Calculations on Trimodal Elastomeric Networks. Effects of Chain Length and Composition on Ultimate Properties

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ABSTRACT: Polymer networks having a bimodal distribution of network chain lengths can be prepared by end-linking two sets of chains having different molecular weights. These unusual elastomers frequently have better mechanical properties than those having a unimodal distribution, which suggests that trimodal distributions could possibly yield further improvements. The theory of bimodal networks based on chains with finite extensibility was therefore extended to trimodal networks. Specifically, networks having various compositions of very long, long, and short chains were characterized with regard to their toughness in elongation. The results showed that a trimodal network prepared by incorporating small numbers of very long chains into a bimodal network of long and short chains could have significantly improved ultimate properties.

I. Introduction

It is possible to prepare elastomeric polymer networks by end-linking functionally terminated chains with a multifunctional end-linking reagent. An important example would be hydroxyl-terminated chains of poly(dimethylsiloxane) (PDMS) [$-Si(CH_3)_2O-$] endlinked with tetraethoxysilane [$Si(OC_2H_5)_4$] in a tin-catalyzed condensation reaction.[1−5] The molecular weight of the network chains (the molecular weight M_c between cross-links) is then simply the molecular weight of the linear precursor chains used in the end-linking process. This permits control of both M_c and the functionality of the cross-links. An additional advantage of preparing a network in this manner is the possibility of reducing the number of dangling-chain imperfections, i.e., chains attached to the network at only one end. Finally, there is the opportunity to control the network chain-length *distribution*, and this is the subject of the present investigation.

Virtually any desired distribution can be obtained by using these specific chemical reactions. The one of greatest practical interest, however, turns out to be the bimodal distribution obtained by end-linking two sets of chains, one unusually short and the other having the much longer lengths generally associated with ruberlike elasticity.[1,5] A comparison between unimodal and bimodal distributions is shown in Figure 1. The upper portion of the figure presents the number distribution and the lower portion the weight distribution. These unusual bimodal elastomers frequently have better mechanical properties than those having a unimodal distribution, in that they simultaneously have large values of the ultimate strength and maximum extensibility, thus giving them remarkable toughness. This has given rise to the hope that *trimodal* distributions could possibly yield further improvements. This is also illustrated in Figure 1, by the conversion of a bimodal distribution into a trimodal upon addition of some unusually long chains to the network structure.

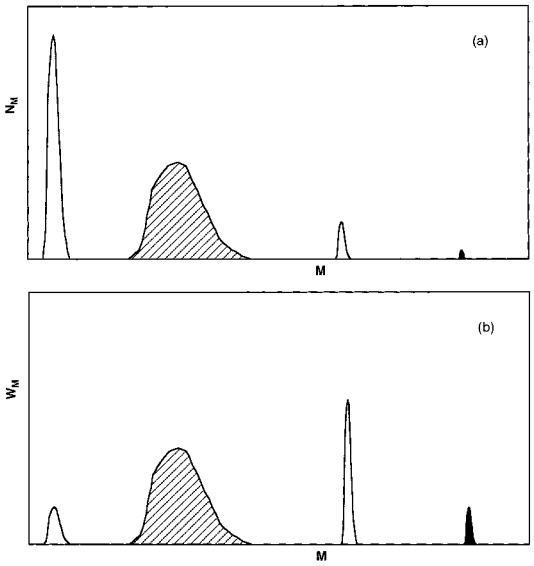

Figure 1. Sketches of network chain-length distributions, in terms of (a) the number N_M of chains having a given molecular weight M and (b) the weights W_M of such chains. The curves with diagonal hatching represent a unimodal distribution, the pairs of dotted ones a bimodal distribution, and the black ones a possible third component for converting a bimodal distribution into a trimodal one.

Although there have been attempts to evaluate the mechanical properties of trimodal elastomers, this has not been done in any organized manner.[6,7] The basic problem is the large number of variables involved, specifically three molecular weights and two independent composition variables (mol fractions); this makes it virtually impossible to do an exhaustive series of relevant experiments. For this reason, the only experi-

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ments of any type that have been carried out have involved arbitrarily chosen molecular weights and compositions.[6−8] Not surprisingly, further improvements were not always obtained and have generally been only modest. For example, converting a bimodal distribution of short and long chains into a trimodal one by introducing an additional set of short chains gave rather discouraging results.[6] Some theoretical studies,[9−17] however, indicate that it should be possible to do calculations to identify those molecular weights and compositions which maximize further improvements in mechanical properties.

