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M. A. Sharat^{ab}; J. E. Mark^a

^a Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, OH, USA ^b United Arab Emirates University, Al Ain, United Arab Emirates

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ELASTOMERS WITH POLYSULFIDIC CROSS LINKS VIEWED AS BIMODAL NETWORKS

M. A. Sharaf* and J. E. Mark

Department of Chemistry and the Polymer Research Center,
The University of Cincinnati, Cincinnati, OH 45221 USA

*United Arab Emirates University, Al Ain, United Arab Emirates

ABSTRACT

Elastomers cured with sulfur frequently have improved mechanical properties when the curing conditions are chosen so as to give cross links that consist of chains of sulfur atoms. If such polysulfidic cross links themselves act as elastomeric network chains, then a bimodal network is produced, albeit inadvertently. Interpretation of its properties requires, accordingly, changes in the description of the network structure, most importantly the replacement of one tetrafunctional cross link by two trifunctional ones separated by a new network chain. Illustrative calculations can be used to elucidate the deformation of such networks in terms of the molecular models much used to characterize simpler, unimodal elastomers. More detailed calculations give results in good agreement with experiment.

INTRODUCTION

There are now a variety of ways of covalently cross linking polymer chains into an elastomeric network (1-3). In the case of unsaturated polymers, such as natural rubber and polybutadiene, sulfur cures immediately come to mind. Historically, they ushered in the entire era of reversibly deformable commercial elastomers and are still of great industrial importance (2,4). They also provide an excellent opportunity for investigating the effect of the nature of the cross link on the elastic properties of the network structure it produces. Specifically, sulfur atoms themselves tend to form chains (1,5) and this tendency can be manipulated by proper choice of additives to the curing reaction (6,7). In this way either monosulfidic or polysulfidic cross links can be produced.

The appropriate reactions have in fact been carried out, on natural rubber and styrene-butadiene rubber (7). In both cases, the networks having polysulfidic cross links were found to have larger values of the elongation modulus, tensile strength, and maximum extensibility (7). Since natural rubber has a very strong tendency to undergo strain-induced crystallization and styrene-butadiene rubber has little or none (8), the marked difference in crystallizability would seem to be irrelevant. This, then, puts the focus of the attention on the nature of the polysulfidic cross links, in particular their lengths.

*Permanent Address. Cairo University - Beni-Suef, Beni-Suef, Egypt.

Of greatest importance is the fact that these sulfur chains, if sufficiently long, would be "elastically effective", i.e., would contribute to the modulus by increasing their end-to-end distances and decreasing their entropies in response to an imposed stress. Such a network would have a *bimodal* distribution of network chain lengths, albeit inadvertently. This is intriguing since bimodal networks are known frequently to have superior mechanical properties (3), such as those cited above. The largest improvements obtained have been observed when the shorter chains have only about a half-dozen skeletal bonds (3,9), and the polysulfidic cross links could certainly be of this length (1).

The present investigation explores this idea of viewing polysulfidically cross-linked elastomers as bimodal networks. Issues to be considered are (i) the total number of elastically effective chains, (ii) the functionality of the cross links that join them, (iii) the extent to which the deformation is non-affine, and (iv) the effects of these parameters on the Flory-Erman elastic equation of state (3,10-13) used to predict values of the elongation modulus. Calculations are carried out both to illustrate the expected changes and to provide more detailed results for comparisons with experiment.

STRUCTURAL CONSIDERATIONS

Cross Links That Are Elastically Ineffective as Chains

Monosulfidic cross links shown schematically by



are clearly tetrafunctional. Since they have essentially negligible length, they are elastically ineffective as network chains. For a network of this type with ν chains, the reduced stress or modulus in elongation defined by (3,14)

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})] \tag{1}$$

is (3, 10-13)

$$[f^*] = A_\phi \nu kT \tag{2}$$

where f is the equilibrium value of the force, A^* the original cross-sectional area, $\alpha = L/L_i$ the relative length of the sample or its elongation, ν the number of network chains per unit volume, k the Boltzmann constant, and T the absolute temperature. The structure factor A_ϕ is unity for an affine deformation and

$$A_\phi = 1 - 2/\phi \tag{3}$$

for the very non-affine deformation exhibited by a phantom network, where ϕ is the cross-link functionality (3, 10-13). As shown in the above sketch, $\phi = 4$ for the monosulfidically cross-linked networks.

