meric dielectric materials and polymers having nonlinear optical properties.

Acknowledgment. Prof. Robert Reeves, Matt Rutten, and S. Y. Kim were instrumental in obtaining oxidation resistance data. Prof. R. G. Bass generously provided information on the preparation of the hydrazines. Their contribution is gratefully acknowledged. This work has been supported, in part, by a grant from the Office of Naval Research.

Registry No. I (copolymer), 115077-22-0; I (SRU), 115077-25-3; II (copolymer), 115077-23-1; II (SRU), 115077-26-4; III (copolymer), 115077-24-2; III (SRU), 115077-27-5; IV, 115077-20-8; V, 115077-21-9; O$_2$, 7782-44-7; [4-(hydrazinophenyl)phenyl]sulfone, 70714-83-9; 1,4-bis(1-chloro-2,2-dicyanovinyl)benzene, 103134-51-6; 1,3-bis(1-chloro-2,2-dicyanovinyl)benzene, 108090-23-9.

References and Notes

(1) Cassidy, P. E. *Thermally Stable Polymers*; Marcel Dekker: New York, 1980.

(2) (a) Stille, J. K.; Harris, F. W. *J. Polym. Sci. Polym. Chem. Ed.* **1968**, *6*, 2317. (b) Stille, J. K.; Bedford, M. A. *Ibid.* **1968**, *6*, 2331. (c) Gilliams, Y.; Smets, G. *Makromol. Chem.* **1969**, *128*, 263.

(3) Connell, J. W.; Bass, R. G.; Sinsky, M. S.; Waldbauer, R. O.; Hergenrother, P. M. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2531.

(4) Moore, J. A.; Robello, D. R. *Macromolecules* **1986**, *19*, 2667.

(5) Tokunga, D.; Hattori, T.; Kubo, T. *Chem. Abstr.* **1957**, *52*, 112911.

(6) This monofunctional hydrazine was prepared from hydrazine hydrate and (4-chlorophenylphenyl)sulfone (Aldrich Chemical Co.) by the method employed for the synthesis of bifunctional monomer as described in ref 5.

(7) (a) Wallenfels, K. *Chemia* **1966**, *20*, 303. (b) Wallenfels, K.; Thiem, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 261.

(8) (a) Moore, J. A.; Robello, D. R., submitted for publication in *Macromolecules*. (b) Robello, D. R. Ph.D. Dissertation, Rensselaer Polytechnic Institute, 1986.

J. A. Moore* and Parag G. Mehta

Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

Received March 21, 1988

Large-Scale Heterogeneities in Randomly Cross-Linked Networks

Large-scale imperfections in network structures are known[1,2] to influence the solvent permeability, the diffusion of small and large molecules (electrophoresis), and more indirectly the swelling and the elastic properties of gels. Light-[3-5] and neutron-scattering[6] studies have shown the existence of concentration heterogeneities at submicrometer scales in gels synthesized under very different conditions. The competition between dilution effects and an effective attraction induced by chemical cross-linking often produces density fluctuations already in the reaction bath (all kinds of syneresis).[1,7] Here we would like to focus on a more paradoxical situation when the large-scale concentration heterogeneities do not appear during the gelation but only in the gel swollen at equilibrium. We discuss a random cross-linking of semidilute solutions of long precursor chains and argue that self-similar cross-linking density fluctuations may exist even far beyond the gel point and are revealed by the swelling of the network.

