Entanglement Effects in Elastomers: Macroscopic vs Microscopic Properties

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Supporting Information

ABSTRACT: This Perspective highlights how entanglement effects on rubber elasticity can be unveiled by a combination of different macroscopic and microscopic methods, taking advantage of new developments in proton low-field NMR spectroscopy as applied to bulk and swollen rubbers. Specifically, the application of a powerful yet routinely applicable double-quantum method, combined with a back-extrapolation procedure over results measured at different degrees of swelling, allows one to characterize the recently introduced “phantom reference network” state, which only reflects contributions of actual cross-links and topologically trapped entanglements. We further present an assessment of the qualitative yet popular Mooney−Rivlin analysis of mechanical data, where the influence of entanglement contributions on the fitted, purely empirical parameters $C_1$ and $C_2$ is reconsidered in the context of different tube models of rubber elasticity. We also review the impact of entanglements on results of equilibrium swelling experiments and address the validity of the common Flory−Rehner approach, where we stress its qualitative nature and the need to use NMR observables for a correct estimation of the relevant volume fractions. We discuss semiquantitative estimations of the cross-link density from these macroscopic experiments with its microscopic determination by NMR on the example of lowly cross-linked synthetic and natural poly(isoprene) rubber prepared by a novel UV-based curing protocol of dried latex based upon thiol−ene chemistry, which in contrast to previously studied thermally peroxide-cured natural rubber contain only small amounts of short-chain defects. We find that the entanglement effects in these samples can best be described by the Heinrich−Straube tube model with positive scaling exponent $\nu > 0.3$ as well as by the slip-link model of Ball et al./Edwards−Vilgis with a slip parameter $\eta > 0.1$. A comparison with literature results demonstrates that these findings are not universal in that the apparent entanglement contribution depends significantly on the sample (in)homogeneity, i.e., of the NMR-determined fraction of inelastic defects and spatial cross-linking inhomogeneities. This means that conclusions on the validity or invalidity of specific tube theories cannot be drawn without careful consideration of the network microstructure.

I. INTRODUCTION

The theoretical foundations of our understanding of entropic rubber elasticity have been laid more than 80 years ago.1,2 While these early theories provide a qualitative description of some mechanical properties, e.g., uniaxial stress−strain curves, deviations on the detail level are clearly apparent, in particular for lowly cross-linked systems. The subsequent decades have witnessed the development of a multitude of strain energy functions based upon molecular models and corresponding stress−strain predictions.3−16 The earliest attempts, for example the model of Ronca and Allegra,3 were based upon specific anisotropic constraints to the cross-link fluctuations, which were assumed to be isotropic in the original phantom model.2

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Most modern theories are based upon the tube model of rubber elasticity and all have in common that they assume an additive contribution of chemical cross-links described by one of the classic theories, possibly refined by finite-extensibility terms, and the entanglement contribution, modeled by slip links or a suitable tube-like constraint to the conformational freedom of all segments rather than just the ends.

With increasing complexity (i.e., number of fitting parameters), fits of simple uniaxial-extension data to such predictions becomes ambiguous, stressing the importance of either probing more complex (in particular biaxial) deformation modes or, alternatively, the microscopic observation of the structure or the dynamics of individual chains or segments. In this context, neutron scattering techniques have been used to probe the anisotropic stretching of labeled network chains and the anisotropy of the tube-constrained segmental motion, suggesting the validity of a specific tube deformation law. It should be noted that these results have been criticized with regards to the approximations used in the fit of the structure factor and to the contribution of defects.

Another important and extensively used molecular-scale technique to characterize elastomers is solid-state NMR, possibly applied on a simple low-field instrument. In particular, the robust double-quantum (DQ or, more generally, multiple-quantum, MQ) technique represents a more quantitative alternative to $T_2$ relaxometry and has been used extensively to estimate the overall cross-link density and assay the sample homogeneity and defect contents. More recently, it was also used to probe the thermodynamic state and the inhomogeneous chain deformation in swollen samples as well as to characterize the actual chain stretching in strained samples. A more indirect $^1$H NMR spin probe technique as applied to biaxially strained samples was further used to assay the validity of specific network models for the description of local deformation.

Here, we highlight how a combination of three different techniques for the characterization of elastomers, i.e., uniaxial stress–strain, equilibrium swelling, and $^1$H DQ-NMR experiments, thus combining macroscopic and microscopic observables obtained from bulk and swollen samples, can help to reveal the influence of entanglements. This allows for conclusions on the applicability of specific network models. As a specific example, we present new data measured on latex-based natural and synthetic polyisoprene rubber prepared by a novel UV-based curing protocol.

We discuss the Mooney–Rivlin (MR) method as the most popular yet purely empirical approach to mechanical data analysis. It is well-known that the MR strain energy function does not provide a consistent description of mechanical data and that the naive interpretation of the fitted $C_{20}$ parameter in terms of the entanglement contribution is incorrect. However, the literature provides an ample database of fitted apparent MR parameters $C_1$ and $C_2$, and it is a valid question to ask whether this data is of any use. We thus revisit the problem of separating the relative contributions of permanent cross-links and entanglements to $C_1$ and $C_2$ when they are fitted over a defined deformation range. It turns out that the predictions of many of the above-mentioned theories differ qualitatively in this aspect, enabling a distinction.

It is noted that the sample preparation (e.g., the use of a specific curing system) has been shown to exert a decisive influence on the MR parameters even in the same base polymers, which stresses the need to use a molecular-scale characterization technique such as DQ-NMR to assess the microstructure.

In this latter study, we were able to unambiguously reveal that peroxide-based cross-linking of natural rubber leads to substantial defect contents and pronounced cross-linking inhomogeneities. The specific and complex processes in latex-based rubbers, involving precuring, drying, and postcuring, were also revealed with the same technique, demonstrating again substantial differences between sulfur- and peroxide-based curing.

The most relevant insights arise from the application of DQ-NMR to the study of partially swollen rubbers. To this end, we have recently established the “phantom reference network”, which refers to a back-extrapolated NMR observable representative of the unswollen bulk that only reflects contributions from permanent cross-links, as reviewed in this Perspective. The observables from all techniques are converted to semi-quantitative measures of the cross-link density, and the linear correlations between them can be used to draw consistent conclusions on the magnitude of entanglement effects.

This Perspective is structured as follows: In the following section, we review what we consider the most established strategies for elastomer characterization by the three mentioned techniques, with a critical discussion of their limitations. The third section is devoted to a discussion of the influence of entanglements in each of the techniques. We put particular emphasis on the predictions of modern theories of entangled rubber elasticity and how these can be tested on the basis of the parameters obtained from the popular Mooney–Rivlin analysis. The fourth section is devoted to a comparative discussion of actual experimental data on a series of lowly cross-linked poly(isoprene) rubbers. We finally conclude on the use of such multimethod studies, combining macroscopic and microscopic insights, in establishing a broader data basis to ultimately obtain a universal picture of entanglement effects in rubbers.

II. REVIEW OF EXPERIMENTS AND ANALYSIS STRATEGIES

In the following, we discuss the different experimental strategies and the associated theoretical background related to an estimation of the most relevant structural parameter of polymer networks, i.e., the average molecular weight between cross-links, $M_c$, by the different techniques.

