VOLUME 66, NUMBER 12 PHYSICAL REVIEW LETTERS 25 MARCH 1991

Experimental Evidence for Inhomogeneous Swelling and Deformation in Statistical Gels

E. Mendes, Jr.,(1) P. Lindner,(2) M. Buzier,(3) F. Boué,(3) and J. Bastide(1)

(1)*Institut Charles Sadron (Centre de Recherche Macromoléculaire–EAHP), 67083 Strasbourg CEDEX, France*

(2)*Institut Laue-Langevin, Grenoble, France*

(3)*Laboratoire Léon Brillouin, Saclay, France*

(Received 2 August 1990)

Polymer concentration correlations in a network swollen by a solvent are studied by small-angle neutron scattering. The network is made by statistical cross-linking of long chains in solution. At small scattering vectors, the intensity strongly increases upon swelling. Upon stretching, unusually oriented isointensity lines ("butterflies") are observed. These effects are well described by a model of fractal heterogeneities of cross-linking giving rise to nonhomogeneous swelling or deformation.

PACS numbers: 61.41.+e, 64.60.Cn, 64.70.Pf, 82.70.Gg

According to most current theories the properties of polymer networks are determined by their structural units alone, namely, the elementary meshes that connect two nearest-neighbor cross-links. No correlations are thought to exist on distance scales larger than the average mesh size.[1-3] These approaches have not been entirely satisfactory, as their description of the elastic properties of rubbers and gels is essentially limited to semiquantitative estimates of behavior. On a microscopic scale, they cannot explain a striking anomaly which has been found recently in studies of the structure of rubbers by small-angle neutron scattering (SANS). A network containing small free labeled (deuterated) chains was subjected to a uniaxial deformation and the isointensity lines were mapped using a bidimensional neutron detector. The pattern observed was anisotropic, as expected, but unexpectedly was oriented in the wrong direction.[4,5] The observed double-winged figures, called "butterfly patterns," had their long axes aligned in the stretching direction.[4] This phenomenon has attracted attention because its understanding might bring new elements to the theoretical debate of the modeling of microstructural properties of networks.[6-8]

In this Letter, we present the results of two experiments designed to shed some light on this situation. We look for the existence of butterfly patterns in a somewhat different situation, namely, the uniaxial elongation of statistically cross-linked gels. The appearence of such figures was predicted recently for such a case on the basis of establishment of correlations between substructures larger than the average mesh size.[9] This new model establishes a connection between the butterfly phenomenon and a strong increase of scattering intensity predicted to appear in a swelling experiment. Thus, we investigate by SANS the swelling and the stretching of networks synthesized under conditions as close as possible to the model assumptions.

Semidilute solutions are good reference systems for discussing the structure of gels. They can be viewed as homogeneous networks of finite lifetime and the way they scatter light or neutrons is well described by existing theories.[3] When a contrast is established between the polymer and the solvent, their neutron-scattering intensity $I(q)$ has an Ornstein-Zernicke form $I(q) \sim I(0)/(1+q^2\xi^2)$ for $q\xi < 1$. ξ is the correlation length scale beyond which the elementary segments of the chains can be considered as randomly distributed; on length scales larger than ξ correlations along any given chain are screened out. From geometrical arguments, one expects $\xi \sim \phi^{-0.77}$, ϕ being the polymer volume fraction; $I(0)$ is predicted to be proportional to $\phi^2\xi^3$, i.e., to $\phi^{-0.31}$. Experimental results are in good agreement with these scaling laws.[3,10]

As mentioned above, the correlation length in homogeneous gels should not be larger than the size of the average mesh. Moreover, it should not differ very much from the correlation length of a semidilute solution of the same polymer concentration.[3] The intensity scattered by gels has been related for $q\xi < 1$ to the dynamical fluctuations of the polymer concentration.[3,11] These fluctuations are governed by both the osmotic pressure of the gel and its shear modulus. Transforming a semidilute solution into a gel by establishing permanent junctions between chains can only increase the elasticity, i.e., raise the shear modulus and decrease the osmotic pressure. The first effect is the larger and thus the balance is in favor of a decrease of the dynamical fluctuations. As a result, for homogeneous gels having no defects, one expects $I(q)_{\text{gel}} \leq I(q)_{\text{solution}}$.

