Self-Similar Chain Conformations in Polymer Gels

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We use molecular dynamics simulations to study the swelling of randomly end-cross-linked polymer networks in good solvent conditions. We find that the equilibrium degree of swelling saturates at $Q_{\mathrm{eq}} \approx N_e^{3/5}$ for mean strand lengths $\bar{N}_s$ exceeding the melt entanglement length N_e. The internal structure of the network strands in the swollen state is characterized by a new exponent $\nu = 0.72 \pm 0.02$. Our findings can be rationalized by a Flory argument for a self-similar structure of mutually interpenetrating network strands, agree partially with the classical Flory-Rehner theory, and are in contradiction to de Gennes' c^*-theorem.

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Polymer gels [1–5] are soft solids governed by a complex interplay of the elasticity of the polymer network and the polymer/solvent interaction. They are sensitive to the preparation conditions and can undergo large volume changes in response to small variations of a control parameter such as temperature, solvent composition, pH, or salt concentration. In this Letter we reexamine a classical but still controversial problem of polymer physics [1,2], the equilibrium swelling of a piece of rubber in good solvent.

We discuss below the two basic theories addressing this situation, the classical Flory-Rehner theory [1] and de Gennes' c^*-theorem [2]. Both are supported by part of the experimental evidence gathered by combining thermodynamic and rheological investigations with neutron or light scattering [6–10]. Here we use computer simulations [11–15], since they offer some advantages in the access to and the control over microscopic details of the network structure. We concentrate on the role of entanglements in limiting the swelling process of defect-free model networks and, in particular, the structure of the network strands in the swollen gel [16]. Questions relating to the structural heterogeneity on larger length scales and the butterfly effect [10,17] will be addressed in a future publication.

For networks prepared by cross-linking a dry (i.e., solvent-free) melt of linear chains, the strands have Gaussian statistics, i.e., the mean-square end-to-end distance is related to the average length, $\bar{N}_s$, by $\langle r^2\rangle_{\mathrm{dry}} \propto b^2\bar{N}_s^{2\nu}$, where $\nu = 1/2$ and b is the monomer radius. The same relation also holds for all internal distances, leading to the characteristic structure factor $S(q) \sim q^{-1/\nu}$ for the scattering at wave vector q from a fractal object.

The classical Flory-Rehner theory [1] writes the gel free energy F as a sum of two independent terms: a free energy of mixing with the solvent (favoring swelling and estimated from the Flory-Huggins theory of semidilute solutions of linear polymers) and an elastic free energy (due to the affine stretching of the network strands which are treated as Gaussian, concentration-*independent*, linear entropic springs). Minimizing F yields $Q_{\mathrm{eq}} \propto \bar{N}_s^{3/5}$ for the equilibrium degree of swelling. The Flory-Rehner theory implies that the structure factor of long paths through the network is of the form $S(q) \sim q^{-2}$ both locally, where the chains are unperturbed, and on large scales, where they deform affinely ($\langle r^2\rangle_{\mathrm{eq}} \propto \langle r^2\rangle_{\mathrm{dry}} Q_{\mathrm{eq}}^{2/3}$) with the outer dimensions of the sample. The stretching should be visible in the crossover region around $q \approx 2\pi/(b\bar{N}_s^{1/2})$ with $S(q) \sim q^{-1}$.

More recent treatments are based on the scaling theory of semidilute solutions of linear polymers [2] and the idea that locally, inside of so-called "blobs," the chains behave as isolated, *self-avoiding* walks with $\nu \approx 3/5$. On larger scales, the solution behaves as a dense melt of Gaussian blob chains. In the case of swollen *networks*, a controversy exists whether the size of the network strands is determined by the *global connectivity* or by the *local swelling*. Quite interestingly, the first view [17–19] leads again to the Flory-Rehner result $Q_{\mathrm{eq}} \propto N_s^{3/5}$. In contrast, de Gennes' c^*-theorem [2] asserts that the macroscopic swelling is limited only by the *local* connectivity, which begins to be felt at the overlap concentration $c^* \propto \bar{N}_s/(b\bar{N}_s^{\nu})^3$ of a semidilute solution of linear polymers of average length $\bar{N}_s$, corresponding to $Q_{\mathrm{eq}} \propto \bar{N}_s^{4/5}$. The c^*–theorem predicts $S(q) \sim q^{-5/3}$ for $q > 2\pi/(b\bar{N}_s^{3/5})$ as well as unusual elastic properties due to the *nonlinear* elasticity of the network strands [14,20].