A. Equilibrium Swelling Experiments. The most common approach to the analysis of swelling experiments is the Flory–Rehner (FR) theory, as based upon the separability hypothesis of the free energies of chain stretching and mixing. Taking advantage of comparisons with NMR experiments (see below), we have in recent years addressed many of the practical and theoretical problems related to this approach; for a review see ref 45. As the bottom line, we found that FR theory is well applicable in poor and theta solvents, but limitations are expected in good solvents. This is a result of excluded-volume statistics of the chains, which challenges the validity of the treatment of the elastic response. The good news is, however, that the FR equation can still be applied and that the good-solvent effects are phenomenologically accounted for by an (apparently!) concentration-dependent Flory–Huggins interaction parameter $\chi$, as addressed extensively in the literature. Ultimately, one must of course always expect a certain level of systematic error related to the derived absolute values of the obtained molecular weight $M_c$.

On the basis of a study of samples with variable effective cross-link functionality $f_c$, we found that the FR equation as based upon the phantom model for the elastic response


\[ M_{cu, sw} = - \frac{\rho_s V_d \phi_{p, ed}^{1/3}}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} f - 2 \] (1)

gives the most consistent representation of the data. This was also stressed much earlier by Cohen and co-workers.\textsuperscript{54} Usually, \( f = 4 \) for elastomers made from long precursor chains. As to the other parameters, \( \rho_s \) is the polymer density, \( V_d \) the solvent molar volume, \( \phi_p = V_p / V \) the polymer volume fraction at swelling equilibrium, and \( \phi_{p, ed} = \phi_p (1 - \omega_{def, sw}) \) the volume fraction of elastically active polymer; i.e., it is corrected for elastically inactive network defects as determined by DQ NMR (see below).

This last issue turns out to be rather relevant, as we find that the fraction of nonload-bearing chains in the swollen state can be rather high, much higher in fact than the amount of extractable sol. Note that the NMR determination of \( \omega_{def, sw} \) to be used for \( \phi_{p, ed} \) in eq 1 must be determined in the swollen state using a perdeuterated solvent. It will be shown below that \( \omega_{def, sw} \) can further be substantially bigger than \( \omega_{def} \) determined in the bulk, in particular in rather lowly cross-linked networks. The defects comprise dangling chains as well as sol. Yet, for rubbers made from long chains, such as the samples addressed below, the sol content is usually rather low.

It should be noted that during swelling experiments it is sometimes mandatory to exclude air and UV light in order to avoid gradual network degradation. This has been demonstrated to be a potentially serious problem for natural rubber swollen in toluene.\textsuperscript{32} Such adverse effects can be monitored by swelling kinetics studies, as addressed in the Supporting Information.

**B. Characterization of Tensile Properties.** Rubber materials generally exhibit strongly nonlinear stress–strain behavior, and the elasticity in the lower deformation range can often be described qualitatively by the Mooney–Rivlin (MR) law.\textsuperscript{42} It is again stressed that the MR law must be considered as empirical, as it has no immediate theoretical justification in terms of an entanglement model and since the underlying strain energy function fails qualitatively in the description of mechanical data in more complex (mostly biaxial) deformation modes.\textsuperscript{10,15} However, it represents the most popular approach to simply parametrize the nonlinear tensile behavior. The relevant MR equations for uniaxial extension read

\[ \sigma = 2C_1 (\lambda - \frac{1}{\lambda^2}) + 2C_2 \left( \lambda - \frac{1}{\lambda^2} \right) \] (2)

\[ \sigma_{ed} = \frac{\sigma}{\lambda - \frac{1}{\lambda^2}} = 2C_1 + \frac{2C_2}{\lambda} \] (3)

where \( \lambda = l / l_0 \) is the deformation (stretch ratio) determined by \( l_0 \) and \( l \) as the initial and final lengths of the sample before and after application of force, respectively. By plotting the reduced Mooney stress (\( \sigma_{ed} \)) against the reciprocal \( 1/\lambda \), a linear relationship, eq 3, is often found or is simply imposed, and the apparent MR constants \( C_1 \) and \( C_2 \) can be determined by linear regression in a range of small to intermediate deformations, i.e., \( 1.3 < \lambda < 2.5 \) for our data to be discussed below and in many references (see e.g. ref 10).

Sample data are shown in Figure 1 in order to highlight the limitations often posed by actual data and to demonstrate why a two-parameter description based upon a linear fit over a limited data range is practically sufficient. An upper limit (lower limit for \( 1/\lambda = 0.4 \)) for the linear fit is chosen to avoid the region of strain hardening due to strain-induced crystallization and finite extensibility. One may of course try to capture these effects with a more complicated model,\textsuperscript{6,8,13,43} yet this comes at the expense of additional uncertainties with regards to its applicability and limitations. A lower limit (upper limit \( 1/\lambda = 0.77 \)) is of practical origin and avoids the low-\( \lambda \) region where \( \sigma_{ed} \) often shows a strong upturn (in fact, a divergence) due to uncertainties in the determination of \( \lambda \) on many tensile testers. An adjustment by \( \Delta \lambda \) can be attempted by fitting the region up to 3% strain to eq 2 using \( \lambda - \Delta \lambda \) instead of \( \lambda \) as argument. The inset of Figure 1 demonstrates that the upturn can partially be removed in this way, but uncertainties remain. From the inset, it is however clear that the problem does not significantly affect data below \( 1/\lambda = 0.8 \).

For the analysis and comparison of the results to other techniques, it is common practice to take an empirical approach and use the predictions from rubber elasticity theory,\textsuperscript{52,53} again using the relations based upon the phantom model:

\[ E = \frac{3\rho_p RT}{M_{c,E}} \frac{f - 2}{f} \] (4)

\[ 2(C_1 + C_2) = \frac{\rho_p RT}{M_{c,MR}} \frac{f - 2}{f} \] (5)

\[ 2C_{1/2} = \frac{\rho_p RT}{M_{c, C_{1/2}}} \frac{f - 2}{f} \] (6)

As discussed above in the context of swelling experiments, our previous studies on model elastomers\textsuperscript{56} suggest that the phantom model is better applicable than the affine model even in bulk rubbers, even though this issue is still a subject of current discussion.\textsuperscript{54} In any way, the affine and phantom predictions differ only in the constant factor \( (f - 2)/f \), which only affects the absolute values but not the correlations between them,\textsuperscript{59} given constant functionality \( f \). Of course, the phantom model does not explicitly treat entanglements, but it is again common practice to apply one of the classic models to estimate their density from their modulus contribution. In the above equations, we distinguish \( M_{c,MR} \) obtained from the \( \lambda \rightarrow 1 \) limit of the MR analysis, reflected by eq 5, which should be comparable to \( M_{c,E} \).
Realizing that in an undeformed sample $R^2 = R_0^2 = M_{c,NMR}$ can be related to the (apparent) network chain molecular weight

$$M_{c,NMR} = \frac{d_{ref} \cdot f - 2}{\nu/m/2\pi} \quad (8)$$

where for instance $d_{ref,NMR} = 617$ Hz kg/mol for natural rubber (NR = 100\% cis-polyisoprene). The functionality of the cross-links $f = 4$ enters again through application of the phantom model, which was recently shown to provide an improved correlation even in bulk samples.36

Importantly, with our method we can reliably determine from the DQ buildup curve not only the structure-averaged $D_{uv} = (D_{uv}/\text{sample}) \sim 1/M_{c,NMR}$ described by an averaged version of eq 7 but also its distribution in an inhomogeneous sample. The distribution function can be determined by a previously published, optimized numerical procedure.58 The most practical second parameter is the numerically calculated standard deviation $\sigma$ of the distribution in terms of a dimensionless width parameter $\sigma/D_{uv}$. In the following, $M_{c,NMR}$ always represents an average value obtained from $D_{uv}$.