The present theoretical study attempts to achieve this goal. Specifically, it extends the previous molecular theory of bimodal networks[12] to the case of trimodal networks, in an attempt to predict the maximum elastic free energy that may be stored before the network chains reach their ultimate extensibilities. This maximum energy, referred to as the "toughness" of the network, is correlated with the ultimate strain, obtained when the macroscopic deformation equates to the maximum allowable deformation at the molecular level. The calculations indeed do show that in some cases the introduction of chains at a third molecular weight into a bimodal elastomeric network may further improve both its maximum extensibility and toughness.

II. Theory and Method

A. The Model and Assumptions. The networks under investigation are perfect networks formed by end-linking. The trimodal networks consist of short (S), long (L), and very long (VL) chains which are assumed to be well dispersed prior to and during the end-linking process. Thus the numbers of S, L, and VL chains in any sufficiently long path are proportional to their number fractions in the network. The end-to-end, series arrangement of chains in such a path leads to the definition of the deformation field for each type of chain as[12]

$$\lambda = \sum_{i=1}^{3} \phi_i \lambda_i \tag{1}$$

where λ_i is the extension ratio of the three types of chains, λ is the macroscopic extension ratio, and ϕ_i is the number fraction of the ith type of chain in the network, with $\phi_1 + \phi_2 + \phi_3 = 1$. The assumption of the relationship given by eq 1 and the formulations of stress based on this relation resulted in satisfactory agreement with experimental results for bimodal networks. An alternative model would be the parallel arrangement of the different-length chains. The extension ratio of each type of chain in this arrangement is defined as

$$\lambda_S = \eta_0 \lambda \qquad \lambda_L = (n_S/n_L)\eta_0 \lambda \qquad \lambda_{VL} = (n_S/n_{VL})\,\eta_0 \lambda \tag{2}$$

for the short, long, and very long chains, respectively. Here, n_S, n_L, and n_{VL} represent the number of repeat units of the three types of chains, and η_0 is the internal parameter which renders the stored elastic free energy of the network a minimum in the undeformed state, i.e., when $\lambda = 1$. Evaluation of η_0 will be discussed in more detail below. It should be noted that the assumption of parallel arrangement of chains emphasizes the contribution of the short chains to the elasticity of the network and therefore underestimates the contributions from the high extensibility of the long chains to enhanced ductility observed in experiments on bimodal networks. It should be noted, however, that the form of the strain function given by eq 1 does not directly imply that the model consists of a series arrangement of chains. The elastic free energy derived below, and the stresses resulting from it, have more general consequences than those of simple series models.

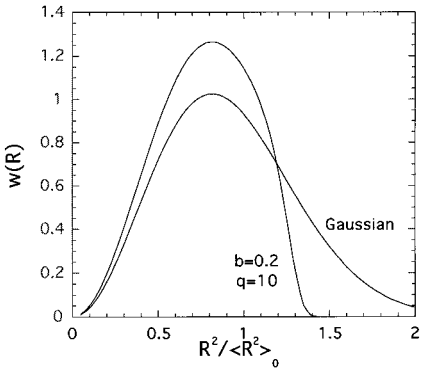

Figure 2. Chain-length distributions $w(R)$, where R is the end-to-end distance of the chain and $<R^2>_0$ its mean-square unperturbed value. One distribution is that for a Gaussian chain (of unlimited extensibility), and the other is the Fixman−Alben result[18] for a chain with limited extensibility, as characterized by the parameters b and q.

