq}}$ in DBP. The normalization with regards to the swelled-state defect content is in line with the Flory–Rehner eq 11, which can then be rearranged accordingly to estimate a value for $\chi$ by fitting. The fit can be significantly be improved by considering a linear dependence on $\phi_{\text{eq}}$ in line with earlier work. The result is

$$\chi(\phi_{\text{eq}}) = 0.28 + 0.39\phi_{\text{eq}}$$

Notably, since $\chi(\phi_{\text{eq}}) < 0.5$ for all samples, DBP turns out to be a good solvent for NBR, a trend which was already supported by the $Q$ scaling of $D_{\text{res,sw}}$ (see Figure 8).

**V. SUMMARY AND CONCLUSION**

Comparing peroxide cross-linked NBR and HNBR elastomers in a multimethod approach comprising different mechanical characterization techniques providing macroscopic properties, and NMR studies of microscopic parameters, a picture emerges which stresses the relevance and nontrivial role of inhomogeneities and in particular nonload-bearing and slowly relaxing defects in the elastomer structure. Our main findings are that the mechanical properties clearly reflect the expected stronger influence of entanglement effects in HNBR as compared to NBR, which is mainly due to the comparably low cross-linking level of the former. The rather large fraction of elastically inactive network defects, which is significantly larger in HNBR, is for both systems found to be reflected in the long-time (low-frequency) mechanical properties.

The NMR data reveal that both elastomer types are characterized by a rather high level of cross-linking inhomogeneities, in contrast to other diene elastomers and comparable only to ethylene propylene diene terpolymer (EPDM) rubbers. Although the NMR responses of NBR and HNBR are rather similar, the comparison with macroscopic observables reveals a high internal consistency only for NBR. The properties of HNBR, in turn, appear to be largely influenced in a complex way by its microstructural complexity, specifically its high content of possibly branched defects, as a direct or indirect consequence of its low reactivity toward peroxide-based cross-linkers. In this regard, the NMR-based assessment of defect contents, comparing experiments on bulk and swollen samples, turned out to be instrumental in elucidating this aspect. The remaining challenge, and a worthwhile research goal, would be to establish a truly quantitative connection of the NMR-detected defect fraction and the time-dependent mechanical properties.

The consistent results for the less defect-dominated NBR stress that the mechanical (and averaged NMR) properties do not appear to be strongly influenced by the rather significant cross-linking inhomogeneity as probed by NMR. A rationale for such a behavior was recently provided by experiments on model-inhomogeneous microgel packings, which support the notion that macroscopic properties are well described by average microstructural parameters (mostly $M_e$). Only if the level of inhomogeneities surpasses a certain (at present not well understood) threshold does one observe deviations from the “mean-field” picture. Notably, such deviations are more pronounced in the swollen state and pose particular challenges for a (sometimes only apparently) quantitative
analysis of results taken on samples swollen to equilibrium or also below.52 Finally, large defect contents combined with low cross-linking and consequently the dominance of entanglement effects, as found for HNBR, pose challenges for the application of theoretical models of entangled rubber elasticity. This concerns the role of finite extensibility and/or time scale of slow relaxation of entangled network and defect chains.5,53

Figure 11. (a) Mooney–Rivlin (MR) representation of the predictions of the two entanglement models for an elastomer with $G_e = 0$. The dashed line is the linear dependence assumed in eq A1. (b) Stress–strain data as a function of the deformation ratio for four representative NBR and HNBR samples. (c) MR representations of the same data with and without the correction of inaccuracies in strain. The short dashed lines mark the original fitting limits from (b), and the solid lines represent the results of the MR fits over the whole inverse deformation range.

Figure 12. Dependence of the fitted moduli on the cross-linker content from MR analyses (large symbols) as compared to fitting results of the two tube models (small symbols from Figure 1).

■ APPENDIX. MOONEY–RIVLIN ANALYSIS

In the literature, it is rather customary to estimate the entanglement contribution to the modulus from linear stress–strain data by way of the Mooney–Rivlin (MR) formula:

$$\sigma_{\text{red}} = \frac{\sigma}{\lambda - \lambda^{-2}} = 2C_1 + \frac{2C_2}{\lambda} \quad (A1)$$

Here, $2C_1$ and $2C_2$ are customarily assigned to $G_c$ and $G_e$, respectively. It is stressed that this is only an operational approach, as the underlying MR strain energy function is known to be inadequate for describing rubbers in other deformation modes.44,56 The main idea is to obtain numerical values $2C_1, 2C_2$ that quantify the deviation from neo-Hookean behavior (for which $C_2 = 0$). The mentioned assignment has been critically discussed in the literature4,56,57 and can be mapped onto different models for the entanglement contribution. This is demonstrated in Figure 11a for the example of the extended tube and slip-tube models discussed in the main text. In a normalized MR representation of $\sigma_{\text{red}}$ vs $\lambda^{-1}$, eq A1 with $C_1 = 0$ and $2C_2 = G_e$ is just a straight line. The extended tube model prediction is almost indistinguishable from this line, while the slip-tube prediction deviates systematically but not very much. This is why similar results can be expected from all three approaches.

In the MR approach, the finite-extensibility contribution is necessarily neglected, which is traditionally solved by restricting the fitting range to moderate $\lambda^* \geq 0.5$. The calculation of $\sigma_{\text{red}}$ provides another pitfall, in that larger errors arise for $\lambda^* \to 1$ due to the division by a small number. The main source of error is uncertainties in the actual extension ratio, as already noted in an early study of NBR.13 We solve the problem by fitting $\sigma(\lambda)$ data to a rearranged version of eq A1, replacing $\lambda$ by $\lambda + \Delta\lambda$ and fitting $\Delta\lambda$ (see Figure 11b for examples). The MR representations in Figure 11c demonstrate nicely the success of this procedure, showing near-linear dependencies now also for $\lambda^* \to 1$.

The MR results are compared with the entanglement model results in Figure 12 (large vs small symbols, respectively). It is seen that apart from some systematic deviations for HNBR at low peroxide content, all results are on good mutual agreement with each other. This mainly reinforces that potential issues with the finite extensibility term, which is limited to $G_e$ in the entanglement models (see also Figure 4), are negligible. The quantities $G_c$ and $G_e$ are thus well determined in all cases.

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■ ACKNOWLEDGMENTS

We thank Julia Weichhold and Wolfgang Binder (Institut für Chemie, Halle) for providing the GPC analyses. Helpful discussions with Dr. A. Bischoff (Arlanxeo Deutschland GmbH) are gratefully acknowledged. Financial support was provided by the “VolkswagenStiftung” and the “Niedersächsisches Ministerium für Wissenschaft und Kultur” (MWK), grant ZN 2189.
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