III. CONSIDERATIONS OF ENTANGLEMENT EFFECTS

The proposed experimental strategy to be illustrated in the next section relies on extracting information on entanglement effects by comparison of different methods which depend rather differently on these. In the following, we thus address this issue for the case of mechanical, swelling, and NMR experiments, where in the latter, our comparison of samples measured in the bulk and in the swollen state (using an extrapolation procedure) is of particular relevance.

A. Entanglement Effects on Mechanical Properties.

For the MR model, it is commonly and uncritically, and likely wrongly, assumed that the constants $C_1$ and $C_2$ reflect the contributions of cross-links and entanglements, respectively. This is motivated by the assumption that the topological constraints leading to the entanglement contribution vanish at infinite strain. This is borne out qualitatively by many modern theories of rubber elasticity based upon tube theory,47,79,12,16 but the $\lambda$ dependence turns out to be different from $C_2\lambda^{-1}$ when a correct constitutive model is employed. Most of the mentioned tube models rely on specific assumptions on the deformation of the spatial components ($i = (x, y, z)$) of the tube diameter

$$d_i = d_0\lambda_i^{\nu} \quad (9)$$

where affine tube deformation corresponds to $\beta = 1$ and $\nu = 1$. This general form of a tube deformation law has been suggested by Heinrich and Straube (HS) in the context of their mean-field theory, where $0 \leq \beta \leq 1$ describes the influence of (defect-related) constraint release processes and $\nu$ is the scaling exponent of actual tube deformation.7

For other theories, in particular the molecular stress function model (MSFM) of Wagner31 and the virtual-chain models of Rubinstein and Panyukov (RP),13,16 we find the explicit statement that the entanglement contribution to the modulus, $G_\text{e}$, contributes in equal parts (50–50) to $C_1$ and $C_2$.10,11 As we will see, this statement requires some reconsideration.

In general, the nonlinear contributions to the reduced Mooney stress is most often written the form

$$\sigma_{red} = G_e + G_e\phi(\lambda) \quad (10)$$

where $\phi(\lambda) = 1/\lambda$ corresponds to the MR form. Neglecting finite extensibility effects, eq 10 holds for all but one13 of the cited...
Figure 2. Schematic influence of cross-links, entanglements, and defects on the stress relaxation modulus $G(t)$ of a polymer melt. Since the NMR observable relies on fast segmental motions $>100$ kHz, it is limited to probing properties reflecting $G(t)$ in the indicated region. Adapted from ref 10.

Theoretical treatments based upon molecular (chain) models, but not for possibly improved phenomenological models based upon continuum mechanics. The parameters of these are not readily comparable to results of other methods probing network structure; thus we exclude them in our discussion. From now on, we denote with $G_c$ the contribution of cross-links, which possibly includes topologically trapped entanglements that behave like fixed physical links. $G_e$ reflects apparent entanglement contributions, whose magnitude depends on the particular form of $\varphi(\lambda)$ which may also have an apparent $\lambda$-independent plateau contribution.

The way in which $G_c$ is reflected in the linear stress relaxation modulus is shown in Figure 2. Wagner$^{10}$ argued that the nonlinear response (strain energy function) of a lowly cross-linked elastomer at higher $\lambda$ is qualitatively indistinguishable from that of a terminally unrelaxed (tube-dominated) polymer melt, where chemical links replace entanglements up to a level where the apparent long-time $G_e$ equals the melt plateau modulus $G_p$. Such an assumption is at least in partial variance to experimental observations that often show a linear relation and an entanglement-related intercept when the elasticity modulus is plotted vs the cross-linker content.$^{36,60}$

However, relaxation processes of a long cross-linked but entanglement-dominated chain within the tube are certainly possible,$^{61}$ such that the relaxed modulus and depends non-trivially on the cross-linker content. Trapped entanglements acting as physical cross-links, and possibly following the deformation law of a permanently cross-linked rubber,$^{43,59,62}$ are another issue. Thus, the relaxed modulus $G_{e,app}$ cannot a priori be expected to be proportional to the actual cross-link density, and it may well be lower than $G_e$. Finally in this context, it is also useful to bear in mind that fast-relaxing defects (short loops, dangling ends) effectively dilute the system and reduce the long-time modulus over a large time range (dotted lines in Figure 2).

Turning back to tube-model predictions of $\varphi(\lambda)$, Figure 3 shows a representation of the entanglement-only contribution ($G_c = 0$) normalized to $G_e = 1$ to the Mooney stress for the most relevant of the mentioned theories: MSFM$^{9,10}$ RP1997 simple virtual chain scaling model,$^{12}$ RP2002 extended slip-tube model,$^{16}$ and the HS mean-field tube model.$^7$ For the latter

$$\varphi(\lambda) = \frac{1}{b} \left( \frac{\lambda^b - \lambda^{-2b}}{\lambda^2 - \lambda^{-1}} \right)$$

where $b = v/\beta$. In Figure 3a, it is seen that only the MSFM, RP2002, and HS ($v < 0.5, \beta = 1$) models can account for the (experimentally well substantiated) maximum of $\sigma_{red}$ at slight compression ($\lambda \approx 0.56$).

An interesting observation is that the HS model can, almost perfectly, reproduce the predictions of all other tube models by variation of the tube scaling exponent $\nu$. We are aware of only one treatment that mentioned the close relation of the HS and RP models,$^{14}$ and stress its heuristic use. Specifically, $\nu < 0$ corresponds to an oblate tube constraint, and $\nu = -1/4$ has been claimed to hold for highly cross-linked rubbers.$^7$ A value of $\nu = 1/2$ was in turn attributed to entanglement-dominated rubbers. The MSFM also assumes entanglement-dominated systems,$^7$ assuming an isotropic dilation $\lambda^{1/2}$ of the tube upon uniaxial stretching, which in the anisotropic HS model occurs for the transverse component when $\nu < 0$. This may explain the fit with the larger $\nu \approx -0.57$ exponent. Interestingly, the RP2002 model corresponds to $\nu = -1/4$ even though it explicitly assumes a $\lambda^{1/2}$ scaling of the tube diameter component parallel to the strain. The difference is obviously explained by the different—obviously inverse—way in which the tube constraint is implemented in the different models (virtual chain length versus mean-field harmonic potential).