As in earlier investigations of polymer melts and networks [21–25], we used a coarse-grained polymer model where beads interacting via a truncated, purely repulsive Lennard-Jones (LJ) potential are connected by anharmonic springs. With ϵ, σ, and τ as the LJ units of energy, length, and time, the equations of motion were integrated by a velocity-Verlet algorithm with a weak local coupling to a heat bath at $k_BT = 1\epsilon$. The potentials were parametrized in such a way that chains were effectively uncrossable, i.e., the network topology was conserved for all times. In our studies we did not simulate the solvent explicitly, but rather used vacuum which can be considered as a perfect solvent for our purely repulsive (athermal) network chains. The relevant length and time scales for chains in a melt are the average bond length,

$\sqrt{\langle l^2 \rangle} = 0.965(5)\sigma$, the mean-square end-to-end distance $\langle r^2 \rangle (N)_{\mathrm{dry}} = 1.74(2) l^2 N$ [21], the melt entanglement length, $N_e = 33(2)$ monomers, and the Rouse time $\tau_{\mathrm{Rouse}}(N) \simeq 1.35 \tau N^2$ [26]. In dilute solutions, single chains adopt self-avoiding conformations with $\langle r^2 \rangle (N) \approx 1.8 l^2 N^{3/5}$.

Using this model, it is possible to study different network structures including randomly cross-linked, randomly end-cross-linked [22,23], and end-linked melts [24], as well as networks with the regular connectivity of a crystal lattice [25]. Here we investigate end-cross-linked model networks created from an equilibrated monodisperse melt with M precursor chains of length N at a meltlike density $\rho_{\mathrm{dry}} = 0.85\sigma^{-3}$ by connecting the end monomers of the chains to a randomly chosen adjacent monomer of a different chain. This method yields defect-free trifunctional systems with an exponential distribution of strand lengths N_s with an average of $\bar{N}_s = N/3$. The Gaussian statistics of the strands remains unperturbed after cross-linking [22,27]. The systems studied range from $M/N = 3200/25$ (i.e., the average strand size $\bar{N}_s = 8.3$) up to $M/N = 500/700$ ($\bar{N}_s = 233$), some systems being as large as $MN = 5 \times 10^5$. All simulations used periodic boundary conditions in a cubic box and were performed at constant volume. Starting from $V_{\mathrm{dry}} = MN/\rho_{\mathrm{dry}}$, the size of the simulation box was increased in small steps alternating with equilibration periods of at least five entanglement times $\tau_R(N_e) \approx 1400\tau$. The isotropic pressure P was obtained from the microscopic virial tensor and the condition $P_{\mathrm{eq}} \equiv 0$ was used to define equilibrium swelling with $Q_{\mathrm{eq}} = V_{\mathrm{eq}}/V_{\mathrm{dry}}$. Tests with a part of the networks using open boundaries did not show any significant changes of the results.

