

# Elastomeric Networks with Bimodal Chain-Length Distributions

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Received April 4, 1994

Rubberlike elasticity implies extremely high deformability with essentially complete recoverability, and there are several molecular features a material must have in order to exhibit it.<sup>1-3</sup> It must first consist of long-chain molecules, which have sufficient flexibility and mobility to switch from compact spatial arrangements to more extended ones in response to an imposed strain. These polymer chains, however, must also be interconnected with cross-links into a network structure, in order to achieve the elastic recoverability. This cross-linking procedure also brings about serious disadvantages, however, most notably the intractability of the resulting network structures. For example, they are insoluble in all solvents, thus requiring forfeiting all of the otherwise-useful characterization techniques which rely on putting a material into solution. As a result, there are serious problems in getting the structural information required in establishing structure-property relationships.

The earliest attempts to obtain structural information focused on the cross-link density since the modulus of the elastomer was known to be directly related to it. The methods relied largely on trying to monitor the cross-linking reaction, for example by measuring the amount of sulfur used up in the classic vulcanization process of diene elastomers such as natural rubber. Results obtained were not very reliable, primarily because of side reactions and lack of information on the number of sulfur atoms in a cross-link. More reliable information became available with the advent of more carefully controlled ways to make network structures. The most important of these involves using chains that are reactive only at their ends, for example by having terminal hydroxyl groups.<sup>3-21</sup> The groups can then be end linked using a multifunctional reactant, such as a trisocyanate, to give the desired network structure. Since the only reaction is occurring at the chain ends, the structure is known in that the molecular weight  $M_c$  between cross-links is simply the molecular weight  $M_n$  of the starting chains, and the functionality  $\phi$  of the junctions is the functionality of the multifunctional end-linking reagent. More relevant with regard to the present application is the fact that the *distribution* of network chain lengths is the same as that of the chains prior

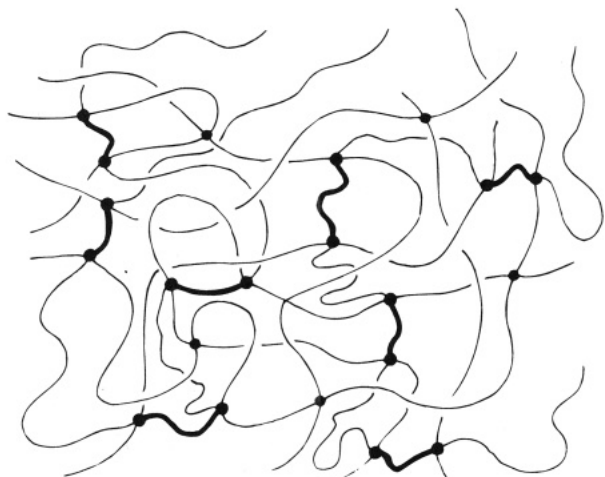
to their end linking, and this, of course, is easy to determine by gel permeation chromatography.<sup>18,22-25</sup>

In fact, the effect of network chain-length distribution<sup>1,2</sup> is one aspect of rubberlike elasticity that has not been studied very much until recently, because of two primary reasons. On the experimental side, the cross-linking techniques traditionally used to prepare the network structures required for rubberlike elasticity have been random, uncontrolled processes, as has already been mentioned.<sup>1-3</sup> On the theoretical side, it has turned out to be convenient, and even necessary, to assume a distribution of chain lengths that is not only unimodal but monodisperse!<sup>2,3</sup>

There are a number of reasons for developing techniques for determining or, even better, controlling network chain-length distributions. One is to check the "weakest-link" theory<sup>26</sup> for elastomer rupture, which states that a typical elastomeric network consists of chains with a broad distribution of lengths, and that the shortest of these chains are the "culprits" in causing rupture. This is attributed to the very limited extensibility associated with their shortness,

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**Figure 1.** Sketch of a bimodal network in which the short chains are arbitrarily drawn in heavier than the long chains, which are more typically associated with rubberlike elasticity.<sup>30</sup> The dots represent the cross-links. Reprinted with permission from ref 30. Copyright 1979 Huthig & Wepf Verlag, Basel.

which is thought to cause them to break at relatively small deformations and then to act as rupture nuclei. Another reason is to determine whether control of chain-length distribution can be used to maximize the ultimate properties of an elastomer. Of particular interest in this regard are networks having bimodal distributions of network chain lengths, more specifically consisting of large numbers of very short chains intimately end linked with the much longer chains normally associated with rubberlike elasticity.