We thus conclude that the HS tube model represents the currently most versatile tube-based approach, as one can in principle use eqs $9$–$11$ in combination with experimental data to
draw conclusions on the value of $\nu$ when it is taken as a free parameter (of course setting $\beta = 1$). It is noted that the early theory of Ronca and Allegra, assuming a specific form of restrictions to junction fluctuations rather than a tube constraint,3 and the tube model of Marrucci4 also predict the experimental maximum in $\sigma_{\text{red}}$ however not at $\lambda \approx 0.56$ but at $\lambda = 1$. Both models predict a quicker decay of $\sigma_{\text{red}}$ with $1/\lambda$ in the compression range than the other models. In elongation, the Marrucci model is similar (but not identical) to the HS model with $\nu = 1/2$.11 Further, the Ronca—Allegra model predicts a constant ratio of $C_1/C_2$ (as it does not consider an independence of cross-link and entanglement effects) and a rather strong, nonlinear, and decisively sigmoidal decay of $\sigma_{\text{red}}$ with $1/\lambda$ in the elongation range. Both latter models are thus not in good accord with experimental data and can safely be neglected.

Figure 3b is of relevance for MR analyses, as it shows that MR fits in the elongation range, when suitably (and experimentally reasonably, see above) constrained to intermediate $1/\lambda$ values, will show finite contributions of $G_e$ to the apparent $2C_1$, even in a purely entangled system. The $50\ldots50$ statement of Wagner10 refers to exactly this situation, while the $50\ldots50$ statement in RP199712 actually refers to the slope around $\lambda \approx 1$. Analyzing the RP predictions, both of which coincide in the elongation range, in the intermediate $\lambda$ range yields $2C_1 \approx 0.2G_e$ and $2C_2 \approx 0.9G_e$ (not conserving the sum!).

Notably, the HS model with values of $\nu$ larger than around 0.3 is for simple linear stress—strain observations practically indistinguishable from the MR form (in particular, considering the uncertainties discussed in the context of Figure 1). The MR form is exactly recovered for $\nu = 1$ (affine tube deformation). Thus, for this range, $2C_1 \approx 0$ and $2C_2 \approx G_e$ in agreement with common operational interpretation of the $C_2$ term.

Another relevant entanglement model is the slip-link theory of Ball, Doi, Edwards, and Warner,5 for which a tube-based treatment of finite-extensibility effects was later developed by Edwards and Vlijminck (EV).6 The best approximation for $\varphi(\lambda)$ in the limit of infinite extensibility ($a = \lambda_{\text{max}}^{-1} \to 0$) is6

$$\varphi(\lambda) = \frac{\lambda}{DD^2} - \frac{1}{D(\lambda + \eta)^2} + \frac{\eta \lambda}{\theta(\lambda + \eta)} \tag{12}$$

where $D = \lambda - \lambda^{-2}$ and $\theta = 1 + \eta \lambda^2$ (correcting a typo in the first term of eq 12 in the original publication). The parameter characterizing the “slippage” of the entanglements is $\eta$. The EV model has been tested in uniaxial extension using MR fits6,64 and also in biaxial deformation.20 The latter work compared it to other molecular theories, among them the HR and RP models, and identified the EV model with $\eta = 0.08$ as the best-fitting tube-based model for the special case of long-chain end-linked PDMS model networks.

Neglecting finite extensibility, the data plotted in Figure 4 show another Mooney representation of the entanglement-only case, now for the EV model in the range of realistic slip parameters $\eta$. It is seen that the linear MR fits to the intermediate $\lambda$ range produce $2C_1 \approx 0$ only in the range $\eta > 0.1$ (significant slip). Thus, in this range, $2C_2 \propto G_e$ with a proportionality factor that decreases with increasing slip, as intuitively expected, since the entanglements are less and less effective. In the range $\eta < 0.1$ we find increasingly large contributions of $G_e$ to the apparent $2C_2$ with roughly conserved sum, approaching the limit $2C_2 \approx G_e$ for vanishing slip, when entanglements behave as phantom-type cross-links.6 The solid line shows for one example that finite extensibility produces an upturn as well as a slight ($\sim 10\%$) offset contribution to the apparent $2C_2$, which is true for any value of $\eta$.

Finally, we mention the “double tube model” of Mergell and Everaers,14 which has been shown to fit data from computer simulations very well.65 It assumes a homogeneous confining potential determined by a tube parameter that combines the effect of both entanglements and actual cross-links. This model is constructed as an interpolation between the RP model and the phantom prediction for permanent cross-links, and it thus covers roughly the same range of apparent $C_{1,2}$ values as the EV model for $\eta \leq 0.1$. A distinction between the models is certainly only possible on the basis of multiaxial mechanical experiments, for which the corresponding equations have not yet been derived.20

Summarizing, one can state that all of the discussed entanglement theories predict that both apparent MR fit parameters $C_{1,2}$ contain entanglement contributions to a variable degree, which for the HS and EV models is parametrized by the tube scaling exponent $\nu$ and the slippage parameter $\eta$, respectively. For approximately $\nu > 0.3$ and $\eta > 0.1$, respectively, the original MR assumption of $2C_1 \approx 0$ and $2C_2 \propto G_e$ holds apparently. A comparison with experimental data from other methods for a series of networks with variable cross-link density can thus help to draw conclusions validity of a specific theories and on the meaning of the two apparent parameters. This is demonstrated by the data in Figure 4b, which show apparent network chain densities from MR fits to the different model

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**Figure 4.** (a) Predictions of the slip-link theory of Ball et al.5 and Edwards—Vlijminck6 for the reduced Mooney stress $\sigma_{\text{red}}$ as a function of inverse strain for the purely entangled case ($G_e = 0$, $G_2 = 1$) on a linear scale for the elongation range, varying the slip parameter $\eta$. The dashed lines with indicated $C_{1,2}$ values are fits over the $0.4\ldots1/\lambda = 0.75$ range, and the solid line includes finite extensibility effects6 with $\lambda_{\text{max}}^{-1} = 10$ for the $\eta = 0.2$ case. (b) Apparent network chain densities derived from $C_1$ and $C_1 + C_2$ values (open and solid symbols, respectively) of MR fits to different tube model predictions as a function of known cross-linked chain density $1/M_e$ for a fixed $1/M_e = 1$. The dashed and solid lines are the respective expectations when $C_2$ is assigned to the full $1/M_e$ contribution.
predictions for a fixed $1/M_f$ as a function of a known $1/M_i$ value, which, as demonstrated below, can be taken from swelling or NMR experiments. First, we note that all models except the EV model for slippage parameters $>0.1$ predict that $1/M_{c,MR}$ calculated from the apparent $C_1 + C_2$ (eq 5) is a rather good measure of the overall constraint density, despite the crude linear approximation over a limited $1/\eta$ range. Second, relevant and meaningful differences among the models arise for $1/M_{c,CL}$ calculated from the apparent $C_1$ only (eq 6). Only the HS model with $\nu > 0.3$ or the EV model with $\eta > 0.1$ yield dependencies with near-zero intercept, indicative of a vanishing entanglement contribution to the apparent $C_1$. All other theories lead to higher intercepts, and its ratio to the intercept of $1/M_{c,MR}$ can be used to constrain the range of valid theories. It is finally noted that model uncertainties will of course lead to nonunity slopes in such a plot, yet the ratio of the intercepts remains to be a valid measure.

B. Entanglement Effects on Equilibrium Swelling.

The interplay of entanglements with the results from equilibrium swelling experiments appears to be relatively clear. A relevant experimental observation is that the apparent $C_1$ vanishes in the limit of highly swollen samples, i.e., for $\phi_g < 0.25$, and Edwards and Vilgis have given a molecular interpretation of this finding in terms of their slip-link theory. It can thus be concluded that swelling experiments should reflect the cross-link contribution, possibly also containing the trapped-entanglement fraction, here jointly denoted as $G_{\epsilon}$.

