

The concept of blobs in the theory of cross-linked polymers

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A theory for the swelling of a gel near the gelatinization threshold is derived by Flory's method [P. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, New York, 1971]. Its correlation functions are calculated. A cross-linked polymer of this sort can be described by making use of the concept of blobs, within which there are correlations characteristic of single branched molecules.

Flory's classic theory¹ describes gels which are far from the gelatinization threshold. Such gels may be thought of as sets of neighboring blobs,² whose properties are the same as those of a single polymer chain. In the present letter we consider a gel obtained near the gelatinization threshold. We show that such a gel can be described in terms of blobs, but within such blobs there exist correlations characteristic of a single

branched molecule. We also present a theory for the swelling of an infinite cross-linked polymer of this sort, and we calculate its correlation functions.

We consider a gel which is produced through the equilibrium polycondensation of monomers in a melt. After its topological structure has been fixed by a rapid cooling, followed by a washing out of molecules of finite size, the gel is placed in a low-molecular solvent, in which its swelling occurs. The topological structure of the cross-linked polymer gel remains unchanged in the process, as it was formed during the preparation of the gel.

The properties of a gel of this sort in molten form have been studied in detail.^{3,4} A key point is the conclusion⁴ that the cross-linked structure of the gel may be thought of as a set of "molecules" of finite dimensions, which are actually parts of this cross-linked structure. The swelling of these "molecules" in the solvent can be described by Flory's method.¹ We denote by l_B the number of monomers of these tree-shaped "molecules." In a molten sample, they have a size $R^{(0)} \approx al_B^{1/4}$, where a is the length of the chemical bond. Their size (R) in the solvent is related to the density of the monomers of the gel, ρ , by the obvious relation $l_B = \rho R^d$, where d is the dimensionality of the space. Using a lattice model, we can calculate the free energy of such a gel in Flory's approximation¹:

$$\frac{F^{(g)}}{T} = \frac{V}{a^d} [(1 - \varphi) \ln(1 - \varphi) + \chi \varphi (1 - \varphi)] + Q \frac{R^2}{[R^{(0)}]^2} \frac{N}{l_B}. \quad (1)$$

Here T is the temperature; $Q \sim 1$; $N = \rho V$ is the number of monomers of the gel; and $\varphi = \rho a^d$ is their fraction by volume. The logarithmic term in (1) reflects the fact that no more than a single monomer can occupy a single site. The second term in brackets, $\sim \chi$, describes the interaction of the monomers with each other and with the solvent. Good solvents have Flory parameters $\chi < 1/2$, and poor solvents have $\chi > 1/2$. The last term in (1) gives the elastic energy of these "molecules," whose number is N/l_B . Their size is found by minimizing (1) with respect to R .

Expanding (1) in powers of φ for the case of low concentrations, we find the following result for a good solvent, $\nu \equiv a^d (1 - 2\chi) > 0$, and for $d < d_c = 8$:

$$R \approx a^{2/(d+2)} \nu^{1/(d+2)} l_B^\nu, \quad \nu = 5/2(d+2). \quad (2)$$

Under θ -conditions, with $d < d_c = 6$, we find

$$R \approx al_B^\nu, \quad \nu = 7/4(d+1) \text{ for } \chi = 1/2. \quad (3)$$

Relations (2) and (3) agree completely with the concept of blobs.² According to (2) and (3), within a blob of this sort, with a size equal to the correlation radius, $\xi = R$, there exist correlations which are characteristic of a single branched molecule with $l_B \sim \rho^{-1/(d\nu-1)}$ monomers. In a study of cross-linked polymer structures one can accordingly use the results of the theory of semidilute solutions.² For example, the surface swelling of a gel at a boundary with a repulsive wall is $\sigma \approx T\xi^{1-d}$, and we find the following expression for the osmotic pressure of a swollen gel:

$$\pi \approx T \xi^{-d} \sim \rho^{d\nu/(d\nu-1)}. \quad (4)$$

We will now calculate the density-density correlation function of the gel, $G^{(g)}(\mathbf{r})$. At small scale, $r \ll \xi$, the function $G^g(\mathbf{r})/\rho = l/r^d$ is proportional to the number (l) of monomers within a sphere of radius r . It follows from scaling considerations that these quantities are related to each other by relations analogous to (2) and (3). We thus find the following expression for the Fourier component of the density correlation function:

$$G_q^{(g)} \equiv \langle \delta \rho_{\mathbf{q}} \delta \rho_{-\mathbf{q}} \rangle \approx \rho \xi^d (q \xi)^{-\nu^{-1}}, \quad q \xi \gg 1. \quad (5)$$