If the polysulfidic cross links were elastically ineffective, ϕ would still be 4 but the number density ν and the modulus $[f^*]$ would be decreased because of the additional volume taken up by these non-contributing chains. The experimental observation (7) that the modulus increases contradicts this, indicating that the polysulfidic chains must be elastically effective at least to some extent.

Cross Links That Are Elastically Effective as Chains

If the polysulfidic cross links are elastically effective as network chains, as shown by the sketch



then the number of new chains is equal to the number μ of such cross links, which is $\nu/2$. Thus ν increases by the factor 1.5, and ϕ decreases from 4 to 3. In the case of an affine network, the modulus would also increase by 1.5, since A_ϕ is a constant at unity. For a phantom network, however, the modulus should be essentially unchanged since the increase in ν would be offset by the decrease (1.5^{-1}) in A_ϕ from $1/2$ to $1/3$.

The possible changes occurring upon network deformation are shown schematically in Figure 1. Part (a) shows a polysulfidically cross-linked network in the undeformed state, with the cross links possibly acting as the short chains in a bimodal network arbitrarily shown with darker lines. Part (b) shows how, in elongation, very long chains might act as though they were tetrafunctionally cross linked by the short chains while the short chains might act as though they were trifunctionally cross linked. That is, stretching the short polysulfidic chains close to their limits of extensibility could make the cross links look tetrafunctional to the very long polymer chains, but still trifunctional to the polysulfidic chains. This might also occur if the polymer chains are very much longer than the polysulfidic chains. In either case, there would then be a bimodal distribution of cross-link functionality ($\phi = 3$ and 4), as well as of network chain length. The modulus in the phantom limit would then be

$$[f^*] = [f^*]_{\text{long}} + [f^*]_{\text{short}} = (1/2)\nu kT + (1/3)(\nu/2)kT = (2/3)\nu kT \quad (4)$$

with the effective values of A_ϕ and $[f^*]$ thus increasing by a factor of $4/3$, from $1/2$ to $2/3$.

The situation could be very different at high degrees of cross linking. In this case, illustrated in part (c) of Figure 1, the lengths of the long chains may become smaller to the extent that all of the network chains appear to be trifunctionally cross linked. The phantom modulus is then predicted to be

$$[f^*] = (1/3)\nu kT + (1/3)(\nu/2)kT = (1/2)\nu kT \quad (5)$$

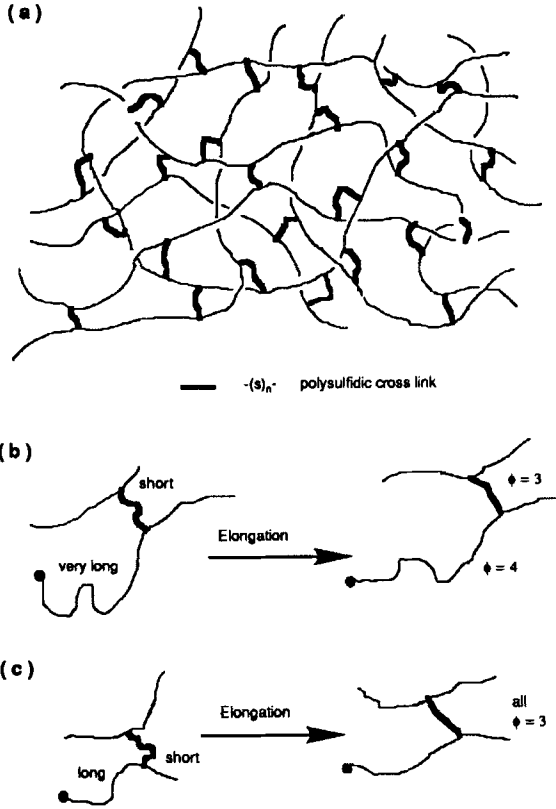


Fig. 1 Sketches showing (a) a network having polysulfidic cross links that can act as short chains in a bimodal network. The other sketches show the effect of elongation on such a short chain attached either (a) to a very long chain, of sufficient length to appear to be tetrafunctionally cross linked while the short chains appear to be trifunctionally cross linked, or (b) to a long chain decreased in length to the point where all chains appear to be trifunctionally cross linked.

