

Outlook

The future development of time-resolved CIDNP may go in the direction all optical spectroscopy has gone by improving the time resolution. Improvement is possible by using higher field spectrometers and more powerful amplifiers. But the ultimate limit is given by the period of the rf frequency which is 2 ns for the highest field commercial spectrometer to date. By coming close to this limit we will be able to measure the kinetics of the geminate processes including the rates of individual nuclear spin states. Another possible direction has been pointed out by Blümlich,²⁵ who suggested combining the advantages of stochastic resonance, low rf and laser power, with time-resolved CIDNP. No attempts have as yet been made to realize that experiment. All time-resolved CIDNP reported so

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far has been on protons. Other nuclei may be investigated in the future. The achievable time resolution is proportional to the gyromagnetic ratio and will accordingly be less for nuclei other than protons.

It is clear that the temporal resolution of CIDNP will never come close to the frontier of optical spectroscopy. However the information obtained by the two methods is highly complementary. The superior information content of high-resolution NMR spectra make it easy to assign kinetics to specific products even if there is a complicated mixture of them. Self-exchange reactions cannot be studied at all with optical methods. Most importantly the detailed spin dynamics being revealed by CIDNP remains obscured in optical measurements.

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Molecular Aspects of Rubberlike Elasticity

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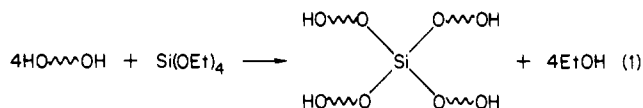
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The elasticity associated with rubberlike materials is very different from that exhibited by atomic or low molecular weight substances such as metals, crystals, and glasses.¹⁻³ In particular, the extensibility of "elastomers" is much higher, frequently amounting to well over 1000%. Most strikingly, such high deformations are generally completely recoverable. The way this recoverability is achieved, however, is the main source of the problems encountered in characterizing rubberlike materials and in developing useful structure-property relationships.^{3,4}

Specifically, elastomers consist of polymer chains and the extraordinarily large numbers of spatial arrangements such molecules can exhibit is the origin of their very high extensibility.¹⁻³ Achieving recoverability requires preventing the chains from irreversibly sliding by one another, and this is accomplished by joining different chains with "cross-links", as is illustrated in Figure 1.³ Relatively few are required, with a typical degree of cross-linking involving only one skeletal atom out of approximately 200. The techniques generally used to introduce cross-links are peroxide thermolysis, high-energy irradiation, and sulfur addition to skeletal or side-chain unsaturation.¹ All are statistical processes, and the number of cross-links thus introduced and their placements along the chains are uncontrolled and essentially unknown. Furthermore, their introduction into the material makes it intractable in that it is no longer soluble in any solvent. The numerous standard characterization techniques based on measurements on isolated chains in solution¹ are therefore categorically

inapplicable. Thus, the very process of forming the required network structure thwarts its characterization. It is the lack of reliable structural information that is the problem in obtaining structure-property relationships in the area of rubberlike elasticity.

Now, however, it is possible to prepare "model" elastomeric networks,⁴⁻¹⁵ which are materials prepared in a way that provides independent information on their structures. An important example is reaction 1 in which



OH --- OH represents a hydroxyl-terminated chain of poly(dimethylsiloxane) (PDMS) [$-\text{Si}(\text{CH}_3)_2\text{O}-$].¹¹ In this approach, some solution characterization technique such as gel permeation chromatography is first used to obtain the number-average molecular weight M_n of the uncross-linked chains and the distribution about this average. Then carrying out the above reaction so as to

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A biographical sketch of the author was published earlier, in *Acc. Chem. Res.* 1974, 7, 218, and 1979, 12, 49. He is spending the 1985-1986 academic year at the IBM Research Laboratory in San Jose, CA.