### Materials and Synthetic Techniques

Most such "bimodal networks" synthesized to date have been prepared from poly(dimethylsiloxane) (PDMS). One reason for this choice is the fact that the polymer is readily available with either hydroxyl or vinyl end groups, and the reactions these groups participate in are relatively free of complicating side reactions.<sup>27</sup> Also, the polymer is noncrystallizable under most conditions because of its very low melting point ( $\sim -40$  °C).<sup>28</sup> These bimodal networks are in fact generally studied at sufficiently high temperatures ( $\sim 25$  °C) to easily avoid contributions from strain-induced crystallization, when desired. The end-linking reactions have generally involved hydroxyl-terminated chains, which are readily obtained from the usual ring-opening polymerizations of the cyclic trimer or tetramer.<sup>29</sup> The ends of the chains are reacted with the alkoxy groups in a multifunctional organosilicate, such as tetraethyl orthosilicate, as described elsewhere.<sup>27</sup> In the application of interest here, a mixture of two polymers is being cross-linked, one component consisting of very short chains and the other, of much longer chains. The resulting network is shown schematically in Figure 1.<sup>30</sup>

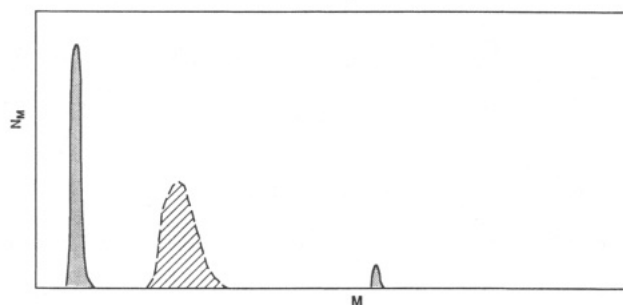
The distribution of network chain lengths in a bimodal elastomer can be extremely unusual, and much different from the usual unimodal distribution

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**Figure 2.** Network chain-length distributions, in which  $N_M$  is the number of chains in an infinitesimal interval around the specified value of the molecular weight  $M$ .<sup>21</sup> The dot-filled areas represent a bimodal distribution, and the diagonal-filled area a unimodal distribution.

obtained in less-controlled methods of cross-linking. Figure 2 shows a schematic distribution, for the important example in which there is simultaneously a large number percent of short chains and a large weight percent of long chains. The major difference is the large amounts of both very short chains and very long chains in the bimodal network, which contrasts sharply with the small amounts of such chains in a typical unimodal distribution. Obviously, such peculiar distributions can be obtained only by carefully-controlled techniques such as the end-linking reactions being described. One of their uses is to test the molecular description of elastomer rupture, as described in the following section.

### Testing of the Weakest-Link Theory

The weakest-link theory<sup>26</sup> was tested by preparing end-linked networks containing increasing amounts of short chains, on the order of 10–20 mol %.<sup>3,30</sup> Remarkably, there were no significant decreases in ultimate properties with these increases in the numbers of short chains, in striking disagreement with the suggested mode of elastomer failure. Apparently, the strain is continually being reapportioned during the deformation, in such a way that the much more easily deformed long chains bear most of the burden of the deformation. Thus, the short chains do not contribute significantly until just prior to rupture. This is consistent with Nature preferring the low-energy route, unless overruled by entropy increases. The flaw in the weakest-link theory is thus the implicit assumption that all parts of the network deform in exactly the same way, i.e., "affinely", whereas the deformation is markedly nonaffine.<sup>3</sup>

The weakest-link issue having been resolved, it became of interest to see what would happen in the case of bimodal networks having such overwhelming numbers of short chains that they cannot be ignored in the network's response. In fact, there turns out to be an exciting bonus if one does put a very large number of short chains into the bimodal network. Specifically, there is a synergistic effect leading to mechanical properties that are better than those obtainable from the usual unimodal distribution! These results are the focus of most of the remaining sections of this Account.

### Elongation Results

**Characterization of Upturns in the Modulus.** This section focuses on the discussion of unfilled

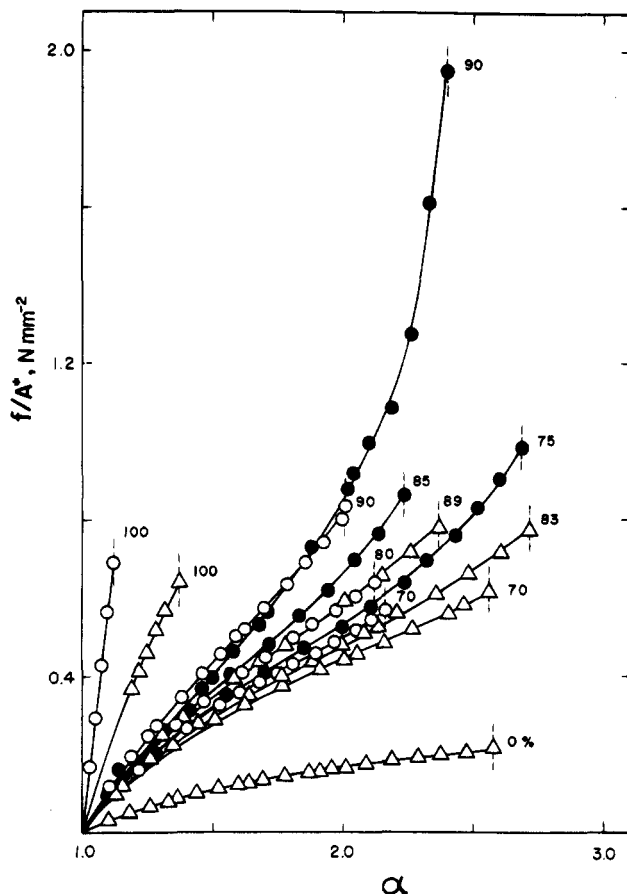
elastomers at high elongations, with an emphasis on ultimate properties (namely, the ultimate strength and maximum extensibility).