B. Distributions. The end-to-end distribution $W(R)$ of a chain is represented by the modified Fixman−Alben expression[12,18]

$$W(R) \propto \exp\left[-\frac{3}{2}\frac{R^2}{<R^2>_0} - \left(\frac{3bR^2}{<R^2>_0}\right)^q\right] \tag{3}$$

where $<R^2>_0$ is the unperturbed mean-square end-to-end distance of the chain, and b and q are parameters that may be adjusted to give a good representation of a chain whose behavior departs from the Gaussian limit. In previous work, the values $b = 0.18$ and $q = 10$ were found to yield reasonable agreement with Monte Carlo results for short model chains.[12]

Figure 2 presents results of calculations based on eq 3 showing the difference between a Gaussian chain and a non-Gaussian chain. The latter can be described as a relatively "stiff chain" in that it does not enjoy the unlimited extensibility of a Gaussian chain. The ordinate represents the normalized radial distribution function, $w(R) = 4\pi R^2$ W(R), of the end-to-end vector, where $W(R)$ is the coordinate form of the distribution. The curve for the Gaussian chain was obtained by setting $b = 0$ in eq 3. The curve for a chain with restricted extensibility was obtained by using $b = 0.2$ and $q = 10$. These parameters are found to satisfactorily approximate the behavior of very short poly(dimethylsiloxane) chains obtained in previous comparisons based on Monte Carlo simulations.[12,19] The unique feature of the non-Gaussian distribution is its abrupt approach to zero at larger values of the end-to-end vector. This results in an upturn of the force-deformation relation of the short chain while the long Gaussian chain exhibits a linear force-extension relation at all levels of strain.

C. Elastic Free Energies. The Helmholtz free energy ΔA_{el} of a deformed trimodal network may be written by extending the treatment for bimodal networks,[12] as

$$\Delta A_{el} = \sum_{i=1}^{3} \frac{\nu_i kT}{2}[I_i + 2(b_i I_i)^{q_i}] \tag{4}$$

where the subscript i stands for the type of the chain, S, L, or VL. The quantity ν_i is the number of ith-type chains per unit volume, I_i is the first strain invariant of the ith type, and b_i and q_i are the coefficients of the modified Fixman−Alben distribution for chains of type i. The first strain invariant of the ith chain in uniaxial deformation is defined as $I_i = \lambda_i^2 + 2/\lambda_i$, where λ_i is the extension ratio experienced by the ith chain. Equation 4 is in a sense a mean-field type of approximation and is not strictly true for non-Gaussian chains. It should be noted that eq 4 is valid for both series and parallel arrangements of the chains. Although eq 4 appears, at first glance, as the simple addition of the elastic free energies of the different length chains, the three terms under the sum-

mation sign, for the series arrangement, are dependent because the extension ratio's λ_i are related by the condition that they should minimize the elastic free energy at all values of the macroscopic extension ratio λ. For given ϕ_i and λ the elastic free energy may be calculated by minimizing eq 4 with respect to any two of the λ_is, the third λ_i being determined by eq 1. Similarly, for the parallel arrangement, the extension ratios for the three types of chains are related through η_0.

D. Deformation Mechanisms. The above procedure of calculating the free energy, however, is valid when the three types of chains are all below their fully stretched lengths. The deformation mechanism in multimodal networks, on the other hand, rests on the assumption that the shorter chains reach their ultimate extensibilities first. With increase of macroscopic deformation, these chains remain at their almost fully stretched lengths, and the remaining chains of larger length continue to extend. Implicit in this assumption, and in the minimization of the elastic free energy, is the effective repartitioning of the deformation among the different elements. For the trimodal networks, the series arrangement suggests that the medium length chains reach their full lengths at the second stage after the short ones have been almost fully stretched, and the network continues elongating by extension of the longest type chains up to their full lengths. Maximum elastic free energy obtains when all three types of chains reach their full lengths.

E. Ultimate Properties. To estimate the ultimate properties such as toughness and extension to break of trimodal networks, an assumption on the maximum extensibility of each type of chain is required. For a model chain of n bonds and equal bond angles, the fully stretched length is $nl\cos(\theta/2)$, l being the bond length and θ the complement of the bond angle. The maximum extension ratio of the ith chain may be expressed as $\lambda_{i,\max} = nl\cos(\theta/2)/\langle r^2\rangle_0^{1/2}$. Substituting $(C_n nl^2)^{1/2}$ for the denominator, where C_n is the characteristic ratio, and representing the number of repeat units of the ith type chain as $M_{i,c}/M_{i,u}$ (where $M_{i,c}$ is the chain molecular weight and $M_{i,u}$ is the molecular weight of the repeat unit of the ith type chain), the expression for the maximum extension of the ith chain is obtained as

$$\lambda_{i,\max} = \left(\frac{\cos(\theta/2)}{M_{i,u}^{1/2} C_n^{1/2}}\right) M_{i,c}^{1/2} \tag{5}$$