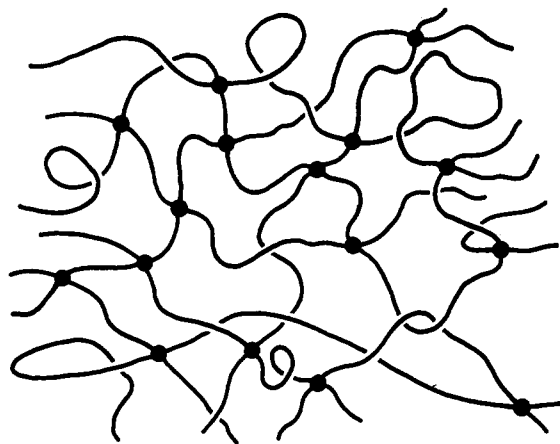
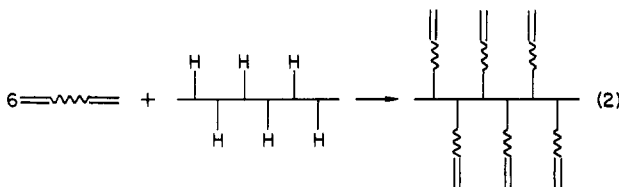
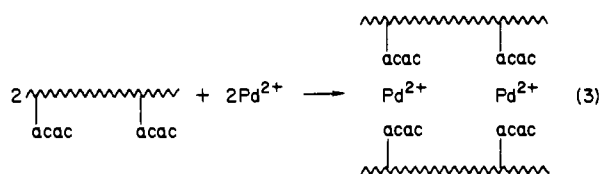


Figure 1. A typical tetrafunctional elastomeric network, with the filled circles representing the cross-links.

exhaustively react all the hydroxyl groups yields a tetrafunctional network in which the very important molecular weight M_c between cross-links is M_n . Also, the distribution of M_c is the same as that of M_n , and the functionality ϕ of a cross-link (the number of chains attached to it) is simply the functionality of the end-linking agent. Network functionalities other than four can be obtained by using vinyl-terminated chains with a multifunctional silane.¹² For example, reaction 2, can



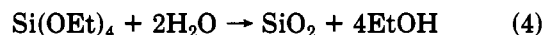
be used to form a hexafunctional PDMS network. These and similar reactions, on side groups as well as chain ends, have now been used to prepare model networks from a variety of polymers including polyisobutylene,¹³ *cis*-1,4-polybutadiene,¹⁴ polyoxides (end linked into polyurethanes with triisocyanates),⁶ and polymers containing acetylacetonate (acac) side groups chelation cross-linked with metal atoms (eq 3).¹⁵ The



use of such materials of known structure in the elucidation of molecular aspects of rubberlike elasticity is the main theme of the present review.

A second area has a similar purpose, but with regard to much more complex elastomeric materials. In most applications, elastomers are filled with particulate substances of high surface area in order to improve their strength and other mechanical properties.^{16,17} Such reinforcing fillers have invariably been introduced by blending them into the polymer prior to its being cross-linked. Obtaining uniform dispersions is exceedingly difficult, particularly since the fillers are generally highly agglomerated, the polymer is invariably of very high viscosity, and premature gelation frequently occurs

because of polymer adsorption onto the filler particles.¹⁸ For this reason, techniques have now been developed for generating filler particles in situ, for example, by the catalyzed hydrolysis (eq 4) of tetraethyl orthosilicate



(TEOS).^{10,18-21} In this way it has been possible to obtain model filled systems in which the particles formed are quite uniform in size and are essentially unagglomerated. These materials of controlled and known filler characteristics thus provide a very complex but important analogue to the unfilled model elastomers of known network structure.