We investigated the equilibrium swelling of our model networks as a function of the average strand length N_s. Figure 1 shows $Q_{\mathrm{eq}}^{-1} N_e^{3/5}$ as a function of the average strand length $(N_e/N_s)^{-3/5}$. In agreement with experimental results for highly cross-linked networks [8,9], our results for short strands are compatible with the Flory-Rehner [1] prediction $Q_{\mathrm{eq}} \propto \bar{N}_s^{3/5}$. They do, however, not allow for an independent determination of the exponent. In contradiction to the original theory, we observe a saturation of the equilibrium swelling degree for large $\bar{N}_s$ [8]. The crossover occurs for $\bar{N}_s \approx N_e$. The extrapolated maximal degree of equilibrium swelling $Q_{\max}(\bar{N}_s \to \infty) = 6.8(3)$ is close to the swelling degree of an ideal Flory-gel with average strand length N_e : $1.15 N_e^{3/5} = 9.5$, where the prefactor is empirically obtained from the slope of the straight line in Fig. 1. In contrast, the corresponding estimate based on the c^*-theorem, $Q_{\mathrm{eq}} \simeq b^3/\sigma^3 N_e^{4/5} \approx 36$, is clearly too high ($b = 1.3\sigma$ is the stastical segment length in good solution). Our interpretation is that to a first approximation entanglements act as chemical cross-links in limiting the swelling of polymer networks. The situation is analogous to an "olympic gel" [2] of topologically linked ring polymers. In contrast to solutions of linear polymers, systems containing trapped entanglements cannot be arbitrarily diluted.

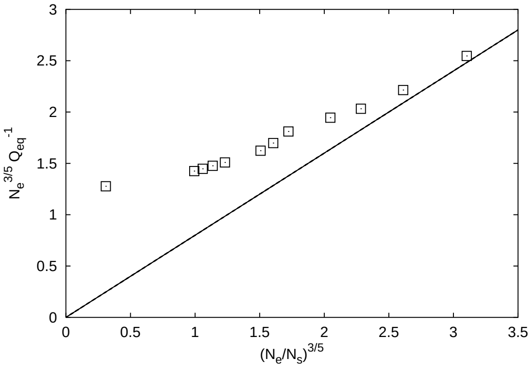

FIG. 1. Strand length N_s dependence of the equilibrium degree of swelling Q_{eq}. The straight line going through zero represents Flory's prediction $Q_{\mathrm{eq}} \propto \bar{N}_s^{3/5}$. The melt entanglement length N_e was used to normalize the axis in order to show that deviations from Flory's theory occur around $N_s \approx N_e$ and that the asymptotic value $Q_{\mathrm{eq}}(\bar{N}_s \to \infty)$ is of the order of $N_e^{3/5}$.

The chain conformations at equilibrium swelling are best characterized by their structure factor $S(q)$. Figure 2 shows $S(q)$ of the precursor chains within the network for our most weakly cross-linked $N = 700$ sample. We have chosen the Kratky representation [$q^2 S(q)$ vs q] to show the deviation from the Gaussian case [$S(q) \propto q^{-2}$] more clearly. The observed power law form $S(q) \propto q^{-1/\nu}$ is characteristic of fractals and common in polymeric systems. However, the observed exponent $\nu = 0.72(2)$ is unexpected. Furthermore, the fractal structure is observed for a q range of $2\sigma \lesssim \frac{2\pi}{q} \lesssim 15.5\sigma \approx b N_e^{0.72}$, suggesting that the mean extension of the effective strands of length N_e is the only relevant length scale in the problem. For

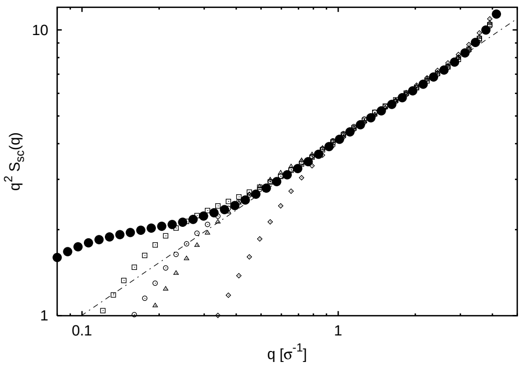

FIG. 2. Single chain structure function in networks at equilibrium swelling in Kratky representation. The straight line corresponds to a power law $q^{2-1/\nu}$ ($\nu = 0.72$). The figure contains scattering data for the precursor chains (•) of length $N = 700$ ($\bar{N}_s = 233$) and for network strands of lengths $N_s = 10$ (◇), $N_s = 40$ (△), $N_s = 70$ (⊙), and $N_s = 100$ (□) within a different network with precursor chains of length $N = 100$ ($\bar{N}_s = 33$).

smaller q, we see the onset of the expected scattering of a Gaussian chain consisting of randomly oriented parts of length $bN_e^{0.72}$. Our precursor chains (even $N = 700$) are too short to see it clearly developed.