It should however be noted that biaxial strain experiments on swollen rubber have shown that an apparently vanishing $C_1$ does not necessarily imply that the classical neo-Hookean model is now valid for the swollen state. Only a more complicated, phenomenological strain energy function could provide the basis for a good fit in these works. This could imply that trapped entanglements do not deform in a simple way, but further work is certainly necessary to elucidate the molecular underpinnings of this finding.

C. Entanglement Effects on NMR Observables. For NMR it is important to consider the dynamic nature of the actual experimental observable, i.e., the residual dipolar coupling constant $D_{\text{res}}$. It reflects fast conformational averaging on time scales up to the $10\sim100$ $\mu$s range. Figure 2 shows that this requirement limits NMR observations to the region around $G_{\epsilon}$. In this range, the NMR measure was in many publications shown to exhibit an almost perfect linear relationship to moduli as well as equilibrium swelling results. In addition, it provides a reliable measure of the nonelastic defect fraction for which $D_{\text{res}} = 0$.

For an assessment of the entanglement contribution in this range, assuming additivity in $D_{\text{res}}$ or related quantities, earlier approaches were based upon a subtraction of an effective entanglement effect by simply subtracting the result measured on an un-cross-linked melt at the same temperature. This approach is identified as ambiguous in the light of Figure 2, since the melt result is a strong function of temperature while the network results is not. Rather, assuming a constant entanglement density and additivity of entangled and cross-linked chain densities, we can write $D_{\text{res}} \sim 1/M_{c,MR} + 1/M_f$ with $M_f$ as the entanglement molecular weight. Exploiting the stably observed linear relationship of $D_{\text{res}}$ with other, macroscopic measures of cross-link density (hopefully $\sim1/M_f$), an extrapolation over a range of different samples consistently identifies an intercept value, i.e., a finite $D_{\text{res}} \sim 1/M_f$ in the limit of an un-cross-linked melt. Truly systematic investigations of $D_{\text{res}}$ obtained by extrapolation vs different other cross-linking measures are as yet rare, and we shall address this issue below.

Note that in vulcanized samples the density of (trapped) entanglements may itself depend on the cross-link density, posing a possible ambiguity. A recent theoretical study, has even suggested that toward lower cross-link densities ($G_{\text{app}} < G_{\epsilon}$ in Figure 2) the linear decay of the NMR-detected $D_{\text{res}}$ toward a finite value ($1/M_f$) should change into a square-root behavior $\sim(1/(M_{M_f}))^{1/2}$ in the very high temperature limit, ultimately approaching zero. This argument is based upon the orientational averaging behavior of the network chain within the tube arising from the dominating entanglement constraints. The resulting decay of $D_{\text{res}} \sim 1/M_{c,MR}$ toward zero is, however, generally not found in experiments since the time scale of large-scale chain motions within the tube is much longer than the NMR experimental time scale at relevant temperatures below sample decomposition, thus preserving the linear decay toward $1/M_{c,MR} \sim 1/M_f$. This is highlighted by the shaded gray region in Figure 2.

NMR studies on swollen samples can also provide valuable insights into entanglement effects, as they can be expected to be removed in the limit of low volume fractions in much the same way as in equilibrium swelling experiments. Qualitatively (see Figure 5), one often (but not always) observes an initial decay of the NMR observable upon swelling measured by the volume degree of swelling $Q = V/V_0$. Operationally, one may just evaluate the pure cross-link contribution $D_{\text{res,c}}$ from the minimum, where the topological unfolding (“desinterspersion” of entanglements) may be assumed to be complete.

We recently refined this qualitative approach, taking into account the $R$ dependence of $D_{\text{res}}$ in eq 7. While the early “desinterspersion” stage is not universal and a strong function of preparation conditions, we consistently for many different rubber types found perfectly affine behavior ($R \sim Q^{1/3} \Rightarrow D_{\text{res}} \sim Q^{2/3}$) beyond the minimum. A back-extrapolation yields what we have termed the “phantom reference network” state, with $D_{\text{res,c}}$ reflecting the bulk contribution from chemical and fixed physical cross-links. Our previous work has indicated an almost perfect intercept-free proportionality with the equilibrium swelling result. This finding, in combination with correlations of $D_{\text{res,c}}$ with apparent MR constants $C_1$ and $C_2$ will be taken up and scrutinized below.

Figure 5. Influence of swelling on the NMR observable $D_{\text{res}}$ for two different samples, showing the extrapolation procedure over the affine deformation range to extract the $D_{\text{res,c}}$ characterizing the phantom reference network (PRN) state, where only chemical cross-links and topologically trapped entanglements contribute. Data replotted from ref 39.
IV. SAMPLE APPLICATION TO LOWLY CROSS-LINKED POLY(ISOPRENE) RUBBERS

We now turn to a demonstration of the principles explained above, discussing and comparing experimental results obtained from a series of natural and synthetic poly(isoprene) rubber (NR and IR, respectively) prepared by a novel UV-based curing protocol of dried latex based upon thiol–ene chemistry. Such samples, in contrast to previously studied thermally peroxide-cured NR, contain relatively small amounts of short-chain defects. In total, we have prepared and investigated 12 NR samples and 10 IR samples, which are simply numbered according to their increasing average cross-link density. Details on the preparation and characterization of the samples can be found in the Supporting Information.

Of particular importance for the discussion are the reported literature values for the entanglement molecular weights $M_{e,rheo}$ estimated from melt rheology, which are 3.9 and 6.4 kg/mol for NR and IR, respectively, as explained by the different microstructures. Literature values in fact vary, and we note that a higher value of 6.1 kg/mol is calculated from the entanglement parameters for NR published in earlier work of Ferry and co-workers. The situation changes dramatically for the swollen state, where entanglement constraints are removed. Samples not too far above the percolation threshold now reveal around 90% nonelastic chains, which decreases quickly with increasing cross-linking to a level below 30% for most samples. This observation is less dependent on the specific cross-linking reaction and has also been made for sulfur-cross-linked NR as well as different kinds of poly(dimethylsiloxane) rubbers. Such high actual defect contents were shown to be in agreement with estimations based upon the density of cross-links in four-functional networks. Since all approximations, we cannot expect perfectly matching values, but we can check whether unique monotonic (in fact, linear) relationships exist. In particular for NMR, where the residual dipolar coupling is an effective monomer-based measure of orientation fluctuation, a number of assumptions must be made, as is the case for the given sample series, the defect fraction is composed of long precursor chains that are highly entangled in the bulk. As they are slightly branched, they may exhibit excessively (if not immeasurably) long relaxation times. It is thus a nontrivial and open question to which extent these defects contribute to the bulk mechanical properties.

B. Correlations of Macroscopic Properties. This section part focuses on the correlations of apparent cross-linking parameters as derived from the different methods. Specifically, we address the network chain densities $1/M_c$, which equal twice the density of cross-links in four-functional networks. Since all estimations are based upon specific models and rely on different approximations, we cannot expect perfectly matching values, but we can check whether unique monotonic (in fact, linear) relationships exist. In particular for NMR, where the residual dipolar coupling is an effective monomer-based measure of orientation fluctuation, a number of assumptions must be made, which renders the $1/M_c,NMR$ values uncertain to at least 50%. However, also the swelling results, in particular when a good solvent is used, are subject to—often neglected—model dependencies that can impose systematic errors of the same order of magnitude.