Testing of Molecular Theories

All of the molecular theories^{1,2,22-25} predict the reduced stress or modulus [f^*] of an elastomeric material to be proportional to the number ν of network chains (i.e., chains extending from one cross-link to the next). It should thus also be directly proportional to the cross-link density and inversely proportional to the average molecular weight M_c of these chains.^{1,26} The proportionality factor is predicted to be a constant for affine deformations, in which the cross-links move linearly with the macroscopic dimensions of the sample. It is also predicted to be a constant, albeit generally considerably smaller, for "phantom" networks, in which the chains can transect one another and the cross-links can fluctuate freely.²²⁻²⁵ Because of the fluctuations, the deformation of a phantom network is very nonaffine. Furthermore, it is the directional character of the fluctuations in the deformed state that diminishes the elongation experienced by the chains and thus the modulus.^{22-25,27} The closeness with which a real network approaches the affine limit depends on the firmness with which the cross-links are embedded within the network structure by chain-cross-link entangling. Since elongating a network stretches out its constituent chains, the entangling and degree to affineness decrease, with a corresponding decrease in modulus. This has been observed in a wide variety of experimental investigations.^{2,7,28}

The entangling around the cross-links increases as the network functionality ϕ increases, and theory thus predicts that increase in ϕ should increase [f^*].²²⁻²⁵ It also predicts that [f^*] should change less with elongation α since the more chains emanating from a cross-link, the less pronounced its fluctuations. Experimental studies on model networks covering a range in ϕ have confirmed both of these expectations.^{7,12}

Knowledge of M_c permits direct estimate of the modulus. There is generally good agreement between theory and experiment,^{5-7,14,15} which suggests that inter-chain entanglements such as the one shown in the

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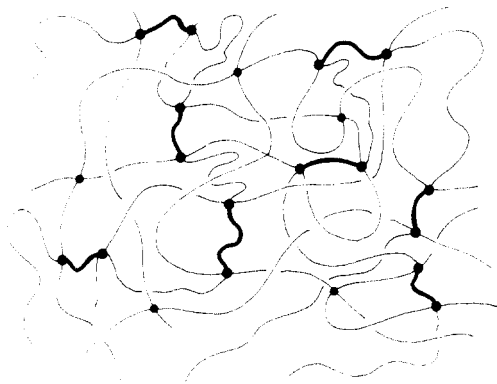


Figure 2. A network having a bimodal distribution of network chain lengths.⁴ The very short polymer chains are arbitrarily represented by heavy lines and the relatively long chains by thinner lines.

lower right-hand corner of Figure 1 do not contribute significantly at elastic equilibrium. There are disagreements²⁹⁻³¹ in this area, however, and this issue has not yet been resolved to everyone's satisfaction.

Bimodal Networks

End linking a mixture of very short and relatively long chains gives a bimodal network, as is shown schematically in Figure 2.⁴ The first application of such networks was in the testing of the "weakest link" theory, in which it is assumed that rupture of an elastomer is initiated by the shortest network chains (because of their very limited extensibility).^{3,4} Bimodal networks containing a relatively small but significant number of very short chains, however, did not show any decreases in ultimate properties. The strain is apparently reapportioned (nonaffinely) within the network so as to ignore as long as possible the difficultly deformable short chains. It is thus the (implicit) assumption of an affine deformation that is the error in the weakest link concept.

An important bonus is obtained if very large numbers (~95 mol %) of short chains are incorporated in a bimodal network. Specifically, the networks are found to have both high ultimate strength and high extensibility, which means they are unusually tough.⁷⁻¹⁰ Apparently the short chains give high values of the modulus and ultimate strength because of their very limited extensibility, and the long chains somehow delay the growth of the rupture nuclei required for catastrophic failure of the sample.

It is also possible to prepare bimodal networks which are spatially as well as compositionally heterogeneous, as is illustrated in Figure 3.⁴ This is done by pre-reacting the short chains to form heavily cross-linked clusters which are then joined to the long chains in the second step of the process.³² Such networks could serve as models for elastomers cured with peroxides which are not totally miscible with the elastomeric matrix.