Using eq 5 in eq 1 leads to the maximum extensibility of the network

$$\lambda_{\max} = \phi_1\lambda_{1,\max} + \phi_2\lambda_{2,\max} + \phi_3\lambda_{3,\max} \tag{6}$$

The force acting on the sample may be obtained by differentiating the elastic free energy with respect to length. The expression for the force obtained in this manner reads as

$$f^* = \frac{\partial \Delta A_{el}}{V_0 \partial\lambda} = \frac{\nu kT}{V_0}\left[\sum_{i=1}^{3} \phi_i (1 + 2q_i b_i^{q_i} I_i^{q_i - 1}) \frac{\partial I_i}{\partial\lambda}\right] \tag{7}$$

Here, V_0 is the reference volume.[1,5] The derivative of the invariants in eq 7 may be performed by adopting eq 1 for the series and eq 2 for the parallel arrangement.

The calculation of the maximum elastic free energy was made as follows: (1) In the first stage, the elastic free energy was calculated for a given λ by minimizing ΔA_{el} with respect to the extension ratios of the two types of chains. λ was then increased and calculations repeated. The value of λ when the shortest chains reach full extension was recorded. (2) In the second stage, the shortest chains were kept at their full extensions, λ was increased, and the elastic free energy was minimized with respect to λ_i of the longest chains. The value of λ was recorded when the medium length chains reached full extension. (3) In the final stage the medium and short chains were kept at their full extensions and λ was increased. This increase was directly reflected on the extension of the longest chains. The value of ΔA_{el} was calculated directly from eq 4. The ultimate value of the stored elastic free energy was obtained by setting $\lambda = \lambda_{\max}$, $\lambda_1 = \lambda_{1,\max}$, $\lambda_2 = \lambda_{2,\max}$, and $\lambda_3 = \lambda_{3,\max}$. It should be noted that although the partitioning of the strain requires minimization of the elastic free energy, the ultimate value is easily calculable by assuming maximum strain for every chain without the optimization procedure. (4) The composition was varied and the calculations repeated.

Table 1. Parameters *b* and *q* for the Distribution Functions

chain type	molecular weight	*b*	*q*
	set 1: Trimodal Network Consisting of Long, Very Long, and Short Chains		
1	10 000	0.0	...
2	100 000	0.0	...
3	400	0.2	10
	set 2: Trimodal Network Consisting of Long, Medium, and Short Chains		
1	10 000	0.0	...
2	1 000	0.1	5
3	400	0.2	10

The values of the maximum stored energies obtained with the above minimization procedure were then divided by the value of the maximum energy that would be stored in a unimodal network at the same extensibility. Throughout the paper, the notation ΔA_{max}(trimodal)/ ΔA_{max}(unimodal) is used to indicate this ratio and is taken as a measure of the increase in toughness of the trimodal network over the corresponding unimodal network.

The elastic free energy was minimized numerically by the routine AMOEBA, taken from ref 20. The details of the minimization technique are described in this reference.

III. Results of Calculations and Discussion

Several different combinations of the three chain lengths and compositions were studied. Here, we report the most meaningful and representative two cases: The first set consisted of long, very long, and short chains with molecular weights of 10 000, 100 000, and 400, respectively. In this set, the long and the very long chains are assumed to be Gaussian and the shorter one non-Gaussian. In the second set, there were long, medium, and short chains with molecular weights of 10 000, 1000 and 400, respectively. It was observed that these two sets are indicative of a pattern from which optimal selection of molecular weights and compositions may be based in general. Table 1 gives the molecular weights and the parameters of the modified Fixman−Alben distribution for the two sets. The distributions obtained with the parameters reported in the table are in qualitative agreement with previous Monte Carlo distributions of chains of comparable lengths.

Normally, it would be difficult or impossible to end-link chains of molecular weight 100 000, because of the very low number density of the reactive chain ends.[21] This should be feasible in the mixtures described, however, because of the much higher chain-end densities in the case of the shorter-chain components in the mixtures.