We first turn to correlations between $1/M_c$ values derived from macroscopic properties, i.e., moduli and swelling results. Figure 7 presents such a correlation based upon the $E$ modulus. We observe significant scatter, which is attributed to the uncertainties of the initial-slope estimation in our tensile tester. Nevertheless, we find an approximately linear correlation with an intercept, indicating additional entanglement effects on $E$. The plot also

![Figure 6](image)

**Figure 6.** Results of the low-field NMR characterization. (a) Distributions of residual dipole–dipole couplings reflecting cross-linking inhomogeneities and (b) apparent, nonelastic defect fractions as compared to previous results obtained on conventionally peroxide-cured NR using dicumyl peroxide (DCP). Plot (b) also shows the high defect fractions determined on swollen samples.
shows the result of an attempt to correct the rubber density for the significant defect fraction found by NMR for swollen samples, using $\rho_{p,el} = \rho_p (1 - \omega_{def})$ for the polymer density in eq 4. The scatter increases substantially, and the apparent cross-link densities reach rather large values.

Figure 8a shows corresponding data, now using the (regarding the better data quality more reliable) results from the MR analyses. In particular, the cross-link density derived from $C_1 + C_2$ should be directly comparable to the value derived from $E$, and we indeed observe a well-defined linear relationship with the swelling results, showing a more reliable intercept, however with a somewhat lower slope. This is not unexpected, as the MR analysis focuses on an intermediate strain range where the Mooney stress may not be linear in $1/\lambda$. As explained in the context of Figures 1 and 3b, such nonlinearities may well be hidden in actual data, leading only to systematic shifts between the two (apparent) parameters $C_1$ and $C_2$. Notably, the $C_1$-only data have a zero intercept within the experimental accuracy, suggesting that $C_1$ indeed reflects the same information as the swelling results, i.e., chemical cross-links plus a fixed-constraint contribution commonly associated with trapped entanglements. This is a common observation that has also been made for sulfur-vulcanized NR. Thus, in the limit of small cross-link densities, entanglements appear to not contribute to $C_1$.

Data including the defect correction for the mechanical data, again using $\rho_{p,el} = \rho_p (1 - \omega_{def})$ in eqs 5 and 6 as based upon NMR on swollen samples, are shown in Figure 8b. The quality of the correlation now appears better, but in particular for the $C_1$-based measure this is deceptive because the large correction for low cross-link densities has a weak effect on the anyways small values. It is thus instructive to focus on the $C_2$ contribution plotted in Figure 8c, which also includes expected values based on the known entanglement molecular weight of the used polymers. The results without defect correction (solid symbols) imply an on average small difference between NR and IR samples, suggesting that the higher literature value of $M_e \approx 6.1$ kg/mol for the former is more reliable. This of course holds only if $C_2$ does turn out to provide a good measure of $G_e$.

However, the effect of the defect correction to the mechanical data is rather dramatic, and unrealistically high values result. While $M_{e,app}$ may well be reduced (its inverse increased) at higher cross-linking, there is no reason that $1/M_{e,app}$ from the melt plateau modulus should be much exceeded in the limit of low cross-link densities. From this, we conclude that the defects, that are unambiguously identified by NMR in the swollen state (and should be used to correct equilibrium swelling analyses), are mechanically active in the bulk; i.e., they do not relax on the time scale of our mechanical testing. This raises the important question whether they would relax on a much longer time scale or are effectively trapped, but an in-depth investigation of this issue is beyond the scope of the present work. For the present...
purpose, we therefore focus on the mechanical results without this defect correction.

A relevant conclusion, to be taken up below, is the somewhat steeper slope observed for the \( C_1 + C_2 \) based measure in Figure 8a. In other words, \( C_2 \) increases somewhat with increasing cross-linking, as is also apparent from Figure 8c. Considering the chemical differences between NR and IR, and the fact that the NR samples cover the higher cross-linking range, we can at least say that \( C_2 \) does not decrease significantly, which allows for conclusions on the appropriate elasticity model.

C. Correlation of Microscopic and Macroscopic Properties. NMR results are compared with swelling results in Figure 9. Before we turn to the comparison of the different correlations with bulk and PRN results, we address the different behavior of the IR samples shown as open squares. As compared to the NR results (solid circles), the slope is steeper. We attribute this to the microstructural differences. It is known that the NMR quantity \( D_{\text{res}} \) depends on the specific dynamics within and beyond a monomer, as a result of different conformational statistics, effective chain stiffness, etc.\(^{75}\) It is thus not surprising that the model-dependent reference coupling for NR, \( d_{\text{ref,NMR}} = 617 \) Hz kg/mol\(^{28}\) must be modified for IR. To achieve this, both data sets were simultaneously fitted to a linear relationship, allowing only for a scaled reference value for the IR data. In this way, we obtained a reference coupling \( d_{\text{ref,IR}} = 811 \) Hz kg/mol. Using this new value in the calculation of \( 1/M_{c,NMR} \), we obtain the solid squares, which perfectly match the NR results. The following discussions always refer to values for IR obtained in this way.

As to the bulk NMR observable, we again and in analogy the \( C_1 + C_2 \) based mechanical observable recognize an almost perfect linear correlation with an intercept attributable to entanglement effects. In contrast, the PRN values (taken on fewer samples due to the high effort involved), now in perfect analogy to the \( C_1 \)-only mechanical data, follow a linear relation with no intercept. This nicely proves the concept that the PRN indeed characterizes the fixed-cross-link contribution and that \( C_1 \) represents a good measure of it. A fortuitous cancellation of errors appears unlikely, considering that all three methods are in qualitative agreement. Also in perfect analogy to Figure 8a, the slope is somewhat steeper for the former, indicating that the entanglement effect reflected in the bulk NMR measure also increases with cross-linking. Note that the present correlation does not suffer from ambiguities related to a possible correction of the rubber density; rather, the NMR measure characterizes the total elastically active fraction in its associated time range (see Figure 2). Thus, there is a proportionality between the short-time entanglement contribution measured by NMR and the \( 1/M_{c,\text{app}} \) reflected in the \( C_1 \) contribution.

Finally, Figure 10 supplies another set of correlations of the NMR results with the MR results. The two graphs show on the y-axis (a) the bulk NMR measure and (b) the PRN result. The correlations are more noisy, mainly due to the limited accuracy of the mechanical data, but the trends are the expected ones and confirm the observations and conclusions so far: The bulk NMR measure and the PRN limit correlate linearly with closer to zero intercept with the \( C_1 + C_2 \) and \( C_1 \)-only measures, respectively, and again, the increasing \( C_2 \) contribution leads to the now flatter slopes of the NMR data versus the \( C_1 + C_2 \) measure along the x-axis.

