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 $Q_{eq} \approx N_s^{3/5}$ for mean strand lengths $N_s$ exceeding the melt entanglement length $N_e$. The internal structure of the network strands in the swollen state is characterized by a new exponent $\nu \approx 0.72\pm0.02$. Our findings are in contradiction to de Gennes’ $c^*$-theorem, which predicts $Q_{eq} \sim N_s^{4/5}$ and $\nu \approx 0.588$. We present a simple Flory argument for a self-similar structure of mutually interpenetrating network strands, which yields $\nu = 7/10$ and otherwise recovers the classical Flory-Rehner theory. In particular, $Q_{eq} \approx N_s^{3/5}$, if $N_e$ is used as effective strand length.

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Polymer gels 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, the equilibrium swelling of a piece of rubber in good solvent.

Experimental gels have been studied extensively by combining thermodynamic and rheological investigations with neutron or light scattering. Here we use computer simulations, 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 and, in particular, the structure of the network strands in the swollen gel. Questions relating to the structural heterogeneity in our gels and the butterfly effect will be addressed in a future publication.

There are several theories for the swelling of polymer networks prepared from a melt of linear precursor chains. In the dry state of preparation, the network strands have Gaussian statistics, i.e. the mean square end-to-end distance is related to the average length, $N_s$, by $\langle r^2 \rangle_{dry} \propto b^2 N_s^{2\nu}$, 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 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 semi-dilute 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 $Q_{eq} \propto N_s^{3/5}$ 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 $\langle r^2 \rangle_{eq} \propto \langle r^2 \rangle_{dry} Q_{eq}^{2/3}$ with the outer dimensions of the sample. The stretching should be visible in the crossover region around $q \approx 2\pi/(bN_s^{1/2})$ with $S(q) \sim q^{-1}$.

More recent treatments are based on the scaling theory of semi-dilute solutions of linear polymers. Locally, inside of so-called “blobs”, the chains behave as isolated, self-avoiding walks with $\nu \approx 3/5$. A blob containing $g$ monomers has a typical diameter $\xi \propto bg^{\nu} = bQ_{eq}^{3/4}$. Chains with $N \gg g$ can again be regarded as ideal, however, with a renormalized chain length $N/g$ and a renormalized monomer size $\xi$. Quite interestingly, refining the Flory-Rehner ansatz along these lines recovers the classical result $Q_{eq} \propto N_s^{3/5}$. Such models imply for the structure factor a crossover from $S(q) \sim q^{-5/3}$ to $S(q) \sim q^{-1}$ at $q \approx 2\pi/\xi_{eq}$, where the blob diameter at equilibrium swelling is given by $\xi_{eq} \propto bQ_{eq}^{3/4}$ and much smaller than the strand extension.

An open point is the length scale on which the systems begin to deform affinely with the macroscopic strain. The two theories mentioned above consider linear entropic springs, where due to the global connectivity (disregarding fluctuation effects) this length scale is given by the strand size. A drastically different point of view has been advanced by de Gennes, who argues that the swelling is limited by the local connectivity, which only begins to be felt at the overlap concentration $c^* \propto N_s/(bN_s^{3/5})$ of a semi-dilute solution of linear polymers of average length $N_s$, corresponding to $Q_{eq} \propto N_s^{4/5}$. As a motivation for his $c^*$-theorem, de Gennes considers crosslinking in dilute solution, but postulates that the same results also hold for swelling of networks prepared by cross-linking dense melts. The $c^*$-theorem predicts $S(q) \sim q^{-5/3}$ for $q > 2\pi/(bN_s^{3/5})$ as well as unusual elastic properties due to the non-linear elasticity of the network strands.

Both, the Flory-Rehner theory and the $c^*$-theorem are supported by part of the experimental evidence. While the results are very sensitive to the details of the preparation process, it seems well confirmed that highly cross-linked networks behave according to Flory’s prediction $Q_{eq} \propto N_s^{3/5}$. On the other hand, SANS experiments and computer simulations of lightly cross-linked gels show the...
weak dependence of the strand extensions on the degree of swelling predicted by the c'-theorem. To our knowledge, all SANS studies have concentrated on the low q Guinier regime (i.e. the radius of gyration of the strands) and no particular attention has been paid to the local chain structure. As in earlier investigations of polymer melts and networks [21,22] we used a coarse-grained polymer model where beads interacting via a truncated, purely repulsive Lennard-Jones (LJ) potential are connected by FENE 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 = 1ε. 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, \( \sqrt{\langle r^2 \rangle} = 0.965(5)\sigma \), the mean-square end-to-end distance \( \langle r^2 \rangle/N_{dry} = 1.74(2)\sigma^2 N \) [20], the melt entanglement length, \( N_e = 33(2) \) monomers, and the Rouse time \( \tau_{Rouse} \) \( \approx 1.35\tau N^2 \) [23]. In dilute solutions, single chains adopt self-avoiding conformations with \( \langle r^2 \rangle/N \approx 1.8\sigma^2 N^{3/5} \).