At scales large in comparison with ξ , the cross-linked structure is represented as a melt of blobs and can be described in the mean-field approximation. From Ref. 5 we find

$$G_q^{(g)} \approx \rho \xi^d (1 + q^4 \xi^4)^{-1}, \quad q \xi \ll 1. \quad (6)$$

The proportionality factor in (6) was found by joining with (5); at $d = d_c$ these expressions become the same as those derived in Ref. 5.

A positive value of π in (4) corresponds to a gel in a limited volume, $V \ll V_{\max}$. The maximum (equilibrium) volume V_{\max} , which the gel occupies in a given solvent, is found from the condition $\pi = 0$. This maximum volume corresponds to the case in which the maximum number of monomers in a blob, $l_B = l_{\max} \approx \tau^{-2}$, is equal to the number of monomers in a volume with a radius equal to the correlation length: $\xi^{(0)} \approx a \tau^{-1/2} \approx a l_{\max}^{1/4}$, for a gel in a melt. The parameter $\tau = p/p_c - 1 \ll 1$ characterizes the proximity to the gelatinization threshold.⁴ At scales large in comparison with $\xi^{(0)}$ the gel has a high degree of cyclization. Because of the numerous cross-linkages, a blob of this sort with $l_B = l_{\max}$ is in contact with its neighbors. At equilibrium, the monomer concentration is therefore automatically established at a level proportional to the threshold for the overlap of branched molecules with $l_B = l_{\max}$:

$$\rho \approx (v a^2)^{-d/(d+2)} \tau^{2(d\nu-1)}, \quad \chi < 1/2. \quad (7)$$

This expression is an analog of Flory's well-known theorem regarding gels.¹

An analysis of relations (1)–(3) under the condition $l_B = l_{\max}$, which describe equilibrium gels, leads to results corresponding to those of Ref. 1. We know that the Flory approach, which we have taken here, gives a good description of polymers because of the mutual cancellation of errors. A rigorous theory for frozen polymer systems confirms the conclusions of this study.

An experimental study of swollen cross-linked polymer structures would be of great interest. In particular, correlation function (5), (6) might be measured directly in experiments on neutron scattering and optical scattering. Under the condition $1 - 2\chi \ll 1$, it should be possible to observe a crossover between the regimes of a good solvent, (2), and a θ -solvent, (3), by varying the scattering wave vector \mathbf{q} (Ref. 2, for example).

We conclude with a few comments regarding the properties of the gel produced by the cross-linking of linear chains of polyfunctional monomers. In a swollen gel of

this sort, each chain consists of “ordinary”² blobs. Taking these blobs as the initial units, we return to the system described above, but with renormalized parameters. The fluctuational regimes studied in this letter prevail at $\tau \ll 1$, when the number of such blobs at the scale of the correlation length ξ is large. For gels far from the gelatinization threshold we would have $\tau \sim 1$, the chains would be essentially non-Gaussian, and the correlation length would be equal to the size of a blob.¹

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¹P. Flory, Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1971.

²P. G. de Gennes, Scaling Concepts in Polymer Physics, Cornell Univ. Press, Ithaca, 1979.

³M. Gordon and G. Scantlebury, J. Polym. Sci. **C16**, 3933 (1968).

⁴S. V. Panyukov, Zh. Eksp. Teor. Fiz. **93**, 1454 (1987) [Sov. Phys. JETP **66**, 829 (1987)].

⁵S. V. Panyukov, Zh. Eksp. Teor. Fiz. **90**, 169 (1986) [Sov. Phys. JETP **63**, 96 (1986)].

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