D. Discussion of Elasticity Models and Comparison with Previous Results. From the correlations discussed above, we could consistently conclude that (i) fixed-constraint contributions (chemical cross-links plus trapped entanglements) to the swelling-derived \( 1/M_{c,j} \) to the \( C_1 \)-based MR measure, and to the extrapolated PRN value from NMR are of identical relative magnitude, and (ii) the entanglement contributions to the mechanical and NMR properties, both as compared to the swelling results, are consistently larger than the fixed-constraint contributions and are increasing slightly with cross-linking. The latter conclusion can be backed up by a final correlation plot comparing two completely independent (in the case of \( C_2 \) of course
describe biaxial stress–strain data\textsuperscript{20} of end-linked model networks of PDMS.

Systems comparable to ours, for which a rather significantly increasing $C_2$ and $C_2 > C_1$ with cross-linking was reported, are thirum-vulcanized NR,\textsuperscript{43,66} sulfur-vulcanized styrene–butadiene rubber (SBR) with a special accelerator system,\textsuperscript{69} and sulfur-cured NR made of short precursor chains.\textsuperscript{27} Note that not all the cited results are strictly comparable, as the way in which the MR plots were evaluated differ. Rather large $C_2$ values have also been found for sulfur-vulcanized latex preparations of NR\textsuperscript{76} and for peroxide-cross-linked poly(ethylene) networks.\textsuperscript{53,77} Analogous results and their interpretation based upon the EV model with larger slippage parameters ($\eta > 0.4$) have been reported for peroxide-cured cis-IR\textsuperscript{63} and radiation-cross-linked polyethylene networks.\textsuperscript{64}

With the exception of the homogeneous sulfur-based NR systems of Vieyres et al.\textsuperscript{38} with small $C_2$, none of the mentioned samples has been probed by NMR with regards to the sample inhomogeneity. We only know from our previous work that peroxide-cross-linked NR is characterized by extensive cross-linking inhomogeneities and a rather large fraction of short-chain defects.\textsuperscript{55} For such samples, Klüppel has reported only slightly increasing $C_2$ values that are initially larger than $C_1$ at low cross-linking. In this limit, and generally in more-defect-rich rubbers, apparent tube scaling exponents appear to be positive (or slippage parameters tend to be larger than 0.1), which means that the apparent $C_2$ is indeed a good measure of the entanglement contributions. This applies to the systems studied herein, for which we can conclude that the x-linking defects appear to contribute to the long-branch defect structures as relevant as the short-chain defect content.

**E. Conclusions.** In summary, we have presented a combined analysis of a series of lowly cross-linked latex-based natural rubber by two different macroscopic techniques (uniaxial stress–strain and equilibrium swelling) and a microscopic technique, i.e., low-field NMR as applied to bulk and swollen samples. NMR on swollen samples, when suitably back-extrapolated to the dry state, referred to as “phantom reference network”, reveals a cross-link-only contribution that is in perfect linear agreement with swelling results. The difference to the bulk NMR result reflects the entanglement contribution, which in turn was found to be proportional to the $C_2$ term from Mooney–Rivlin analysis. The consistency of these findings suggests that the samples can be described by the Heinrich–Straube tube theory with positive scaling exponent $\eta > 0.3$ or the Edwards–Vilgis slip-link model with slippage parameter $\eta > 1$.

We can conclude that the system studied herein, despite its comparably low short-chain defect fraction characteristic for conventionally peroxide-cured NR, is dominated by entanglement constraints whose detailed influence on the mechanical behavior bears a relation to cross-linking inhomogeneities and defect structures with high molecular weight. The former are reflected in the inhomogeneous distribution of residual dipole–dipole couplings measured by NMR in the bulk, while the latter are revealed through their fast relaxation in swollen samples and their correspondingly long transverse relaxation times as seen by NMR (note the inverse relation). However, such large defect structures appear to contribute to the long-time elastic properties of bulk samples probed in the tensile tests, where they suffer a significant slowdown. The role of such possibly very slow or even topologically frustrated relaxation of these components will be the focus of future studies.

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**Figure 11.** Comparison of the independent microscopic and macroscopic measures of the entanglement contribution from NMR (difference between bulk and PRN) and MR $C_2$, respectively. Linearly interpolated PRN values were used for the samples for which an experimental value was not available. The correlation coefficient $R$ for the linear regression is 0.79.
More refined discussions should possibly also include the assessment of the actual fraction of trapped entanglements, which was here simply treated as additive to the apparent chemical cross-link density.

We expect our experimental strategy, in particular the use of NMR in assessing the sample (in)homogeneity and defect content, and the phantom reference network based separation of cross-link and entanglement contributions, to be of much use in understanding the large qualitative differences in the mechanical behavior of rubbers prepared by different protocols. In addition, a wider-scale application of biaxial stress–strain experiments is desirable, as this is the only strategy which allows for a truly objective distinction between different elasticity models.\textsuperscript{18–20} Obviously, a final and universal elucidation of the molecular underpinnings of entanglement effects on rubber elasticity must comprise a detailed assessment of the network inhomogeneity and defects.

**ASSOCIATED CONTENT**

*Supporting Information*

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

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Marie-Luise Trutschel has been a PhD student since 2011. She studied Medical Physics at the Martin-Luther-University Halle-Wittenberg (Halle, Germany) and received her Diploma in 2011. Since 2009 she has been working with Prof. Kay Saalwächter on the study of structure and dynamics in polymer melts, blends, and elastomers by multiple-quantum NMR experiments and complementary techniques.

Walter Chassé received his Diploma (2007) and Ph.D. (2013) degrees in physics from the Martin-Luther-University Halle-Wittenberg (Halle, Germany). He worked in the group of Prof. Kay Saalwächter, investigating structure, formation, and thermodynamic properties of polymer networks by various NMR techniques and swelling experiments. In 2013, he moved to Radboud University Nijmegen, working as a postdoctoral fellow in the lab of Prof. Arno Kentgens. He is involved in a DPI project developing high-field NMR methodology for the investigation of semicrystalline polymers and the influence of stress on the phase composition.

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Correction to Entanglement Effects in Elastomers: Macroscopic vs Microscopic Properties

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In our previous publication,1 eq 1 needs to be replaced by

\[ M_{c,sw} = -\frac{\rho_w V_p \phi_p^{1/3}}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} \frac{f - 2}{f} \]  

(1)

The previous version of the above Flory–Rehner equation incorporated an earlier suggested2 and in the meantime revised3 incorrect account of a fraction of elastically inactive defects \( \omega_{def,sw} \) as determined by NMR experiments in the swollen state. In short, the previous version incorporated a modified \( \phi_{p,el}^{1/3} = [(1 - \omega_{def,sw})\phi_p]^{1/3} \) dependence on the polymer volume fraction at swelling equilibrium in the numerator. The dependence on \( \phi_w \) however, merely relates to the geometric deformation of the sample as a whole, not to the fact that a part of the material is inactive. Rather, the fraction of elastically active material \( \omega_{el} = 1 - \omega_{def,sw} \) is to be used to correct the resulting overall density of active network chains \( 1/M_c \) resulting in eq 1.

The revision affects the results shown in Figures 8a–c and 9 of the paper and mostly affects the samples with the lowest \( 1/M_c \). The effects of the correction are rather minor, amounting to changes in the slopes and intercepts of the linear fits to the data by on average less than 10%. For an exemplary demonstration, the corrected versions of the previous Figures 8a and 9 are shown.