Since the scattering from the *precursor chains* could be affected by polydispersity effects, we have investigated the conformations of the *network strands* as a function of their contour length N_s. For high q, all structure functions fall on top of each other and show the same fractal structure with $S(q) \sim q^{-1/0.72(2)}$ (Fig. 2). The complementary Fig. 3 shows a log-log plot of the mean-square strand extension $\langle r^2 \rangle_{\mathrm{eq}}(N_s)$ versus their length. In agreement with the results for the structure functions, we find a power law $\langle r^2 \rangle_{\mathrm{eq}} \propto b^2 N_s^{2\times 0.72}$ for strands which are shorter than the effective strand length N_e and therefore *subaffine* deformations. Long strands, on the other hand, deform affinely with $\langle r^2 \rangle_{\mathrm{eq}} = \langle r^2 \rangle_{\mathrm{dry}} Q_{\mathrm{eq}}^{2/3}$.

Clearly, the results of our simulations do not agree with the predictions of any of the theories presented in the introduction. While the neglect of entanglements seems to be fairly simple to repair by treating them as effective cross-links (with N_e supplanting the average strand length $\bar{N}_s$ [19]), the fractal structure of the strands and the exponent $\nu = 0.72(2)$ come as a surprise. In the following, we discuss a possible explanation for the stronger swelling of network strands ($\nu \approx 0.72$) than of single chains ($\nu \approx 3/5$) under good solvent conditions.

We begin by recalling Flory's argument [1] for the typical size $R_F \propto bN^\nu$ of a single polymer chain of length N and statistical segment size b in a good solvent. The equilibrium between an elastic energy $\propto R_F^2/(b^2 N)$ of a Gaussian chain stretched to R_F and a repulsive energy $\propto b^d R_F^d (N/R_F^d)^2$ due to binary contacts between monomers in d dimensions leads to $\nu = 3/(d + 2)$.

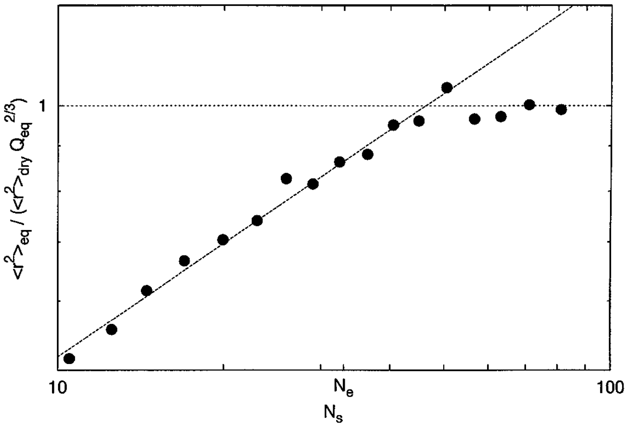

FIG. 3. Log-log plot of the mean-square end-to-end distance $\langle r^2 \rangle_{\mathrm{eq}}$ of the individual network strands within a single network ($\bar{N}_s = 33$) at equilibrium swelling $Q = 5.8$ versus strand length N_s. The straight line corresponds to a power law $\langle r^2 \rangle_{\mathrm{eq}} \sim N_s^{2\nu}$ with $\nu = 0.72$. The data are normalized to an affine deformation $\langle r^2 \rangle_{\mathrm{eq}} = Q_{\mathrm{eq}}^{2/3} \langle r^2 \rangle_{\mathrm{dry}}$.