Non-Gaussian Theory

Since it was concluded that the increases in modulus and ultimate strength are due to limited chain exten-

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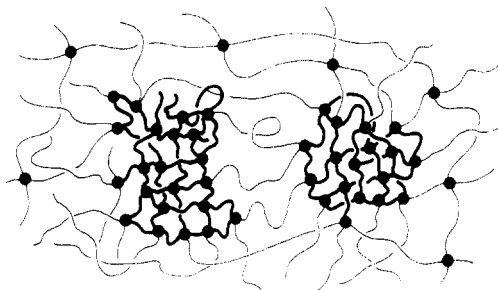


Figure 3. A bimodal network which is spatially as well as compositionally heterogeneous with respect to chain length.⁴

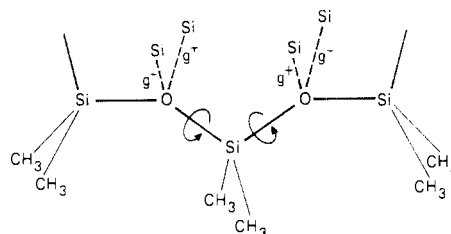


Figure 4. The poly(dimethylsiloxane) chain, illustrating how typical conformations have different energies and frequencies of occurrence because of the different interactions they engender (after ref 33).

sibility, it became important to try to interpret these results in terms of a non-Gaussian theory of rubberlike elasticity. The novel approach taken utilized the wealth of information which rotational isomeric state (RIS) theory³³ provides on the spatial configurations of chain molecules. Comparisons between theoretical and experimental values of properties dependent on the spatial configurations of the chains give the energies for the permitted conformations, some of which are shown for the PDMS chain in Figure 4. Specifically, Monte Carlo calculations based on the RIS approximation were used to simulate spatial configurations, and thus distribution functions for the end-to-end separation r of the chains.³⁴ These distribution functions are used in place of the Gaussian function in the standard three-chain network model² in the affine limit to give a molecular theory of rubberlike elasticity which is unique to the particular polymer of interest.³⁵⁻³⁷ Most important, it is applicable to the regions of very large deformation where limited chain extensibility gives rise to elastomeric properties significantly different from those in the Gaussian limit. One important result is an improved understanding of the increases in modulus observed in short-chain networks at very high elongations.

Interpenetrating Networks

If two types of chains differ in their end groups, it is possible simultaneously to end link them into two networks that interpenetrate^{38,39} one another. Such a network could, for example, be made by reacting hy-

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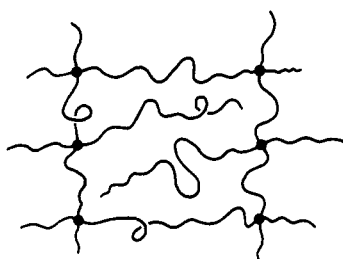
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Figure 5. A bimodal interpenetrating network, in which the short-chain cross-links are represented by filled circles and the long-chain ones by open circles.

(a) Excess difunctional chains



(b) Monofunctional chains

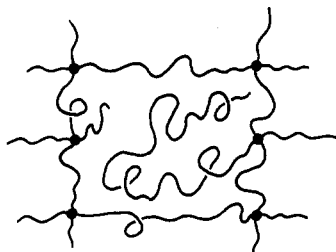


Figure 6. Two methods for preparing networks having dangling chains of known length, present in known concentration.

droxyl-terminated PDMS chains with tetraethylorthosilicate while reacting vinyl-terminated PDMS chains with a multifunctional silane.⁴⁰ A bimodal network of this type is shown in Figure 5. Interpenetrating networks in general can be very unusual with regard to both equilibrium and dynamic mechanical properties.^{38,39}

Dangling-Chain Networks

Mechanical properties can be adversely affected by network irregularities such as dangling ends (chains attached to the network at only one end),^{41,42} and it is therefore very important to characterize their effects. Model networks containing dangling chains of known lengths and concentrations can be prepared in several ways, two of which are shown in Figure 6. If, during