Some elastomeric networks show a large and rather abrupt increase in modulus at high elongations.<sup>1,2,4,18,31,32</sup> This increase is very important since it corresponds to a significant toughening of the elastomer. Its molecular origin, however, had been the source of some controversy.<sup>33</sup> It had been widely attributed to the "limited extensibility" of the network chains, i.e., to an inadequacy in the Gaussian distribution function, specifically that it does not assign a zero probability to a configuration unless its end-to-end separation  $r$  is infinite. However, the increase in modulus had generally been observed only in networks which could undergo strain-induced crystallization, which could account for the increase in modulus, primarily because the crystallites thus formed would act as additional cross-links in the network.

This type of reinforcement from strain-induced crystallization is typified by results reported on the ultimate properties of *cis*-1,4-polybutadiene networks.<sup>3,18,34</sup> The higher the temperature, the lower the extent of crystallization, and this was found to diminish the ultimate properties. In fact, the upturns diminish and eventually disappear upon an increase in temperature.<sup>34,35</sup> The effects of an increase in swelling were found to parallel those for an increase in temperature, as was expected, since diluent also suppresses network crystallization. This indicates that the reinforcing upturns in modulus were due to strain-induced crystallization rather than limited-chain extensibility.

Attempts to observe upturns from non-Gaussian effects in noncrystallizable networks prepared by the usual random cross-linking techniques were not successful,<sup>32</sup> presumably because such networks were incapable of the large deformations required to bring about the effects of limited-chain extensibility. Such upturns have been observed,<sup>34-36</sup> however, by the use of some of the end-linked, noncrystallizable model PDMS networks. These networks have high extensibilities, presumably because of their very low incidence of dangling-chain network irregularities. They have particularly high extensibilities when they are prepared from a mixture of very short chains (around a few hundred  $\text{g mol}^{-1}$ ) with relatively long chains (around 18 000  $\text{g mol}^{-1}$ ), giving a bimodal distribution of network chain lengths. Apparently the very short chains in such networks are important because of their limited extensibilities, and the relatively long chains because of their ability to retard the rupture process.

As will be documented below, stress-strain measurements on such bimodal PDMS networks exhibited upturns in modulus which were much less pronounced than those in crystallizable polymer networks such as natural rubber or *cis*-1,4-polybutadiene. Furthermore, they are independent of temperature and are not diminished by incorporation of solvent. These characteristics are what is to be expected in the case of



**Figure 3.** Typical plots of nominal stress against elongation for (unswollen) bimodal PDMS networks consisting of relatively long chains ( $M_c = 18\,500 \text{ g mol}^{-1}$ ) and very short chains [1100 ( $\Delta$ ), 660 ( $\circ$ ), and 220 ( $\bullet$ )]. Each curve is labeled with the mole percent of short chains the network contains, and the area under each curve represents the rupture energy (a measure of the "toughness" of the elastomer). Reprinted with permission from ref 38. Copyright 1981 John Wiley & Sons, Inc.

limited chain extensibility.<sup>33,37</sup> The results on this system will therefore be extremely useful for the reliable evaluation of the various non-Gaussian theories of rubberlike elasticity.

These stress-strain isotherms in elongation on bimodal PDMS networks were generally obtained in the vicinity of 25 °C, a temperature sufficiently high to suppress strain-induced crystallization. The results thus determined were of considerable interest since they indicated that the bimodal nature of the distribution greatly improved the ultimate properties of the elastomer.<sup>3,7,17,18</sup> This is illustrated in Figure 3,<sup>38</sup> in which data on PDMS networks are plotted in such a way that the area under a stress-strain isotherm corresponds to the energy required to rupture the network. If the network consists entirely of the short-chain component, then it is brittle (which means that the maximum extensibility is very small). If the network consists of only the long-chain component, the ultimate strength is very low. In neither case is the material a tough elastomer. As can readily be seen from the figure, the bimodal networks are much improved elastomers in that they can have a high

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ultimate strength without the usual diminished maximum extensibility. This corresponds to high values of the energy required for rupture, which makes them unusually tough elastomers, even in the unfilled state.<sup>24</sup>

Since this internally-generated improvement in properties is of considerable practical and fundamental interest, a number of studies on PDMS elastomers were carried out to determine its dependence on the molecular weights of the short chains,<sup>39</sup> the proportions of short and long chains,<sup>39,40</sup> and cross-link functionality.<sup>23,40,41</sup> These results can be used to optimize the improvements in properties obtained.

