

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

$$M_{c,sw} = - \frac{\rho_p V_s \omega_{el} \phi_p^{1/3}}{\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2} \frac{f - 2}{f} \quad (1)$$

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 ϕ_p , 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.

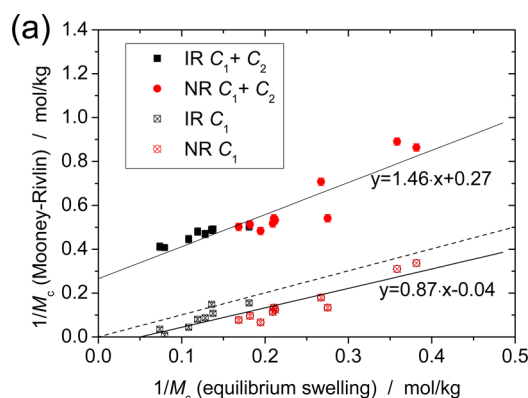


Figure 8. Correlation of the network chain densities calculated from the MR parameters with the analogous quantity derived from equilibrium swelling experiments. (a) Total effective network chain density (from $C_1 + C_2$) and high-strain contribution (from C_1) reflecting mainly chemical cross-links.

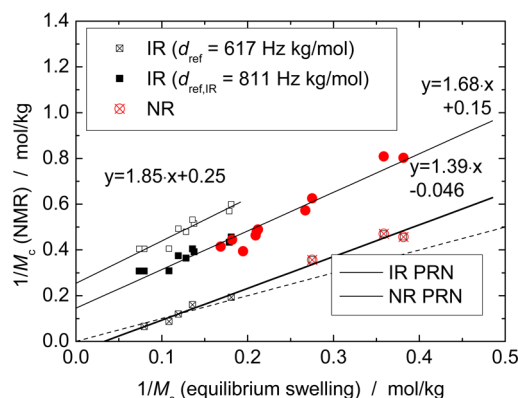


Figure 9. Network chain densities from NMR as compared to swelling results. The solid lines are linear fits with indicated parameters, and the dashed lines have a slope of unity. The crossed symbols denote the NMR values obtained by extrapolation from experiments on swollen samples, i.e., the phantom reference network (PRN) state.

REFERENCES

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- (3) Chassé, W.; Lang, M.; Sommer, J.-U.; Saalwächter, K. Correction to Cross-Link Density Estimation of PDMS Networks with Precise Consideration of Networks Defects. *Macromolecules* **2015**, 48, 1267–1268.

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