

Theory of structurally disordered polymers

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A topological disorder, which has not been considered previously, plays a governing role in a scaling theory for polymer networks.

The modern scaling theory of polymer structure^{1,2} is based on the assumption of a complete spatial separation of the various chains of the polymer because of a strong mutual repulsion of the monomer units. This assumption is known as Flory's theorem, according to which the equilibrium density of units in the structure is found from the condition $\rho_p \approx \rho^* = N/\xi^3$ at the threshold for the overlap of dilute and semidilute solutions of chains. Here $\xi \approx a^{2/5} B^{1/5} N^{3/5}$ is the size of an isolated chain of the structure, which has N units of size a , and B is the second virial coefficient of their interaction.

In this letter we show that Flory's theorem applies only to polymer structures which are topologically equivalent to a regular lattice and whose synthesis would be described better as art than science. As a rule, the structure of real polymers is far from regular. We will derive a simple scaling theory for such polymers.

The elasticity of polymers originates in the entropy. An increase in entropy due to structural disorder leads to a corresponding increase in the elastic force π_{el} of stretched chains in the polymer. This compressional force causes the chains to overlap markedly, and they form a semidilute solution. At equilibrium, the osmotic pressure π_{osm} of such a solution is balanced by the elastic force: $\pi_{el} = \pi_{osm}$. The difference between these two forces, $\pi = \pi_{el} - \pi_{osm}$, is equal to the external pressure. If the deformation of the structure is slight, this difference determines the elastic modulus:

$$\pi = E(\lambda / \lambda_q - 1), \quad \lambda = (\rho_0 / \rho)^{1/3}, \quad \lambda_q = (\rho_0 / \rho_q)^{1/3}. \quad (1)$$

Here ρ_0 is the density of units under the synthesis conditions, λ and ρ are the linear modulus of expansion and the density of the polymer, and λ_q and ρ_q are the equilibrium values.

In a semidilute solution, the chains are Gaussian chains² made up of noninteracting "blobs," each having a size equal to the correlation radius ξ and consisting of g monomer units. Treating these blobs as the building blocks, we can use the classical Flory theory³ to describe the elasticity of the Gaussian networks that result. From that theory we find

$$\pi_{el} = \nu T \alpha \lambda^2, \quad \alpha = \langle R^2 \rangle / \langle R^2 \rangle_0, \quad (2)$$

where T is the temperature, ν is the density of chains, α is the chain expansion factor, and $\langle R^2 \rangle$ and $\langle R^2 \rangle_0$ are the mean square distances between the ends of the chains in free space under the experimental conditions and during the formation of the network, respectively. Using Eqs. (1) and (2) along with the scaling laws²

$$\pi_{osm} \approx T / \xi^3, \quad g = \rho \xi^3, \quad (3)$$

we can express the equilibrium and elastic properties of disordered polymers in terms of the microscopic characteristics of the blobs.

For definiteness we consider a polymer formed by cross-linking a semidilute solution of chains beyond their ends. The dimensions of the chains of this polymer under the experimental conditions and under the synthesis conditions, consisting of respectively N/g and N/g_0 blobs, are

$$\langle R^2 \rangle = \xi^2 N / g, \quad \langle R^2 \rangle_0 = \xi_0^2 N / g_0, \quad (4)$$

and the dimensions of the blobs are related to the numbers of units, g and g_0 , by $\xi \approx a^{2/5} B^{1/5} g^{3/5}$. Here

$$\xi_0 \approx a^{2/5} B^{1/5} g_0^{3/5}, \quad g_0 = \rho_0 \xi_0^3. \quad (5)$$

Using (2)–(5) and $\nu = \rho / N$, we find the following expression for the equilibrium density of units in the network:

$$\rho_q \approx a^{-6/5} B^{-3/5} g_0^{-1/5} N^{-3/5}, \quad g_0 \approx a^{-3/5} B^{-3/4} \rho_0^{-5/4}. \quad (6)$$

In contrast with Flory's theory,¹ the quantity ρ_q depends on not only the experimental conditions but also the parameter g_0 , which is a measure of the degree of

disorder of the topological structure. Flory's theorem $\rho_q \approx \rho^*$ holds only for polymers which are synthesized strictly at the threshold for the overlap of dilute and semidilute solutions of chains, $g_0 \approx N$, which have an approximately regular topological structure. The greatly disordered networks obtained in a semidilute solution, $g_0 \ll N$, swell to a much lesser extent: $\rho_q \gg \rho^*$.

Determining the elastic modulus from (1)–(6), we find

$$E \approx \rho_q T g_0^{1/4} N^{-3/4} \approx \rho^* T g_0^{-9/20} N^{-11/20}. \quad (7)$$

The elastic characteristics are thus more sensitive than the equilibrium parameters in (6) to a disorder.

Scaling law (6) for g_0 holds only in the case of a large value of the perturbation-theory parameter⁴ $Z_0 = B_0 g_0^{1/2} / a^3 \gg 1$. In the opposite case $Z_0 \lesssim 1$, the chains are Gaussian under the synthesis conditions, and from the relation $\langle R_0^2 \rangle = a^2 N$ we find the expression $g_0 \approx 1 / \rho_0^2 a^6$ for the parameter g_0 in (6) and (7). For polymers produced in a melt we would have $g_0 \ll 1$, and the quantities ρ_q and E —even for short chains with $N \sim 100$ —could be much larger than their values for regular networks, ρ^* and $\rho^* T / N$.

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

²P. G. de Gennes, *Scaling Concepts in Polymer Physics*, Cornell U. Press, Ithaca, New York, 1979.

³P. J. Flory, *J. Am. Chem. Soc.* **78**, 5222 (1956).

⁴I. M. Lifshitz *et al.*, *Usp. Fiz. Nauk* **127**, 353 (1979) [*Sov. Phys. Usp.* **22**, 123 (1979)].

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