Measurements of the mechanical and optical properties of these networks as a function of temperature and degree of swelling were used to test further the conclusion cited above that crystallization or other intermolecular organization was not the origin of the improved properties.<sup>3,17,18,24,42-44</sup> As already mentioned, stress-strain measurements on such bimodal PDMS networks exhibited upturns in modulus which were much less pronounced than those in crystallizable polymer networks such as natural rubber or *cis*-1,4-polybutadiene. In another experiment, temperature was found to have little effect on the Mooney-Rivlin isotherms for bimodal PDMS networks, as would be expected in the case of limited chain extensibility.<sup>24</sup> Stress-temperature ("thermoelastic") and birefringence-temperature measurements showed no discontinuities or discernible changes of slope,<sup>24</sup> and swelling can even make the upturns in modulus more pronounced.<sup>33,37</sup> Apparently, the enhanced upturns are due to the chains being stretched out in the solvent dilation process, prior to their being stretched further in the elongation experiments. In contrast, as has already been mentioned, the upturns in crystallizable polymer networks disappear upon sufficient swelling.<sup>35,36</sup>

The above findings argue against the presence of any crystallization or other type of intermolecular ordering.<sup>33,37</sup> and the upturns thus seem to be intramolecular in origin. In addition, infrared and Raman spectroscopy indicate that bond-angle distortion is of relatively minor importance, at least in PDMS networks.<sup>45</sup> The observed increases in modulus and ultimate strength therefore have to be due to the limited extensibility of the very short network chains. In qualitative terms, increases in their end-to-end distances greatly decrease the number of their spatial configurations, their entropies plummet, and the elastic force rises correspondingly. It is possible to characterize this non-Gaussian limited extensibility more quantitatively in a number of ways, some of which are described below.

Quantitative characterization of this limited chain extensibility requires, of course, a non-Gaussian distribution function<sup>2</sup> for the end-to-end separation  $r$  of the short network chains. Ideal for this case is the

distribution obtained by Fixman and Alben<sup>46</sup> and recommended particularly for very short chains. It was found to give a much better approximation to the highly reliable Monte Carlo simulated results than does the Gaussian limit, particularly in the most important region of very high extension.<sup>47</sup> The parameters in the Fixman-Alben distribution function can be adjusted to give very good approximations to the Monte Carlo distributions for the short PDMS chains. These Fixman-Alben distributions can then be combined with the constrained-junction theory and reasonable values of the constraint parameter  $\kappa$ <sup>47</sup> to calculate stress-strain isotherms in elongation for bimodal PDMS networks. The observed upturns in the reduced stress [ $f^*$ ] at high values of the elongation  $\alpha$  were well reproduced by the calculated results.<sup>47</sup> Other non-Gaussian distribution functions have also been successfully used for this purpose,<sup>48,49</sup> as can be the van der Waals theory of rubberlike elasticity.<sup>50,51</sup>

Another approach, Monte Carlo simulations, utilizes the wealth of information that rotational isomeric state theory provides on the spatial configurations of chain molecules. In brief, Monte Carlo calculations based on the rotational isomeric state approximation are used to simulate spatial configurations and thus distribution functions for the end-to-end separations of the chains.<sup>3,52</sup> These distribution functions are then used in place of the Gaussian function in the standard three-chain model<sup>2</sup> in the affine limit to give the desired non-Gaussian theory of rubberlike elasticity. Stress-strain isotherms calculated in this way are strikingly similar to the experimental isotherms obtained for the bimodal networks.<sup>3,52</sup> The overall theoretical interpretations are thus quite satisfactory and would encourage other applications of these distributions, for example to segmental orientation in networks containing very short chains. Such segmental orientation is of critical importance, for example, with regard to strain-induced crystallization.