This means that the increase in modulus from the increased number of chains is offset by the decrease in functionality, and the result is the same as that obtained by treating the network as a simple unimodal network with functionality four.

Some of these ideas regarding cross-link functionality in bimodal networks and their possible changes with M_c are considered more quantitatively elsewhere (15).

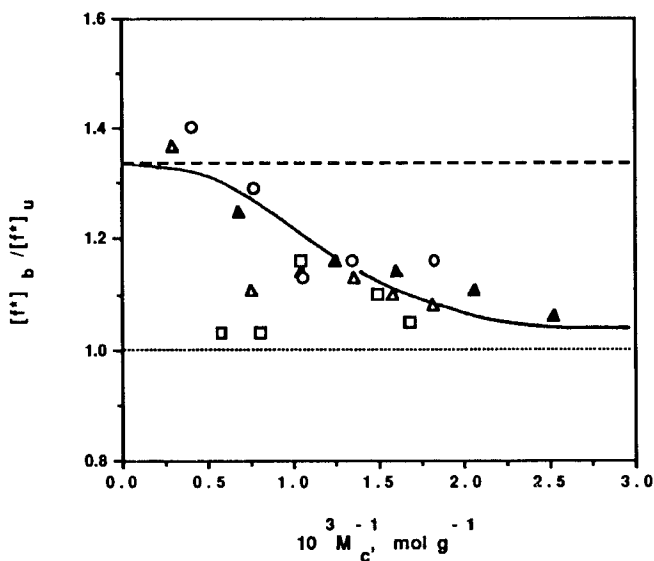


Fig. 2 Values of the ratio of the phantom modulus calculated on the assumption of a bimodal (b) and unimodal (u) distributions, as described in the text, shown as a function of the inverse molecular weight between cross links. The points correspond to NR-DPG (Δ), NR-CBS (\blacktriangle), SBR-DPG (\square), and SBR-CBS (O).

COMPARISONS BETWEEN THEORY AND EXPERIMENT

To evaluate the experimental data it is necessary to make the reasonable assumption that the modifications of the curing scheme used to increase the lengths of the sulfur cross links (6,7) did not also change other structural features of the network. It is then possible to use the swelling equilibrium results presented (7) to estimate factors by which the modulus has changed by making the sulfur cross links chainlike.

As mentioned above, there are relevant results (7) for both natural rubber (NR) and styrene-butadiene rubber (SBR). In some cases, the curing system involved diphenylguanidine (DPG) and in others N-cyclohexylbenzo-thiazole-2-sulphenamide (CBS). In all cases, the conditions were such as to give predominantly polysulfidic cross links.

The property of primary interest is the ratio $[f^*]_b/[f^*]_u$ of the value of the phantom modulus calculated on the assumption that these networks have a bimodal distribution of cross-link functionality, as described above, to the value calculated on the assumption that they are unimodal. The results are shown in Figure 2 as a function of degree of cross

linking, as measured by the reciprocal of the molecular weight M_C between cross links. This ratio is seen to have a value very close to unity at high degrees of cross linking (low values of M_C), as expected. It increases with increase in M_C , approaching the expected value of $4/3$ in the limit of large M_C . This could be due to the effectively bimodal distribution of values of ϕ , as described above. Alternatively, it could be due to the deformation becoming more nearly affine because of the increased network chain interpenetration at large M_C (3,10,11). The relative importance of the two effects could be gauged by studying networks having values of ϕ different from those studied here. This would avoid the possibility of having the change in A_ϕ exactly offset the change in v .

In any case, interpretation of the experimental results on polysulfidically cross-linked elastomers in terms of a bimodal distribution of network chain lengths does seem justified.

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