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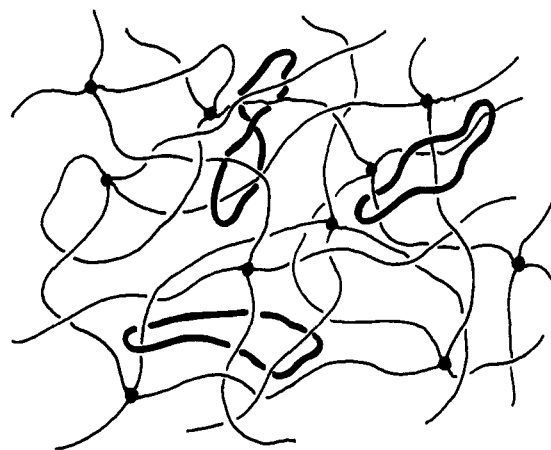


Figure 7. Cyclics trapped by linear chains which passed through them prior to being end linked into a tetrafunctional network.⁴⁵

the end-linking process, more difunctional chains are present than is required to react with all the functional groups on the end-linking molecules, then the known excess number of chain ends is equal to the number of dangling ends. In this method, the dangling chains must of course have the same average length as the elastically effective chains. The second method overcomes this limitation by the inclusion of monofunctional chains of any desired length. In this way the dangling chains can be either much shorter or much longer than the elastically effective chains. A mixture of dangling chain lengths can also be introduced as is, in fact, shown in the lower portion of Figure 6.

Studies^{41,42} of the mechanical properties of such networks show that dangling-chain irregularities do significantly decrease ultimate properties, as should be expected.

Sorption and Extraction of Diluents

End-linking functionally terminated chains in the presence of chains with inert ends yields networks through which the unattached chains "reptate".^{43,44} Networks of this type have been used to determine the efficiency with which unattached chains can be extracted from an elastomer, as a function of their lengths and the degree of cross-linking of the network. The efficiency was found to decrease with increase in molecular weight of the diluent and with increase in degree of cross-linking,^{43,44} as expected. It was also found to be more difficult to extract diluent present during the cross-linking than to extract the same diluents absorbed into the networks after cross-linking. Such comparisons can provide valuable information on the arrangements and transport of chains within complex network structures.

It was also found that if relatively large PDMS cyclics are present when linear PDMS chains are end linked, approximately one quarter are permanently trapped by one or more network chains threading through them, as is shown in Figure 7.⁴⁵ It should be possible to correlate the fraction of a cyclic trapped with its effective "hole" size, as estimated from Monte Carlo sim-

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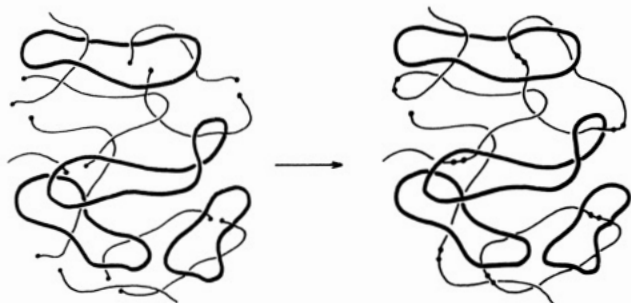


Figure 8. Preparation of a "chain mail" network, not having any cross-links at all. Linear chains passing through the cyclics are difunctionally end linked to form series of interpenetrating cyclics, which would be a gel.⁴⁵

ulations³⁵ of its spatial configurations.

It may also be possible to use this technique to form a network having no cross-links whatsoever. Mixing linear chains with large amounts of cyclic and then difunctionally end linking them could give sufficient cyclic interlinking to yield an "Olympic" or "chain mail" network, as is illustrated in Figure 8. Such materials could have highly unusual equilibrium and dynamic mechanical properties. Attempts to prepare some are in progress.