Consider a reaction bath well in the semidilute regime. It can be visualized as a melt of "blobs" of size ξ_r, which scales as the screening length of the excluded volume interaction or as the distance between interchain contact points. Introduce now, at random and rapidly, some cross-links in this solution. Depending on the concentration in the reaction bath φ_r, a fraction of them will react on the same chain and will form small loops:[8] these junctions are lost with respect to the interchain gelation process. Only the tie points that form interchain bridges will contribute to the elasticity. Let us call $\rho(\varphi_r)$ the interchain cross-linking density, i.e., the ratio of the number of interchain tie points and monomer units. We avoid here the delicate question of estimating the number of intrachain cross-links and use $\rho(\varphi_r)$ instead of the total number of introduced cross-links. We can thus consider that everything happens as if a certain fraction of permanent cross-links was placed at random upon the interchain contact points, which can be viewed as forming the sites of a lattice of coordination number 4 (and unknown topology). This means that the problem can also be regarded as a site percolation,[9] on a lattice with a site having the blob size (cf. ref 10). As pointed out first by Daoud,[10] the statistical cross-linking of a semidilute solution contains therefore two separate questions: the "true" gelation of the chains and the "percolation" of the blobs. We would like to focus here on a frequent regime of chain length, concentration (φ_r), and cross-linking density when the two following conditions are satisfied:

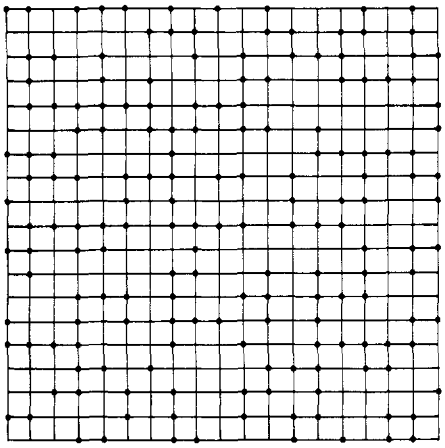


Figure 1. Schematic representation of a two-dimensional reaction bath well above the chain gelation threshold. The size of the lattice site is ξ_r. For sake of simplicity, the chains, which are random walks on this lattice, are not shown on the figure. Black dots represent the interchain cross-links, placed at random.

(i) $\rho(\varphi_r) \gg 1/Z$, where Z denotes the weight-average polymerization index of the precursor chains.

(ii) $P_b = g\rho(\varphi_r) \lesssim P_c$, with P_b denoting the fraction of linked blobs and g being equal to the number of monomer units per blob. P_c is the gelation threshold in the percolation model.

The first condition ensures that a sufficiently regular gel is formed: one expects a vanishing sol fraction and even a small fraction of dangling ends (with respect to the number of elastically effective strands). On the other hand, condition ii implies that a noticeable disorder remains in the spatial repartition of cross-links: a given junction may or may not be neighbor to another one on the lattice of the interchain contact points, as illustrated schematically in Figure 1. When junctions are located on neighboring lattice sites, a "frozen blob" is formed. When swelling, it will be difficult to move these cross-links apart from each other since they are connected by a chain segment which is already in a optimal excluded volume conformation. Frozen blobs are often connected and form clusters of first topological neighbors.[11,12] The important point is that the

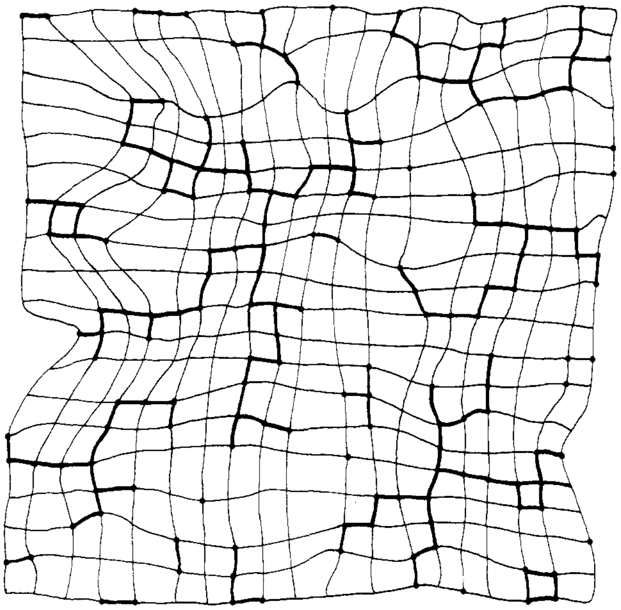


Figure 2. Schematic representation of the two-dimensional gel of Figure 1, overswollen by the addition of solvent. The clusters of first chemical neighbor junctions (frozen blobs), which do not swell, are represented by thick solid lines. The small clusters, which penetrated large clusters in the reaction bath, are here desinterspersed by the swelling of the interstitial medium. The desinterspersion effect and the resulting large-scale heterogeneities should be more pronounced in the three-dimensional case.