**Strain-Induced Crystallization.** PDMS networks were found to be unsuitable for characterizing the effects of bimodality on strain-induced crystallization, because of their very low crystallization temperatures. The polymer chosen instead for these end-linked bimodal networks was poly(ethylene oxide), which has a relatively high melting point ( $\sim 65^\circ\text{C}$ )<sup>28</sup> and thus readily undergoes strain-induced crystallization.<sup>53</sup> The aspect of relevance here is the use of these networks to elucidate the dependence of strain-induced crystallization on network chain length distribution. A decrease in temperature was found to increase the extent to which the values of the ultimate strength of the bimodal networks exceed those of the unimodal ones.<sup>53</sup> This suggests that bimodality facilitates strain-induced crystallization, possibly through increased orientation of the very long chains, into crystallization nuclei. Similar conclusions have been

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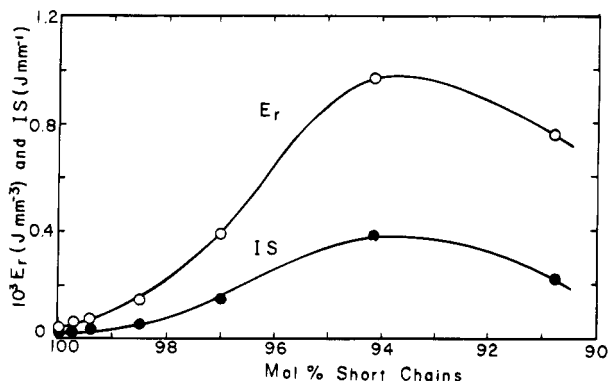
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**Figure 4.** The energy required for rupture and the impact strength (as measured by the falling-dart test) shown as a function of composition for bimodal PDMS networks in the vicinity of room temperature.<sup>55</sup> The molecular weights of the chains were 220 and 18 500 g mol<sup>-1</sup>.

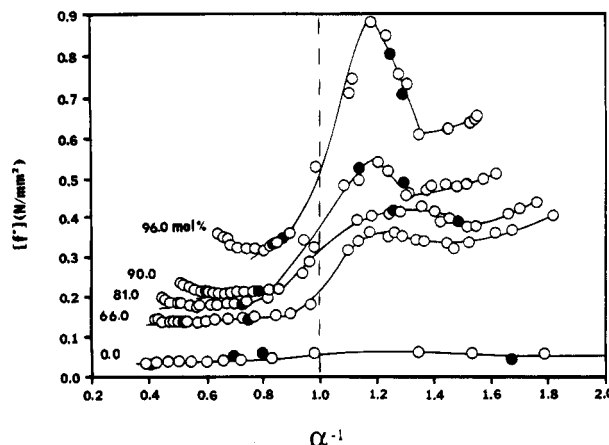
reached in studies of elongated bimodal networks of poly(tetrahydrofuran).<sup>54</sup>

**Thermosets.** In practical terms, the above results demonstrate that short chains of limited extensibility may be bonded into a long-chain network to improve its toughness. It is also possible to achieve the converse effect. Thus, bonding a small number of relatively long elastomeric chains into a short-chain PDMS thermoset greatly improves both its energy of rupture and its impact resistance, as is illustrated in Figure 4.<sup>55</sup> Approximately 95 mol % short chains gives the maximum effect for the molecular weights involved. Lower concentrations give smaller improvements than can otherwise be achieved, and higher concentrations will gradually convert the composite from a relatively hard material to one that is more rubberlike.

### Results in Other Mechanical Deformations

**Biaxial Extension.** There are numerous other deformations of interest, including compression, biaxial extension, shear, and torsion. In the case of compression ( $\alpha < 1$ ), the equation of state is the same as that for elongation ( $\alpha > 1$ ). Some of these deformations are considerably more difficult to study than simple elongation and, unfortunately, have therefore not been as extensively investigated. Equi-biaxial extension is equivalent to compression and can more conveniently be imposed by inflation of sheets of the elastomer.<sup>2</sup> Results of this type obtained by inflating sheets of unimodal and bimodal networks of PDMS are illustrated in Figure 5.<sup>56,57</sup> Upturns in the modulus are seen to occur at high biaxial extensions, as expected. Also of interest, however, are the pronounced maxima preceding the upturns. This represents a challenging feature to be explained by molecular theories addressed to bimodal elastomeric networks in general.

**Shear.** Elastomeric networks can be studied in pure shear by stretching a sheet of the material, having a large ratio of width to length, in the direction perpendicular to the width. Results of such shear



**Figure 5.** Representative stress-strain isotherms for unimodal and bimodal PDMS networks in uniaxial extension (left side of figure) and biaxial extension (right side).<sup>56</sup> Each curve is labeled with the mol % of the short chains present in the network. The open circles represent data points measured using increasing deformations, and filled circles represent data obtained out of sequence to test for reversibility.

measurements on some unimodal and bimodal networks of PDMS have been reported.<sup>58</sup> The bimodal PDMS networks showed large upturns in the pure-shear modulus at high strains which were similar to those reported for elongation and biaxial extension.