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Entanglement effects in elastomers: macroscopic vs. microscopic properties

Supporting Information

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I. MATERIALS AND CHEMICALS

Natural concentrated rubber (NR) latex (high ammonia, 60 wt.-% dry rubber content) was obtained from a Malaysian supplier. Isoprene rubber (IR) latex (Kraton IR-401 BU, 63 wt.-% dry rubber content) with 90 % cis-1,4-, 2 % trans-1,4- and 8 % 3,4-isoprene units and a molecular weight in the range from 1,500,000 to 2,500,000 g/mol was purchased from Kraton Polymers. Ethyl-2,4,6-trimethyl benzoyl phenyl phosphinite (Lucirin TPO-L) was used as photoinitiator and was supplied by BASF. The crosslinking agent trimethylol propa-ntriis-3-mercapto propionate (TriThiol) was obtained from Bruno Bock Thiochemicals. All other chemicals were purchased from Sigma-Aldrich and were used without further purification.

In total, we have prepared and investigated 12 NR samples and 10 IR samples, which are numbered according to their increasing average crosslink density.

Preparation of UV crosslinked NR and IR latex. The photochemical pre-vulcanization of both NR and IR latex was carried out by emulsifying 1.0 phr (parts per hundred parts of rubber) Lucirin TPO-L and 1.0 phr TriThiol in 2.0 phr deionized water. This emulsion was then added to 10.0 kg NR and IR latex, respectively, with a dry rubber content of 40 wt-%. Both latex formulations were stirred at room temperature by means of a magnetic agitator for 2 hours and were UV pre-vulcanized in a falling film photoreactor [1, 2]. The falling film reactor was tailor made and consisted of a reactor tube with an inner diameter of 135 mm. The reactor tube was made of glass and comprised an inlet for the latex mixture at the top and an outlet at the bottom. A medium pressure Hg lamp (Heraeus) with an arc length of 25 cm was positioned in the center of the reactor tube. The UV lamp was equipped with a quartz cooling tube and was flooded with inert gas (nitrogen). The lamp power was regulated by a power unit ranging from 800 to 3500 W. The latex mixtures were pumped continuously from a storage vessel to the top of the falling film reactor with an eccentric screw pump. By employing a flow rate of 1.3 L/min a continuous and stable liquid falling film was obtained with a film thickness between 0.5 and 1.0 mm. The outlet of the reactor tube was connected to a collecting vessel where the pre-cured latex was collected after each illumination cycle.

The UV pre-vulcanization of NR as well as IR latex was carried out with a lamp power of 800, 3000 and 3500 W corresponding to a light intensity of 0.4, 0.9 and 1.1 J/cm², respectively (wavelength range between 240 and 460 nm). The latex formulations were conveyed through the photoreactor at least five times and after each cycle a sample was collected. In the UV-assisted crosslinking of NR latex, additional crosslink agents (emulsion with 1.0 phr photoinitiator and 1.0 phr TriThiol) were added to the pre-cured latex between the third and fourth illumination cycle to replace the consumed chemicals and to enhance the crosslink density. With respect to the pre-vulcanization of IR latex, however, the amount of crosslink chemicals did not exceed 1.0 phr, since highly pre-cured IR latex particles suffer from poor film formation properties.

To obtain IR latex samples with higher crosslink densities (IR08 IR10), solid films were photochemically post-vulcanized. An emulsion with 1.0 phr Lucirin TPO-L and 1.0 phr TriThiol was added to the pre-cured IR latex and then solid films were prepared using a coagulant.
The dashed lines indicate the degradation process. The former were dried at 120°C in a conventional coagulant dipping process. Preparation of dipped latex films. Solid films were prepared from the photochemically pre-cured NR and IR latex by a conventional coagulant dipping process. Porcelain forms were cleaned with deionized water and acetone and were then immersed in a coagulant solution containing calcium salts (coagulant), calcium carbonate (release agent) and surfactants. The former were dried for 10 minutes at 120°C for 20 s. After the drying step (20 min, 120°C) the thickness of the latex films ranged from 200 to 300 μm.

II. EQUILIBRIUM SWELLING MEASUREMENTS

Equilibrium swelling experiments were performed at 21°C and evaluated as described in our previous work [3, 4], using toluene as solvent (molar volume \( V_s = 106.2 \) mL/mol and density \( \rho_s = 0.87 \) g/cm\(^3\)). For each sample, ten test specimens were weighed on an analytical balance (\( w_i \), accuracy \( \sim 0.01 \) mg) and then placed in glass vials with toluene. After 48 h the swollen samples were removed from the vials, blotted with a tissue paper to remove the excess solvent and weighed immediately (\( w_d \)). The samples were dried under vacuum at 50°C until constant weight (\( \sim 24 \) h) and weighed again (\( w_d \)). The sol fraction is then given by \( 1 - w_d/w_i \) and was found to range between 15 and 5% and to decrease with the degree of crosslinking, except for the most lightly crosslinked IR sample, where 37% were found.

It must be noted that during the swelling experiments in toluene it is mandatory to exclude air and UV light in order to avoid gradual network degradation [3]. This is demonstrated in Fig. 1, where results of swelling kinetics experiments are shown. For these studies, swelling of the 10 specimens was started simultaneously in 10 different vials, and then the samples were taken out, quickly wiped and weighed and put back for further swelling, one after the other and with increasing time intervals. Values beyond 1 hour swelling time are again averaged over all 10 samples. It is seen that 20 min are sufficient for the equilibration of the small sample pieces (20 50 mg), thus easily avoiding an influence of the slow degradation in case inert conditions are not easily realized.

For the evaluation of the Flory-Rehner equation as discussed in the paper, we used a polymer density \( \rho_p = 0.92 \) g/cm\(^3\) for NR, and an interaction parameter \( \chi = 0.427 + 0.112\phi_p^2 \) for the pair NR/toluene [5].

III. CHARACTERIZATION OF TENSILE PROPERTIES

Uniaxial tensile tests were performed with a Zwick tensile tester Z010 at extension rates of 0.02, 0.06, 0.5, 5 and 500 mm per minute. With a specimen length of 75 mm, this corresponds to strain rates of 0.0044, 0.013, 0.111, 1.11 and 111 ms\(^{-1}\), respectively. Most results analyzed in the paper refer to experiments at 0.5 mm/min, and no significant changes were found for lower strain rates, confirming that the samples were relaxed at any given strain. The stress-strain curves were obtained at room temperature and the dimensions of the tensile samples were in compliance with ASTM Standard D412-98a. Young's modulus (E) was calculated from the initial linear slope of the stress-strain curve below 5% strain according to Hooke's law, \( \sigma = E \varepsilon \), which connects the axial stress (\( \sigma \)) to axial strain (\( \varepsilon \)) at small deformations. The axial strain, \( \varepsilon = (L - L_0)/L_0 \) is a function of the initial length of the sample (\( L_0 \)) and the length after the application of force (\( L \)).

IV. PROTON LOW-FIELD SOLID-STATE NMR SPECTROSCOPY

\(^1\)H double-quantum (DQ) NMR experiments were carried out on a Bruker minispec mq20 spectrometer operating at 20 MHz. \(^1\)H Larmor frequency with a 90° pulse length of about 2.4 μs. The experiments and raw data analysis were performed following previously published procedures [6-9]. Specific information on NMR experiments conducted on toluene-swollen samples (= good-solvent case) can be found in ref. [10].