Figure 3 shows the change in the stored elastic energy for different compositions of the set L/VL/S as a function of average molecular weight. The lowest curve is obtained when the shortest chains first reach full extension during deformation. The four points on the curve correspond to different compositions, i.e., to networks with 0, 1, 2, and 3 mol % of the VL chains. Larger values of M_c correspond to larger amounts of VL in the network. The amount of L chains is kept fixed at 20%. The leftmost point on the curve corresponds to the bimodal network with 0% VL. Results of calculations show a small decrease in relative toughness with

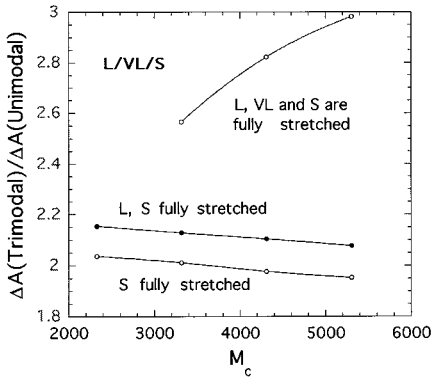

Figure 3. Predicted increases in toughness, as gauged by the ratio of the maximum stored energy for a trimodal network in which all the chains are at full extension, relative to the maximum energy that would be stored in a unimodal network having the same average molecular weight M_c between cross-links, taken to the same extensibility. The designations S, L, and VL refer to results for chains that are short, long, and very long, respectively.

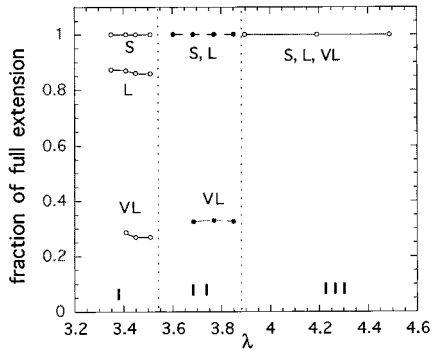

Figure 4. Extent of deformation for each type of chain, represented by the fraction of full extension reached at the specified value of the macroscopic deformation λ.

increasing amount of VL when the short chains are at full extension. This is due to the fact that the VL chains are still very close to the undeformed state, as will be shown in Figure 4. It may be noted that if the VL chains were undeformed they would act as solvent in the system and would lower the stored elastic energy of extension. The middle curve in Figure 3 shows the change in stored elastic energy when both the S and L chains have reached their full extensions. The VL chains are again very close to their undeformed states, as will also be shown in Figure 4. The uppermost curve shows the case when all three types of chains have reached their full extensions, which represents the state of incipient fracture. The toughness values are now much larger than those of the bimodal network that would be obtained with L and S chains alone. More important, toughness increases with increasing amount of VL chains.

The state of deformation of the three types of chains during the deformation process is presented in Figure 4. The ordinate values show the fraction of full extension of each type of chain as a function of macroscopic extension ratio. It consists of three parts marked by I, II, and III. The first part represents the state when the short chains have reached their full extension. The different points are for different compositions as described in Figure 3. Region II represents the state when the S and L chains have reached full extension. Both regions I and II indicate that the VL chains are at 25−30% of their full extensions when the other components

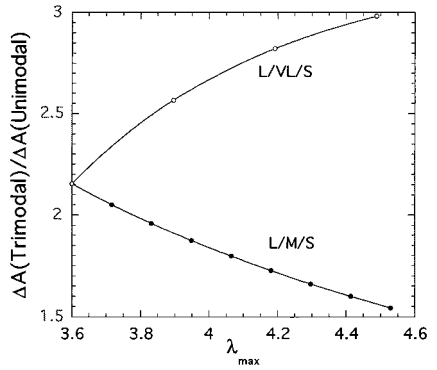

Figure 5. Predicted increases in toughness for the two types of trimodal network described as sets 1 and 2 in Table 1. The results are shown as a function of the extension ratio bringing about full extension of each type of chain at the composition chosen.

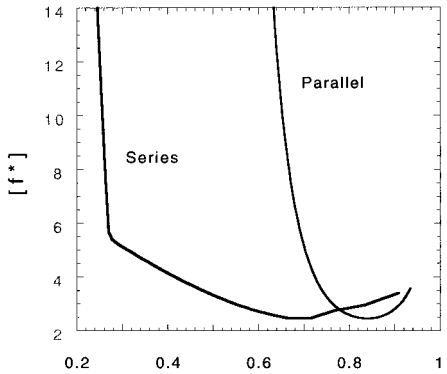

Figure 6. Predicted stress−strain isotherms for a typical L/VL/S network, in which the chains are placed in a series arrangement (heavy line) and a parallel arrangement (thin line).

are at their full extensions. This is important because the network can further be deformed significantly until the VL chains reach their full extensions, as shown in part III of Figure 4.