**Torsion.** Very little work has been done on elastomers in torsion (twisting a cylindrical sample around its long axis).<sup>2,59,60</sup> The same types of bimodal PDMS networks showed rather different behavior in torsion<sup>61</sup> in that no unambiguous upturns in modulus were observed at large deformations. It has not yet been established whether this is due to the inability, to date, of reaching sufficiently large torsions, or whether this is some inherent difference in this type of deformation.

**Tear.** Tear tests have been carried out on bimodal PDMS elastomers,<sup>13,15</sup> using the standard "trouser-leg" method. Tear energies were found to be considerably increased by the use of a bimodal distribution, with documentation of the effects of compositional changes and changes in the ratio of molecular weights of the short and long chains. As is shown in Figure 6, the increase in tear energy did not seem to depend on tear rate.<sup>13</sup> This observation is important in that it suggests that viscoelastic effects are not of paramount importance in explaining the observed improvements.

A subsequent series of tear tests<sup>15</sup> established the dependence of the tearing properties on the composition of the bimodal networks and the lengths of the chains used to prepare them. The maxima in curves showing the dependence of tearing energy on the amount of the short-chain component then identifies the composition giving the greatest increases in tear energy. Also of interest are results showing how the tensile strength depends on the ratio of molecular weights of the two components. There is an increase in strength with a decrease in the molecular weight

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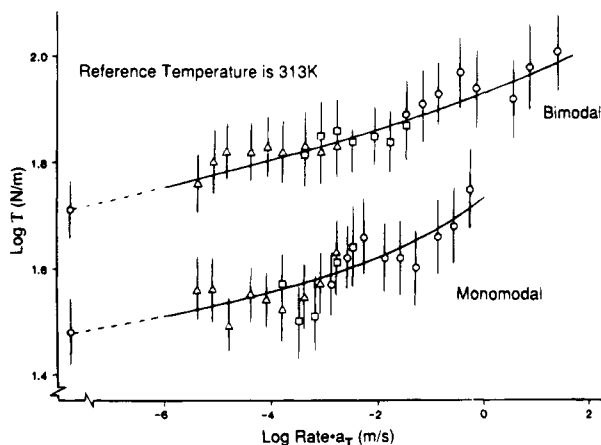
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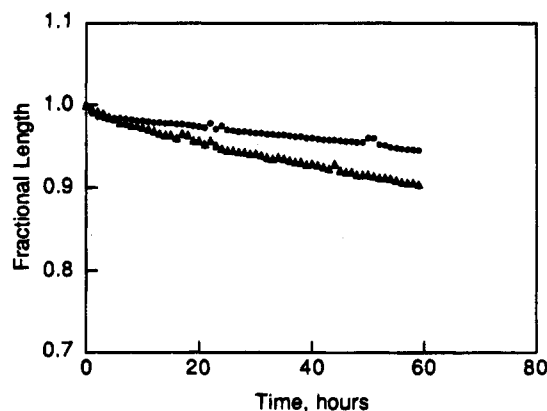
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**Figure 6.** Tearing energy master curves for monomodal (unimodal) and bimodal PDMS networks as a function of the tear rate.<sup>13</sup> Both types of network had an average  $M_c$  of  $6800 \text{ g mol}^{-1}$ , and the bimodal one consisted of 70 mol % chains having  $M_c = 930 \text{ g mol}^{-1}$  combined with chains having  $M_c = 20.5 \times 10^3 \text{ g mol}^{-1}$ .



**Figure 7.** Effect of cyclic compressive stress on unimodal ( $\Delta$ ) and bimodal ( $\bullet$ ) PDMS networks represented as the dependence of fractional length on time.<sup>63</sup>

of the short chains, but this must eventually become a decrease when the chains become too short. It would obviously be important to carry out additional studies to establish the molecular weight at which this occurs.

**Cyclic Deformations.** Some Rheovibron viscoelasticity results have been reported for bimodal PDMS networks.<sup>62</sup> One of the important conclusions reached was that the long chains promoted crystallinity by giving additional mobility to the short network chains.

Some measurements have also been made on permanent set for PDMS networks in compressive cyclic deformations.<sup>63</sup> As can be seen from Figure 7, there appears to be less permanent set or creep in the case of the bimodal elastomers. This is consistent with some early results for polyurethane elastomers,<sup>64</sup> in which cyclic elongation measurements on unimodal and bimodal networks indicated that the bimodal ones survived as much as an order of magnitude more cycles before the occurrence of fatigue failure.