Nevertheless, gels are often intrinsically heterogeneous at scales larger than the average mesh size.[9] We focus here on a semidilute solution of polymer volume fraction ϕ_r and correlation length ξ_r which is subsequently statistically cross-linked. We will consider the case when the number of junctions is large enough that no sol fraction remains after cross-linking. The random arrangement of cross-links in space creates regions where the cross-linking density is higher than average. This disorder can be described as a site percolation: The "hard" regions have the topology of percolation clusters. For a sufficiently high cross-linking density, they are substantially interpenetrated and the larger ones have a self-similar structure [as schematically shown in Fig. 1(a)]. In the prepared state, these clusters should not be detectable by a scattering technique because there is no "contrast" between the cross-linked and the uncross-linked entanglements. When put in contact with an excess of solvent, however, such gels should swell heterogeneously. The solvent is essentially absorbed by the regions in between the clusters, where the chains can still move with respect to each other. The polymer concentration would then be different inside the clusters than in the rest of the gel. The more densely cross-linked regions are expected to be less deformed than the average of the gel; thus, the swelling should result in a partial expulsion of smaller clusters from the larger ones. Moreover, the random arrangement of the more cross-linked regions should be destroyed by the swelling [see Fig. 1(b); for simplicity, undeformed clusters are drawn]. Thus, in the expanded gel, one expects the length scale of the fluctuations of monomer concentration (characterized by a new correlation length ξ_c) to be now larger than the average distance between cross-links. For scales larger than ξ_r, one can argue that the swelling may be described through a direct analogy with the dilution of percolation clusters: For $1/\xi_c < q < 1/\xi_r$, one expects $I(q) \sim q^{-8/5}$, where $\frac{8}{5} = D(3-\tau)$ depends on the polydispersity of the clusters (described by τ) and on their fractal dimension D. One expects $\xi_c \sim \phi^{-5/3}$ and $I(0) \sim \phi^{-5/3}$, where ϕ is the monomer volume fraction.[12]

We now turn to elongated gels. In the case of deformation of homogeneous networks, the scattering intensity should decrease relative to the isotropic case for q parallel to the stretching axis, as in all chain-orientation processes. Thus, the isointensity curves should have a long axis perpendicular to the stretching direction.[13] On the contrary, in the case of heterogeneous networks, this normal anisotropy is expected to be at least partially masked at low q by another phenomenon: It is reasonable to expect that the strongly cross-linked regions deform less than the weakly cross-linked ones. Thus, upon stretching of the sample, the clusters should separate, as in the case of swelling, but now in the direction parallel to the stretching [see Fig. 1(c); for simplicity, the clusters are drawn undeformed]. As a result, one expects the gel to become less homogeneous in this direction and the scattering intensity to increase at low q. In the perpendicular direction, the dimension of the sample is contracted, due to Poisson's effect: The more cross-linked clusters, if they deform less than the average, should interpenetrate more in this direction. Thus, the scattering intensity should decrease in the perpendicular direction. The scattering has been calculated under a further simplification: Any deformation of clusters and chains directly induced by the shear strain has been neglected; only variations of cluster shapes due to changes with elongation of the screening of excluded volume interactions have been taken into account. The resulting calculated isointensity curves exhibit butterfly patterns, with a long axis parallel to the stretching direction (Fig. 2). This model is the only one of which we are aware that predicts the appearance of such butterfly patterns in swollen gels that have been deformed.

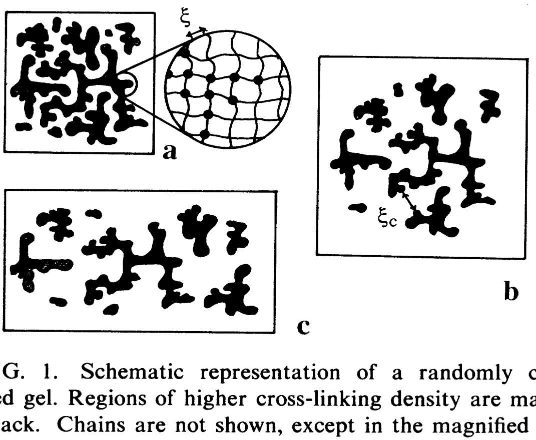

FIG. 1. Schematic representation of a randomly cross-linked gel. Regions of higher cross-linking density are marked in black. Chains are not shown, except in the magnified inset of (a), where the black dots represent the cross-links. (a) Preparation state; (b) gel swollen with respect to the preparation state; (c) uniaxially extended gel [with respect to the state of (b)]. The deformation of the clusters, smaller than the macroscopic one, is not represented.

Statistically cross-linked gels were prepared using a Friedel-Crafts reaction.[14] Polystyrene chains ($M_w \sim 7 \times 10^5$) were dissolved at a concentration ϕ (by volume) of 0.1 in 1,2-dichloroethane. Small amounts of cross-linker [1,4-bis(chloromethyl)benzene at concentration c_x equal to 0.8% in mole/mole] and coreactor ($SnCl_4$, 2% mole/mole) were then added to the solution. This mixture was heated at 60 °C for two days. Under washing in tetrahydrofuran, the residual sol fraction was very low, less than 0.1%. Then, the samples were dried, polished, and reswollen by placing the desired amount of solvent (deuterated toluene) inside the cells used for

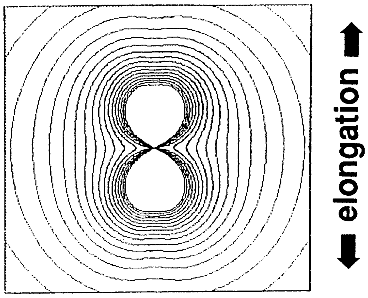

FIG. 2. Example of calculated isointensity curves for a correlation length equal to 50 Å before deformation and for an elongation ratio equal to 1.35. Range of scattering-vector amplitude: $0.005\ \text{Å}^{-1} < q < 0.1\ \text{Å}^{-1}$.