cluster size distribution may be very large, implying large-scale cross-linking density fluctuations. In the framework of the percolation model, the number density n_s of clusters of s frozen blobs drops (for large s) according to a power law, cut at a certain characteristic size $s^*(P_b)$:[9,13]

$$n_s(P_b) = s^{-\tau}f(s/s^*)$$

where f denotes the crossover function.

The typical size s^*, which determines the evolution of the spread and of the moments of the distribution, diverges when the blob gel point is reached: $s^* = (P_c - P_b)^{-1/\sigma}$. The exponents τ and σ are respectively equal to 2.2 and 0.46.

The clusters are expected to be widely branched (even self-similar) and interspersed, the smaller ones being embedded in the larger ones. In the present case of very large chains, the existence of these blob clusters should be practically undetectable in the reaction bath. The fluctuations of the cross-linking density would indeed tend to shrink locally the net. However, since the chains pass in general through several clusters, this effect is very likely weak. Thus, the polymer concentration in the reaction bath is expected to remain practically as uniform as in the original solution. In the reaction bath, we have therefore a subtle interspersion of two media: the frozen blob clusters with a "high" cross-linking density and the "interstitial" medium with a lower cross-linking density. If we take the gel out of the reaction vessel and put it in a excess of a good solvent, the clusters will swell less than the interstitial medium. During the swelling, the smaller clusters could even be expelled from the inside of the larger ones (see Figure 2). Such a desinterspersion may be possible since cross-links belonging to different clusters, although "spatial" neighbors in the reaction bath, are connected only through a long chemical path along the net.[12,6] As mentioned above, the expansion of the frozen blob should be negligible. Then, the radius of gyration R_s of a cluster of s frozen blobs is expected to scale as $R_s \simeq s^{\nu}\xi_r$. If the desinterspersion of the clusters was complete, ν would be that of lattice animals, i.e., $^1/_2$.[15,16] In any case, the value of ν could be expected to be in between its value in the reaction bath, 0.4, and $^1/_2$. The interstitial medium, having a lower cross-linking density, should swell to a new concentration (φ_i) that is smaller than φ_r, to which will correspond a screening length ξ_i larger than ξ_r. Therefore, the overswollen gel can be pictured as branched objects ("fractals"[14]) of local concentration (φ_r) (at the scale of the frozen blob), bathing in a less concentrated medium, comparable, in a first approximation, to a semidilute solution. These heterogeneities in an overswollen gel can be detected by the scattering spectrum, which we expect to be very different from that of a semidilute solution.

The scattering spectrum of a semidilute solution exhibits two main regimes:[7]

(1) For $q\xi < 1$,

$$S(q) \simeq \frac{1}{q^2 + \xi^{-2}}$$

With q scattering vector amplitude in this regime, $S(q)$ will appear almost flat in a log–log plot.

(2) for $q\xi > 1$,

$$S(q) \rightarrow 1/q^{5/3}$$

In the overswollen gel, the additional contrast in polymer concentration, arising from the presence of clusters in a less concentrated medium will lead to three main regimes instead of two.

(1) For $qR^* < 1$, with R^* being the radius of gyration of the characteristic clusters of size s^*

$$S(q) = 1 - q^2\frac{\langle R_g^{\,2}\rangle_z}{3}$$

where $\langle R_g^{\,2}\rangle_z$ is the z-average square radius of the frozen blob clusters which scales as $R^{*2} \simeq s^{*2\nu}\,\xi_r$;[15] i.e., the scattering will be that of the Guinier regime of the polydisperse clusters.