Using this model, it is possible to study different network structures including randomly cross-linked, randomly end-cross-linked [21,22] and end-linked melts [23] as well as networks with the regular connectivity of a crystal lattice [24]. Here we investigate end-cross-linked model networks created from an equilibrated monodisperse melt with \( M \) precursor chains of length \( N \) at a melt-like density \( \rho_{dry} = 0.85\sigma^{-3} \) by connecting the end monomers of the chains to a randomly chosen adjacent monomer of a different chain. This method yields defect-free tri-functional systems with an exponential distribution of strand lengths \( N_s \) with an average of \( N_s = N/3 \). The Gaussian statistics of the strands remains unperturbed after crosslinking [21,22]. The systems studied range from \( M/N = 3200/25 \) (i.e. the average strand size \( N_s = 8.3 \)) up to \( M/N = 500/700 \) (\( N_s = 233 \)), some systems being as large as \( M \cdot N = 5 \cdot 10^5 \). All simulations used periodic boundary conditions in a cubic box and were performed at constant volume. Starting from \( V_{dry} = MN/\rho_{dry} \), the size of the simulation box was increased in small steps alternating with equilibration periods of at least 5 entanglement times \( \tau_e(N_s) \approx 1400\tau \). The isotropic pressure \( P \) was obtained from the microscopic virial tensor and the condition \( P \approx 0 \) was used to define equilibrium swelling with \( Q_{eq} = V_{eq}/V_{dry} \). Tests with a part of the networks using open boundary conditions 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 \( N_s \). Fig. 1 shows \( Q_{eq} \cdot N_e^{3/5} \) as a function of the average strand length \( (N_e/N_s)^{-3/5} \). Our results for short strands are compatible with the Flory-Rehner [1] prediction \( Q_{eq} \approx N_s^{-1/2} \), but do not allow for an independent determination of the exponent. In contradiction to this theory we observe a saturation of the equilibrium swelling degree for \( N_s \leq N_e \). The crossover occurs for \( N_s \approx N_e \). The extrapolated maximal degree of equilibrium swelling \( Q_{max} = 6.8(3) \) close to the swelling degree of an ideal Flory-gel with average strand length \( N_e : 1.15 \cdot N_e^{3/5} = 9.5 \), 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, \( Q_{eq} = b^3/\sigma^3 N_e^{3/5} \approx 36 \), 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 crosslinks in limiting the swelling of polymer networks. The situation is anogous to an “olympic gel” [3] of topologically linked ring polymers. In contrast to solutions of linear polymers, systems containing trapped entanglements cannot be arbitrarily diluted.

The chain conformations at equilibrium swelling are best characterized by their structure factor \( S(q) \). Fig. 2 shows \( S(q) \) of the precursor chains within the network for our most weakly crosslinked \( N = 700 \) 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 \( S(q) \propto q^{-(\nu+1)} \) 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 \( 2\sigma \lesssim 2 \pi q \lesssim 15.5\sigma \approx 0.72 \), suggesting that the mean extension of the effective strands of length \( N_e \) is the only relevant length scale in the problem. For 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 to 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 \( \langle r^2 \rangle_{eq} (N_s) \) versus their length. In agreement with the results for the structure functions, we find a power law \( \langle r^2 \rangle_{eq} \sim b^2 N_s^{2/0.72} \) for strands which are shorter than the effective strand length \( N_c \) and therefore sub-affine deformations. Long strands, on the other hand, deform affinely with \( \langle r^2 \rangle_{eq} = \langle r^2 \rangle_{dry} Q_{eq}^{2/3} \).

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 \( N_c \) supplanted by the average strand length \( N_s \)), 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 [4] 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

\[
\nu = \frac{3}{d+2}.
\]  

The simplest models for swollen networks have the regular connectivity of a crystal lattice. In agreement with the c*-theory 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 \( R_F Q^{-1/3} \propto b N_s^{1/3} \) as dense globules. In contrast, if the corresponding semi-dilute solution is compressed, the chains shrink only weakly from \( R_F \) to the Gaussian coil radius \( R \propto b N_s^{1/2} \). Instead, they become highly interpenetrating with \( N \propto N_s^{1/2} \) of them sharing a volume of \( R^3 \). Moreover, at least the simplest model for highly crosslinked networks prepared in the dry state, \( n \propto N_s^{1/2} \) mutually interpenetrating regular networks with strand extensions of the order of \( R \) [24], cannot possibly comply with the c*-theory, 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.

The consequences can be estimated using a simple Flory argument. Instead of a single polymer, we now consider a group of chains which can swell but not desinterpenetrate, i.e. \( n \propto N_s^{1/2} \) chains of length \( N \) which span a volume \( R_F^3 \). The equilibrium between the elastic energy \( \propto n R_F^2 (N/R_F^d)^2 \) and the repulsive energy \( \propto b^d R_F^d (N/R_F^d)^2 \) leads to

\[
\nu = \frac{4 + d}{4 + 2d}.
\]
Quite interestingly, this *local* argument reproduces in three dimensions with $Q_{eq} \sim N^{d/(d+2)} = N^{3/5}$ and $R_{FR} \sim Q^{1/d}N^{3/2} = N^{7/10}$ the results of the classical Flory-Rehner theory of gels. However, in analogy to the Flory argument for single chains, Eq. (6) 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, $G^{3/5}$, should be sub-affine 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. 3 and 6).

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 [16,17,26] and predicts local chain structures characterized by $\nu = 5/8$. (ii) Eq. (6) can also be derived along the lines of [13,19,24] from an equilibrium between the elastic energy of blob chains and the osmotic pressure of a semi-dilute 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 only expected below the original correlation length $\xi_{prep}$ for systems prepared by cross-linking semi-dilute 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 $\nu = d/(d+2)$. 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 [7,10].

In summary, we have used large scale computer simulations and scaling arguments to investigate the swelling behavior of defect free model networks prepared at melt density. We find that for networks with average strand lengths $\bar{N}_e > N_e$ the swelling is limited by entanglements to $Q_{eq} \approx N_e^{3/5}$ and that the strands locally exhibit a fractal structure characterized by an exponent $\nu \approx 7/10$ which should be directly observable in neutron scattering experiments.

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