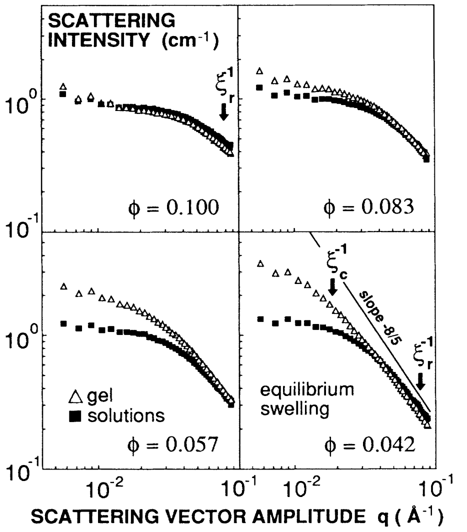

FIG. 3. Isotropically regrouped neutron-scattering intensities vs scattering-vector amplitude for a gel at different concentrations ϕ and for the corresponding semidilute solutions (of same ϕ).

SANS. Samples of the same gel ($\phi=0.09\pm0.01$) were uniaxially elongated in an airtight container. The stretching ratio λ (length divided by initial length) ranged from 1 to 1.85.

Four spectra corresponding to the same gel swollen at different concentrations ϕ are plotted in Fig. 3, together with those of semidilute solutions at the same concentrations.[15] At the concentration of the state of preparation ($\phi=0.1$), the signal of the solution and the gel coincide almost exactly; the effects of the cross-linking are not detectable in this state. When the same amounts of solvent are added to the two types of systems, $I(q)$ increases much more at low q in the gels than in the solutions. This means that, upon swelling, the fluctuations of concentration increase much more at large length scales in gels than in the equivalent solutions. We have seen above that such behavior is not predicted by the standard theories of homogeneous gels and cannot be explained by dynamical fluctuations in polymer concentration since such fluctuations must be smaller in gels than in solutions. Thus, as predicted by the new model discussed above, the large concentration fluctuations probed here must be quenched and produced by heterogeneous swelling process. At equilibrium swelling, the signal tends asymptotically towards a straight line of slope $\frac{8}{5}$, for q in the range $1/\xi_c < q < 1/\xi_r$, in agreement with the model.

The correlation lengths in gels and semidilute solutions were determined by selecting from the log-log representation the data points that level off at low q and fitting them with the equation $I(q)=I(0)/(1+q^2\xi^2)$. This expression for $I(q)$, the classical one for solutions,[3] has been used because it is better suited to the detection of trends than the function proposed in Ref. 9; it allows the comparison of the values found for ξ and $I(0)$ in the cross-linked and uncross-linked systems together with the comparison of the values obtained in our measurements with those available in the literature for solutions. The variation of ξ as a function of ϕ for the solutions is in good agreement with the expectation $\xi\sim\phi^{-0.77}$ (Fig. 4); the absolute values agree well with those reported in the literature.[10] In the case of the gels, ξ increases more strongly with ϕ (Fig. 4); the exponent found (over the limited range of concentrations) is -1.65 ± 0.15, in agreement with the variation expected for ξ_c from the model.[9] With regard to $I(0)$, the difference between the gels and the solutions is larger. The values for the solution are in approximate agreement with the expected $\phi^{-0.31}$ law. However, the exponent is much higher in the case of the gels (-1.5 ± 0.1), and close to the value expected from the model.[9]

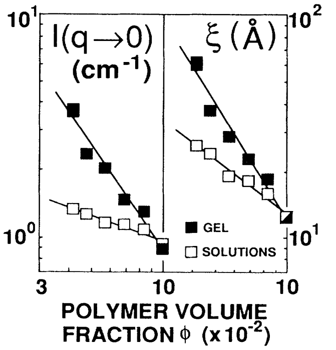

FIG. 4. Correlation lengths ξ and zero-angle extrapolated intensities vs polymer volume fraction for a given gel at different swelling degrees and for a series of semidilute solutions. Apparent exponents: gel, $I(0)\sim\phi^{-1.5}$ and $\xi\sim\phi^{-1.65}$; solutions, $I(0)\sim\phi^{-0.37}$ and $\xi\sim\phi^{-0.78}$.