(2) For $1/R^* < q < 1/\xi_r$, $S(q)$ should vary as

$$S(q) = 1/q^{1/\nu(3-\tau)}$$

in analogy to the intermediate regime of the scattering by polydisperse randomly branched molecules.[17,18] The effective exponent $(3-\tau)$ arises from the polydispersity of the clusters. This regime extends more and more toward small q vector amplitudes when one approaches the blob gelation threshold. In principle, the scattering by the interstitial semidilute medium should also be considered. However, in this q range, the variation of the intensity with the scattering vector amplitude (q) is much slower than the above power law decrease, except eventually in the crossover region of $q \simeq 1/\xi_r$.

(3) Eventually for $q\xi_r > 1$, we expect $S(q) \rightarrow 1/q^{5/3}$ since we explore the chains inside the blobs.

Some possible situations are represented on Figure 3, differing mainly by their behavior at the crossover regions. Since $(3 - \tau)/\nu$ is close to 5/3, a single scaling form should appear in some cases in a rather wide range of $\boldsymbol{q}$ vector amplitude. The closer one is to the blob percolation threshold, the larger is this power law regime.

In conclusion, it seems that a gel prepared by random cross-linking of long chains will exhibit large-scale fractal heterogeneities, when swollen at equilibrium, even when the reaction has been stopped far beyond the gel point.[19] This results from a natural fluctuation of the cross-linking density, always occurring in the reaction bath. The simplest verification of the self-similar nature of the concentration fluctuations, over a wide range of distance scales,

Macromolecules **1988**, *21*, 2649–2651 **2649**

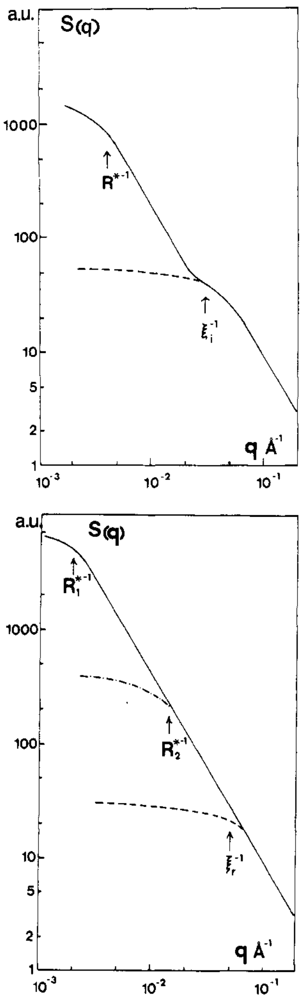


Figure 3. Schematic representations of possible scattered intensities by overswollen networks. (a) Nonnegligible contribution of the scattering by the interstitial medium at $q \simeq 1/\xi_i$ (ξ_i = screening length of the interstitial medium); (- - -) scattering by the interstitial medium alone. (b) Negligible contribution of the scattering by the intersitial regime at $q \simeq 1/\xi_i$; (- - -) scattering by the reaction bath; (—) scattering by very large frozen blob clusters, $P_b^1 \simeq P_c$, R_1^* = typical size of the clusters; (-·-) scattering by smaller frozen blob clusters, $P_b^2 < P_c$, $R_2^* < R_1^*$. The slope in this regime is $(3 - \tau)/\nu \simeq 1.6$.

could be provided by scattering experiments.

Acknowledgment. We are particularly indebted to M. Daoud for illuminating discussions on the vulcanization problem. We gratefully acknowledge helpful and interesting discussions with H. Benoît, F. Boué, M. Buzier, S. J. Candau, E. Pezron, and F. Schosseler.