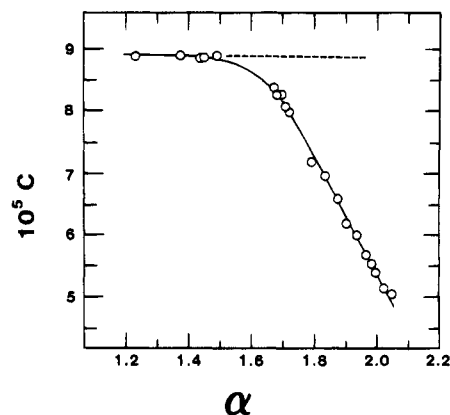
### Nonmechanical Results

**Birefringence.** Birefringence measurements have been shown to be very sensitive to bimodality and have

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**Figure 8.** Strain dependence of the stress-optical coefficient for a bimodal network containing 93.4 mol % short chains ( $880 \text{ g mol}^{-1}$ ), with the rest being considerably longer ( $21.3 \times 10^3 \text{ g mol}^{-1}$ ).<sup>65</sup>

therefore also been used to characterize non-Gaussian effects resulting from it in PDMS bimodal elastomers.<sup>65,66</sup> This is illustrated in Figure 8, which shows the effect of strain on the stress-optical coefficient (defined as the ratio of the birefringence to the stress).<sup>65</sup> There is seen to be a large decrease in this coefficient over a relatively small range in elongation, presumably from the limited extensibility of the short chains in the bimodal structure. It is therefore a sensitive way of characterizing non-Gaussian effects in network deformation.

**Freezing Points of Absorbed Solvents.** This type of experiment is based on the fact that solvent molecules constrained to small volumes form only relatively small crystallites upon crystallization and therefore exhibit lower crystallization temperatures.<sup>67-71</sup> Relevant here is the fact that broad distributions of cavity sizes should give rise to broad distributions of crystallite sizes and crystallite melting points. Some differential scanning calorimetry measurements on solvent molecules constrained in the pores of PDMS elastomers gave evidence for several crystallization temperatures, which could be indicative of an unusual distribution of pore sizes. The effect seemed to be most pronounced for trimodal networks, which are discussed below.

**Related Investigations.** Calorimetric measurements on bimodal poly(ethylene oxide) networks indicated that the short chains seemed to decrease the amount of crystallinity in the unstretched state.<sup>72</sup> This is an intriguing result since, as mentioned above, they increase the extent of crystallization in the stretched state. A similar study on a different polymer, poly(tetrahydrofuran), did not show any decrease, how-

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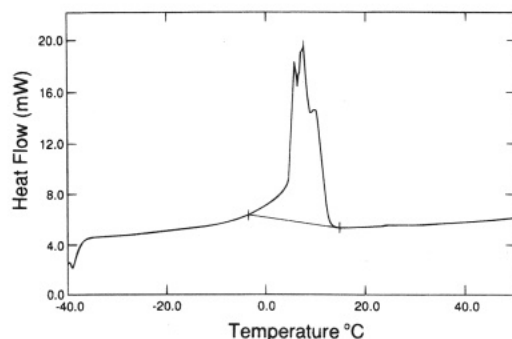
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**Figure 9.** Typical DSC scan for a trimodal PDMS network consisting of 13 mol % chains having a value of  $M_n$  of 417 g mol<sup>-1</sup>, 75 mol % chains having a value of  $M_n$  of 2760 g mol<sup>-1</sup>, and 12 mol % chains having a value of  $M_n$  of  $18.9 \times 10^3$  g mol<sup>-1</sup>.<sup>78</sup> The swelling solvent whose crystallization temperatures were monitored was benzene.

ever.<sup>73</sup> Dynamic light scattering experiments,<sup>74</sup> neutron scattering investigations,<sup>75</sup> and computer simulations<sup>76</sup> have also been used to obtain insight into the dynamics and structure of bimodal elastomers. Swelling equilibrium measurements would, of course, also be of interest.

Some of these related approaches could be very helpful in elucidating precisely how such bimodal networks deform. This is the major unsolved problem in the area, specifically, how the macroscopic deformation is partitioned between the long and short chains, and thus how they "communicate" with each other.

### Trimodal Networks

There has not been much done on the mechanical properties of networks with trimodal distributions of network chain lengths. There seems to be little additional improvement in mechanical properties from adding another set of short chains to the long-chain component,<sup>77</sup> but there are now so many variables with regard to molecular weight and composition that there may well be some combinations that would give further substantial improvements.

As mentioned above, there have been differential scanning calorimetry measurements on solvent molecules constrained in the pores of PDMS elastomers. Some results on networks having a trimodal distribution of network chain lengths are presented in Figure 9.<sup>78</sup> The several crystallization temperatures observed for the benzene in this network could possibly be used to obtain additional information on the pore sizes present.