In the case of the stretched sample, the isointensity lines have, at low q, the shape of *butterfly patterns*, with

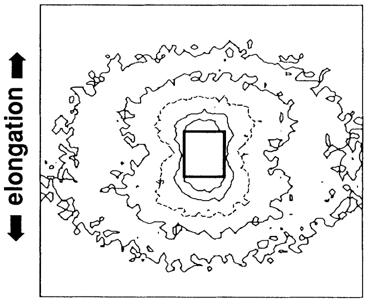

FIG. 5. Experimental isointensity curves for a gel submitted to a uniaxial elongation by a factor $\lambda=1.5$. The rectangle in the center indicates the limits of the beamstop. Range of scattering-vector amplitude: $0.006\ \text{Å}^{-1} < q < 0.044\ \text{Å}^{-1}$.

the long axis aligned with the direction of elongation. An example is shown in Fig. 5. Although less anisotropic, they resemble the ones calculated with the model of heterogeneous gels, in which strain-induced stretching of the clusters and of the chains were neglected (Fig. 2). The results disagree completely with the classical picture: A strong increase of intensity rather than a decrease is observed in the direction of elongation. The qualitative agreement with the new model implies that the deformation process is strongly inhomogeneous, since the classical anisotropy appears to be masked at large length scales. The classical effects only appear at higher q values, where ellipses with the long axis perpendicular to the elongation direction can be seen. Presumably, they reflect a net average chain orientation in elongated gels at small length scales.

The results reported here are the first observation of butterfly patterns in swollen polymer gels. The scattering patterns observed are in qualitative agreement with a recent model of the deformation of gels containing fractal cross-linking heterogeneities greater than the average mesh size of the network and having a large distribution of sizes.[9] Furthermore, the observed neutron-scattering behavior of gels isotropically swollen by solvent is in quantitative agreement with this model. Analogous phenomena may be exhibited by other kinds of systems, provided they contain large substructures having a distribution of sizes. Note that the latter do not need to be fractal; the important requirements are that these substructures be interpenetrated and that the amount of their interpenetration can be modified by a macroscopic strain. In particular, such a picture could explain the *butterfly patterns* that have been observed in rubbers and polymer melts in which free short labeled chains behave as a kind of polymeric solvent.[4,5] Such phenomena, if observed, would mean that in these systems deformation is also far less homogeneous than is usually assumed.

The authors are indebted to C. Lartigue, L. Leibler, and F. Schosseler for fruitful discussions. The manuscript has greatly benefited from critical reading by J. Harden and G. Mc Kenna. We are very grateful to them.

---

[1] P. J. Flory, Proc. Roy. Soc. London **351**, 351 (1976).

[2] R. T. Deam and S. F. Edwards, Philos. Trans. Roy. Soc. London A **280**, 317 (1976).

[3] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, NY, 1979).

[4] R. Oeser, C. Picot, and J. Herz, in *Polymer Motions in Dense Systems,* edited by D. Richter and T. Springer (Springer-Verlag, Berlin, 1988), p. 104.

[5] Butterfly patterns appear also in temporary networks like polymer melts: See J. L. Barea, R. Muller, and C. Picot, in *Polymer Motions in Dense Systems,* edited by D. Richter and T. Springer (Springer-Verlag, Berlin, 1988), p. 86; J. Bastide, M. Buzier, and F. Boue, *ibid.*, p. 112.

[6] F. Brochard-Wyart and P. G. de Gennes, C. R. Acad. Sci. Ser. 2, **306**, 699 (1988).

[7] N. Pistoor and K. Binder, Colloid Polym. Sci. **266**, 132 (1988).

[8] S. F. Edwards and T. C. B. Mc Leish (to be published).

[9] J. Bastide, L. Leibler, and J. Prost, Macromolecules **23**, 1821 (1990).

[10] M. Daoud, J. P. Cotton, B. Farnoux, G. Jannink, G. Sarma, H. Benoît, R. Duplessix, C. Picot, and P. G. de Gennes, Macromolecules **8**, 804 (1975).

[11] T. Tanaka, L. O. Hocker, and G. B. Benedek, J. Chem. Phys. **59**, 5151 (1973).

[12] M. Daoud and L. Leibler, Macromolecules **21**, 1497 (1988).

[13] A. Onuki, in *Space Time Organisation in Macromolecular Fluids,* edited by F. Tanaka, T. Ohta, and M. Doi (Springer-Verlag, Berlin, 1989), p. 94.

[14] C. Collette, F. Lafuma, R. Audebert, and L. Leibler, in *Biological and Synthetic Polymer Networks,* edited by O. Kramer (Elsevier, Amsterdam, 1988), p. 277.

[15] SANS experiments performed at Institut Laue-Langevin, Grenoble (D17 spectrometer), and at Laboratoire Lèon Brillouin, Saclay (PACE spectrometer).