Calculations were also performed for a second set of trimodal networks with different chain lengths, given as set 2 in Table 1. Here, intermediate length non-Gaussian M chains with $b = 0.1$ and $q = 5$ were incorporated into the bimodal network consisting of L and S chains. Calculations showed that the toughness of the trimodal networks obtained in this manner unfortunately remains below the toughness of the original bimodal network. In Figure 5, the relative toughnesses of the two networks, L/VL/S and L/M/S, are compared as a function of λ_{max}. The different points refer to different amounts of VL chains for the upper curve and of M chains in the lower curve.

In Figure 6, the reduced force $[f^*] \equiv f^*/(\lambda - \lambda^{-2})$ for a typical L/VL/S network is presented as a function of inverse extension ratio, as is typically done in Mooney−Rivlin plots.[1,2,5,22] The composition was 20 mol % L, 2 mol % VL, and 78 mol % S, and the values of f^* were obtained by numerical differentiation of the elastic free energy, which is represented in closed form by eq 7. The ordinate values were normalized by dividing with $\nu kT/V_0$, where ν is the total number of chains. The thick and thin lines are for the series and parallel arrangements of chains, respectively. The series arrangement result exhibits a decrease in $[f^*]$ with extension at low values of λ, followed by an upturn of intermediate slope and then a very steep upturn. The decrease in $[f^*]$ with

increasing deformation takes place in the range where all three chains are below their full extensions. An analysis of the deformations of the three types of chains in this range shows that the VL chains are stretched more than the macroscopic extension, and this difference becomes progressively more with increasing extension. As the VL chains share the burden of stretching more than the other two types, the network exhibits an increased extensibility, resulting in the decrease of the reduced force with extension. The mild upturn in the figure results from the fact that the S chains have reached full extension. Similarly, the very steep upturn results from the fact that the S and L chains have reached full extension, and all of the extension is now due to that of the VL chains. The differential of eq 1, $d\lambda = \phi_3\, d\lambda_3$, where the subscript 3 refers to VL, indicates that for small ϕ_3 a small increase in macroscopic extension leads to significant increase in the extension of the few VL chains, thus leading to their very pronounced deformations. The curve for the parallel arrangement of chains was also obtained for the same data as for the series arrangement. The value of η_0 which minimizes the elastic free energy when $\lambda = 1$ was found to be 1.36. The curve exhibits a sharp upturn when the maximum extensibility of the short chains is approached. This results from the unrealistic features of the parallel-arrangement model according to which the short chains dominate the force relation. This is unrealistic, given the fact that results of numerous experimental and theoretical work[5] strongly indicate a communal behavior of the chains in a polydisperse network, with the long ones stretching more to relieve the force on the short ones. The present situation is thus best represented by the series arrangement of the chains.

IV. Conclusions

Results of calculations presented in Figure 5 may be used to generalize the findings of the present work: The ultimate properties of trimodal networks where the third component molecular weight is intermediate between the L and S chains are always lower than those of the bimodal network of L and S chains. This is not surprising, since this represents a change in the direction of a unimodal network.

The ultimate properties of trimodal networks are better than those of bimodal networks only when the third chain type incorporated to the bimodal network of long and short chains is very long. The physical explanation of this conclusion is that the VL chains increase the extensibility of the network and a large amount of additional energy may be stored in the system until the VL chains reach their fully extended lengths.

Calculations carried out for parallel arrangement of chains showed that such a model is not a good representation of multimodal networks because it emphasized the action of the short chains, contrary to experimental observation according to which the ductility of the networks are strongly enhanced by the presence of long chains.

A high priority should also be given to mechanical property measurements on trimodal elastomeric networks prepared in light of the guidance provided by the present calculations. Finally, calculations with a wide range of mole fractions of S and L chains should be performed. This would allow, in particular, a good estimate of how the presence of the VL chains affects the properties of trimodal networks relative to the bimodal ones.

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