The simplest models for swollen networks have the regular connectivity of a crystal lattice. In agreement with the c^*-theorem, they adopt equilibrium conformations with strand extensions of the order of R_F [28]. However, these systems are hardly good models for the swelling process of networks prepared in the dry state, since the hypothetical initial state at melt density has an unphysical local structure with average strand extensions $R_F Q^{-1/3} \propto bN_s^{1/3}$ as in dense globules. In contrast, if the corresponding semidilute solution is compressed, the chains shrink only weakly from R_F to the Gaussian coil radius $R \propto bN_s^{1/2}$. Instead, they become highly interpenetrating with $n_F \propto N_s^{1/2}$ (the Flory number) of them sharing a volume of R^3. Moreover, at least the simplest model for highly cross-linked networks prepared in the dry state, $n_F \sim N_s^{1/2}$ *mutually interpenetrating* regular networks with strand extensions of the order of R [25], cannot possibly comply with the c^*-theorem, if one disregards *macroscopic* chain separation: Either the strands extend to R_F, leading to internal concentrations of $c^* N_s^{1/2}$, or the systems swell to c^*, in which case the strands are stretched to $R_F N_s^{1/6}$. The same conclusions should hold for any network without too many defects, where the *global* connectivity forces neighboring chains to share the same volume *independent* of the degree of swelling.

We now consider a Flory argument for a group of chains which can swell but *not* desinterpenetrate, i.e., $n_F \sim N^{d\nu - 1}$ chains of length N which span a volume R_{FR}^d. The equilibrium between the elastic energy $\propto n_{FR}^2/(b^2 N)$ and the repulsive energy $\propto b^d R_{FR}^d (n_F N / R_{FR}^d)^2$ leads to

$$\nu = \frac{4 + d}{4 + 2d}. \tag{1}$$

Quite interestingly, this *local* argument reproduces in three dimensions with $Q_{\mathrm{eq}} \sim N^{d/(d+2)} = N^{3/5}$ and $R_{FR} \sim Q^{1/d} b N^{1/2} \sim N^{7/10}$ the results of the classical Flory-Rehner theory of gels. However, in analogy to the Flory argument for single chains, Eq. (1) should also apply to subchains of length G with $1 \ll G < N$ which share their volume with a correspondingly smaller number of other subchains. In particular, the local degree of swelling, $G^{1/5}$, should be *subaffine* and *the exponent* $\nu = 7/10$ *should characterize the entire local chain structure* up to the length scale of the effective strand length, N_e. This is in excellent agreement with the main findings from our simulations (see Figs. 2 and 3).

Before we conclude, some additional remarks are in order: (i) For swelling in a theta solvent, the analogous scaling argument yields $Q \sim N^{3/8}$ in agreement with previous theories and experiments [8,9,19] and predicts local chain structures characterized by $\nu = 5/8$. (ii) Equation (1) can also be derived along the lines of [17–19] from an equilibrium between the elastic energy of blob chains and the osmotic pressure of a semidilute polymer solutions. Note that the appropriate blob size is a function of the size G of the subchains under consideration and that isolated chain behavior is expected only below the original correlation length ξ_{prep} for systems prepared by cross-linking semidilute solutions. (iii) Sommer, Vilgis, and Heinrich [29] have argued that the effective inner fractal dimension d_i of a polymer network is larger than $d_i = 1$ for linear chains, leading to stronger swelling with $\nu = (d_i + 2)/(d + 2)$. While the correction goes into the right direction, it is difficult to explain a strand length *independent* effective inner fractal dimension of $d_i = 1.5$ as an effect of the *local* connectivity. (iv) However, such effects may well be important in systems with a sufficient number of defects such as dangling ends or clusters. If the global connectivity is weak, the chains may locally desinterpenetrate, leading to a behavior which agrees much better with the c^*-theorem [7,12].

In summary, we have used large scale computer simulations and scaling arguments to investigate the equilibrium swelling of defect-free model polymer networks prepared at melt density. We find that the chain structure on short scales is *independent* of the network connectivity and characterized by an exponent $\nu \approx 7/10$, while the macroscopic degree of swelling is controlled through an (entanglement limited) effective strand length. The predicted chain structure should be directly observable in neutron scattering experiments.

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Note added.—After this work was finished, we learned of unpublished theoretical work by Rabin [30] and by Erman *et al.* [31] predicting $\nu = 7/10$ in swollen networks.

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