

cal-point phenomena generally (see Fisher and Scesney¹⁷), the true effect is allowed for¹⁴ by the appropriate rescaling, i.e., replacing γ by γ/γ_c in comparing experiments with plots like b, Figure 1, to an excellent approximation. The recent Faraday discussion on gels did reveal a more general lack of awareness, especially of the Scanlan-Case EANC concept. I propose to review the subject at the forthcoming IUPAC microsymposium on cross-linking and networks in Prague.¹⁸

References and Notes

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Comments on "Rubber Elasticity. Flaws in the Theory of Networks"

In the accompanying communication¹ Gordon levels two criticisms at our recent work "Elastically Ineffective Cross-links in Rubbers."² His first comment is that we have treated chain ends with concepts first employed by Flory,³ but no longer considered to be the most applicable approach. Scanlan⁴ and Case⁵ have presented a superior point of view on the elastic activity of cross-links, which Gordon suggests we use. Actually, at the time we first received this comment from Gordon we were about to submit a paper in which, among other things, just such a change had been made, and this work is now published.⁶ Chain ends are not central to the counting of elastically ineffective cross-links, except near the gel point. Hence, the modifications of the numerical results we published earlier² are slight. We agree, however, that if the free-end correction is to be made at all, it should be made with the theory of Scanlan and Case.

In section b of his communication Gordon claims that in Gordon, Ward, and Whitney (GWW)⁷ the correct theory of loop formation in rubbers has been presented. We do not agree that this is the case. (Most of Gordon's work is specific to network formation by condensation reactions of polyfunctional groups, but we are willing to assume that somehow this can be related to rubber vulcanization.)

Our major reservation about GWW is the complete disregard, by fiat, of any correlation between pairs of units which are part of the gel. This includes the case where units

are separated by only a few links, a case that we know dominates the loop formation problem. It is not hard to see that this omission of correlation results in no loop formation. However, we do not accept the hypothesis; nor do we regard GWW's four-parameter fit to condensation rates as proof of the approximation as it applies to loop formation. Furthermore, we do not believe that James and Guth⁸ felt that such a hypothesis was to be made. While it is true that they pursue its consequence in one section (from which GWW quote), they also consider other, indeed strong, correlation schemes. The major thrust of James and Guth's argument is that the elasticity formula obtained is not overly sensitive to the correlation assumed.

GWW do consider certain loops, viz., those formed in the sol. These are not directly equivalent to any of our elastically ineffective loops. As the functionalities along sol loops join the gel such loops may, in fact probably will, become elastically effective in the sense of the topological theories of rubbers.⁹ (By the topological theories we mean those approaches which are based on the number of effective chains in the network, and are independent of the way the cross-links were formed.) Of course, if one adheres strictly to the 1947 James and Guth⁸ ideas, it is the condition of a bond at the moment of formation that counts (but in James and Guth⁸ all network cross-links, including loops, contribute to the elastic modulus). We do not wish to comment on this disagreement here, but feel free to carry out calculations which are of interest to adherents to the topological school.

We think that some of the kinetic equations of GWW could be adapted to the calculation of elastically ineffective looping (as we define it) by allowing for gel loop formation and by statistically monitoring the subsequent connectivity of those loops to the network. This is not a program we intend to implement at this time.

References and Notes

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Motion of Nitroxide Spin Labels Covalently Attached to Synthetic Polymers

The use of nitroxide spin labels to study motion, environment, conformation, etc., in biological systems is extensive.^{1,2} The type of problems involving synthetic polymer systems which can be usefully explored by this technique is not so well established. A few studies on motion in dilute polymer solutions have appeared,³⁻¹⁰ as well as studies on motion in more concentrated solutions^{9,11,12} and also in the pure polymer.^{6,9,12-16} In dilute solution spin labels attached to random coil polymers typically undergo rapid motion ($\tau_R \approx 10^{-10}$ sec) which can be analyzed using theory for motionally narrowed spectra.¹⁷ In solid polymers the motion of the spin label may be several orders of magnitude