Elastomers Filled in Situ

There are three techniques by which silica can be precipitated into an elastomeric material. First, an already-cured network, for example, prepared from PDMS, may be swollen in TEOS and the TEOS hydrolyzed in situ.^{18,19,46} Alternatively, hydroxyl-terminated PDMS may be mixed with TEOS, which then serves simultaneously to tetrafunctionally end link the PDMS into a network structure and to act as a source of SiO₂ upon hydrolysis.^{20,46} Finally, TEOS mixed with vinyl-terminated PDMS can be hydrolyzed to give a SiO₂-filled polymer capable of subsequent end linking by means of a multifunctional silane.^{21,46}

Stress-strain isotherms obtained on in situ filled PDMS show the presence and efficacy of the filler; this is demonstrated by the large increases in modulus, with marked upturns at the higher elongations.^{18,20,21} There are also large increases in the energy E_r of rupture, which is the standard measure of elastomer toughness. Increase in percent filler generally decreases the maximum extensibility α_r , but increases the ultimate strength. The latter effect predominates and E_r increases accordingly. In some cases, extremely large levels of reinforcement are obtained. Such networks behave nearly as thermosets, with some brittleness (small α_r), but with extraordinarily large values of the modulus [f^*].⁴⁰

Transmission electron microscopy⁴⁷ and light scattering and neutron scattering measurements⁴⁸ are being used to study the filler particles. As illustration, an electron micrograph for a PDMS elastomer in which TEOS has been hydrolyzed is shown in Figure 9.⁴⁷ The

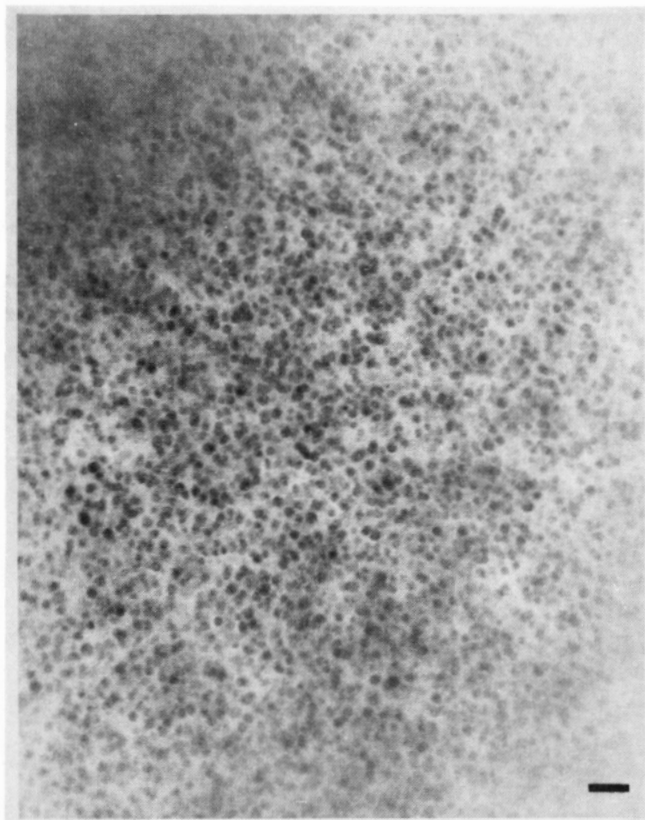


Figure 9. Transmission electron micrograph for a poly(dimethylsiloxane) network containing 34.4 wt % SiO₂ filler introduced by the in situ hydrolysis of tetraethyl orthosilicate.⁴⁷ The length of the bar in the figure corresponds to 1000 Å.

existence of filler particles in the network, originally hypothesized on the basis of mechanical properties,¹⁸ is clearly confirmed. The particles have average diameters of approximately 250 Å, which is in the range of particle sizes of fillers typically introduced into polymers in the usual blending techniques.^{16,17} The distribution of sizes is relatively narrow, with most values of the diameter falling in the range 200–300 Å.⁴⁷

Most strikingly, there is virtually none of the aggregation of particles essentially invariably present in the usual types of filled elastomers. These materials should therefore be extremely useful in characterizing the effects of aggregation and could be of considerable practical importance as well.⁴⁷

Concluding Remarks

Preparing and studying "model" elastomers having controlled and known network structures is seen to provide a great deal of valuable molecular information on rubberlike elasticity. Additional advantages include the preparation of unusually tough elastomers and materials of possibly unique equilibrium and dynamic mechanical properties. Analogous techniques for obtaining model filled systems could well be equally rewarding.

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