References and Notes

(1) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969**, *6*, 1.
(2) Silberberg, A. Proceedings of the Network Group Meeting, 1986 (in press, 1988, and references therein).
(3) Stein, R. S. *J. Polym. Sci., Part B* **1969**, *7*, 657.
(4) Wun, K. L.; Prins, W. *J. Polym. Sci.* **1974**, *12*, 533.
(5) Candau, S. J., et al. *J. Chem. Phys.* **1979**, *17*, 83.
(6) Candau, S. J.; Bastide, J.; Delsanti, M. *Adv. Polym. Sci.* **1982**, *44*, 27.
(7) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(8) Collette, C.; Lafuma, F.; Audebert, R.; Leibler, L. In *Biological and Synthetic Networks*; Elsevier: Amsterdam, 1988, in press.
(9) See, for example: Stauffer, D. *Phys. Rep.* **1979**, *54*, 1. Daoud, M. In *Kinetics of Non-Homogeneous Processes*; Freeman, G. R., Ed.; Wiley: New York, 1987.
(10) Daoud, M. *J. Phys. Lett.* **1979**, *40*, L 201.
(11) Flory, D. J. *Proc. R. Soc. London, Ser. A* **1976**, *351*, 1966.
(12) Bastide, J.; Candau, S.; Picot, C. *J. Macromol. Phys.* **1981**, *B19*, 13.
(13) Leibler, L.; Schosseler, F. *Phys. Rev. Lett.* **1985**, *55*, 810.
(14) Mandelbrot, B. *Fractals: Form, Chance and Dimensions*; Freeman: San Francisco, 1977.
(15) Daoud, M.; Family, F.; Jannink, G. *J. Phys. Lett.* **1984**, *45*, L 199.
(16) Isaacson, J.; Lubensky, T. C. *J. Phys. Lett.* **1980**, *41*, L 469.
(17) Bouchaud, E.; Delsanti, M.; Adam, M.; Daoud, M.; Durand, D. *J. Phys.* **1986**, *47*, 1273.
(18) Schosseler, F.; Leibler, L., unpublished results.
(19) See also: Bastide, J.; Boué, F. *Physica* **1986**, *140A*, 251, references therein.

Jacques Bastide*
Institut Charles Sadron (CRM-EAHP)
6, rue Boussingault, 67083 Strasbourg-Cedex
France and Laboratoire Léon Brillouin, CEN Saclay
91191 Gif-sur-Yvette, France

Ludwik Leibler*
Laboratoire de Physico-chimie Macromoléculaire
Université Pierre et Marie Curie, ESPCI
10, rue Vauquelin, 75231 Paris Cedex 05, France

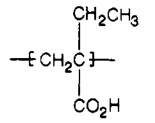
Received April 15, 1988

---

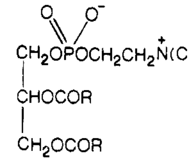
pH-Dependent Vesicle-to-Micelle Transition in an Aqueous Mixture of Dipalmitoylphosphatidylcholine and a Hydrophobic Polyelectrolyte

The capacity to respond to chemical and physical stimuli is an essential characteristic of biological membranes. Intercellular communication and recognition, response to the binding of drugs and hormones, photoreception, and many other critical cellular functions are in fact *membrane* processes in biology and are subject to control as a result of the responsive nature of the bilayer membrane.

We[1] and others[2] have demonstrated several means of preparing *synthetic* bilayer membranes that respond to signals in an analogous fashion. Our approach exploits conformational transitions in membrane-associated polyelectrolyte chains to modulate bilayer structure and permeability. In particular, we have found that addition of the hydrophobic polyelectrolyte, poly(2-ethylacrylic acid) (PEAA, **1**), to aqueous dispersions of natural or synthetic phosphatidylcholines (**2**), renders the lipid membrane exceedingly sensitive to pH.[1a–d] pH sensitivity arises from the cooperative collapse of the polyelectrolyte chain from an expanded, hydrophilic state in basic solutions to a globular, hydrophobic coil upon acidification.[1d,3] Collapse of the chain is accompanied by rapid and quantitative release of vesicle contents,[16] and the fact that release occurs near physiological pH makes this a process of some potential interest in biology and medicine. We present herein evidence that the release of vesicle contents is a result of membrane rupture caused by a reorganization of the surfactant aggregate from vesicular to mixed micellar form.



1



2a, R = $C_{15}H_{31}$

Hydration of dipalmitoylphosphatidylcholine (DPPC, **2a**) at a concentration of 50 μg/mL in 50 mM phosphate

0024-9297/88/2221-2649$01.50/0 © 1988 American Chemical Society