### Networks of Very High Modality

The interpretation of the attractive mechanical properties of bimodal networks has been in terms of a "delegation of responsibilities", with the short chains serving in one role and the long chains in another. If this picture is true, then it would be interesting to prepare and study networks having extraordinarily

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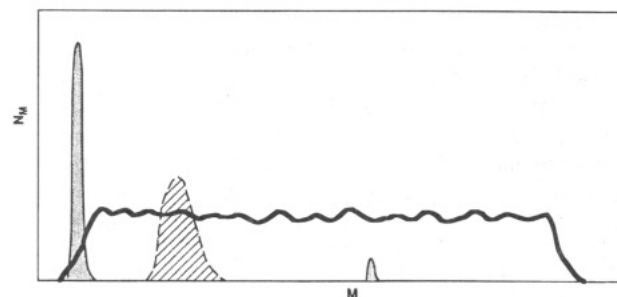
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**Figure 10.** Network chain-length distributions, in which  $N_M$  is the number of chains in an infinitesimal interval around the specified value of the molecular weight  $M$ . A typical unimodal distribution is shown by the area filled with diagonal slashes, a bimodal distribution by the dotted areas, and an extremely broad distribution (obtained by combining separately-prepared polymers) by the unfilled area.

broad molecular weight distributions, in that there would be network chains of all conceivable lengths, available for any conceivable mechanism that would improve properties.<sup>79</sup> Polymer prepared from single polymerizations would not have a broad enough distribution, but the combination of a series of samples of gradually differing average molecular weight could provide the desired broadness. This is illustrated in Figure 10.

### Elastomers That May Have Been Inadvertently Bimodal

Elastomers cured with sulfur frequently have improved mechanical properties when the curing conditions are chosen to give cross-links that consist of chains of sulfur atoms.<sup>80</sup> It has been suggested that if such polysulfidic cross-links can themselves act as elastomeric network chains, then a bimodal network is produced, albeit inadvertently.<sup>81</sup> Calculations conducted to take into account this possible bimodality gave results in good agreement with experiment.<sup>81</sup>

A similar situation may occur in the case of networks end linked using the addition reaction involving vinyl chain ends and hydrogen atoms in an oligomeric poly(methylhydrosiloxane).<sup>82,83</sup> In the case of incomplete reactions, the segments between the reacted silicon atoms on the oligomer may be long enough to act as elastically-effective chains in a bimodal structure. Finally, a bimodal chain-length distribution has also been proposed to explain some unusual properties of polysiloxane networks that have been postcured.<sup>84</sup>

### Other Materials in Which Bimodality Might Be Advantageous

There appear to be other cases where a bimodal distribution of chain length or some other physical property can be advantageous, possibly again through this idea of a delegation of responsibilities.

For example, in the area of thermosets, there seems to be an improvement in mechanical properties when the polymer being cured has a bimodal distribution

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of molecular weights.<sup>85</sup> In this case, the improvements may be due to different morphologies resulting from the fact that the long chains in a bimodal distribution could have considerably lower solubilities than the short chains. Also, it is well-known that the flow characteristics of a polymer during processing<sup>86</sup> can frequently be adjusted by the addition of a small amount of polymer of either very low or very high molecular weight. Another example is in the area of rubber-toughened thermoplastics in which an elastomer is dispersed as domains within the thermoplastic matrix to improve its mechanical properties.<sup>87,88</sup> It has been found that a bimodal distribution of particle sizes gives the largest improvements.<sup>89,90</sup> Perhaps the small particles are most efficient at stopping one type of failure mechanism, and the large particles another type. In a related application, there is the possibility that a mixture of two chemically different particles, such as silica (SiO<sub>2</sub>) and titania (TiO<sub>2</sub>), could have significant advantages in elastomer reinforcement.<sup>91-93</sup>

### Conclusions and Outlook

The very specific end-linking techniques described in this Account can be thought of as a step in the

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application of biomimetic principles<sup>94</sup> for the design of elastomers with improved properties. The techniques used by Nature to produce bioelastomers are, in fact, far more sophisticated than those currently used in the preparation of commercial elastomers. This is well illustrated by the example of the protein elastin produced in mammals for in vivo elastomeric applications.<sup>3</sup> The only cross-linking which occurs along these chains is restricted to lysine repeat units, and these are placed in known numbers and in specified positions in the amino acid sequence. An enzyme, lysyl oxidase, then oxidizes the lysyl side chains and combines them into very stable, aromatic cross-links. This fixes not only the degree of cross-linking but also the network chain-length distribution. These lysine units are also preceded and succeeded along the chain by alanine units, and these are thought to be in rigid  $\alpha$ -helical conformations. This could mean that the potential cross-linking sites are also spatially positioned within the protein matrix, perhaps in a way that minimizes chain-junction entangling. Such careful control of the cross-linking procedure could explain some of the unusually attractive properties of bioelastomers, for example their relatively efficient storage and release of elastic energy.

A better molecular understanding of Nature's ways of preparing bioelastomers and their structure-property relationships could well provide valuable guidance for improving commercially-important materials.

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