Interpretation of Polymer Properties in Terms of Chain Conformations and Spatial Configurations

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Polymeric materials very frequently have physical properties which set them off strikingly from low molecular weight substances. Perhaps the most unusual example which might be cited in this regard is rubberlike elasticity (large, reversible deformability).[1,2] It is exhibited by many polymers when cross-linked into network structures, but not at all by any low molecular weight materials. This unusual and highly useful property, and other unique properties as well, arise from the fact that polymer chains have accessible to them a virtually unlimited number of conformational arrangements, or "spatial configurations", arrived at by different rotations about the single bonds making up the chain backbone.[3-10] Rubberlike elasticity is thus directly comprehended in terms of the long-chain molecules responding to an imposed force by switching from random, relatively compact configurations to less random ones having higher spatial extension along the axis of deformation. Similarly, the fact that the entropy of the polymer network is decreased in the deformation process provides the mechanism for the reversibility. Upon removal of the force, the elastomer returns to its original shape since this restores the entropy to its initial, considerably larger value.[1,2]

Configuration-dependent properties of this type are obviously of the greatest interest and importance in the characterization and utilization of polymeric materials. It is the interpretation, understanding, and prediction of these properties that is the subject of the present Account. The relatively simple molecular models adopted for this purpose are based on the rotational isomeric state approximation, in which each rotatable skeletal bond is assumed to occur in one of a small number of discrete rotational states.[4-11] (This general model has ample precedence of course in related studies of the physical properties of small molecules.) In most chain molecules, these states are located at rotational angles of 0, 120, and $-120°$, and are designated trans (t), gauche positive (g^+), and gauche negative (g^-). A spatial configuration is then specified by the particular sequence of the conformations or rotational states

adopted by the skeletal bonds of the chain. Thus, the average configuration of the chains and their configuration-dependent properties depend on the relative energies of these rotational states. These energies arise from a variety of sources, including the intrinsic torsional potential, and intramolecular interactions such as van der Waals attractions and repulsions, electrostatic and dipolar interactions, and hydrogen bonding.[4,12-14] Although it is possible to calculate such energies from semiempirical potential-energy functions, it is obviously more reliable to determine them through comparisons of calculated and experimental values of at least one configuration-dependent property.

In order to take into account the interdependence of neighboring rotational states, statistical weights are assigned to *pairs* of conformations about adjoining skeletal bonds.[4-11] Each such statistical weight is expressed as a product of simple Boltzmann factors, each an exponential in the energy characterizing one of the intramolecular interactions occurring in the conformational pair being characterized. The statistical weights required to characterize all of the conformations about a given skeletal bond are then arranged as elements of a statistical weight matrix. The sequential multiplication of such matrices, one for each skeletal bond, generates the configurational partition function of the chain.[4,5,8]

This thermodynamic information must be supplemented by structural data in order to calculate the

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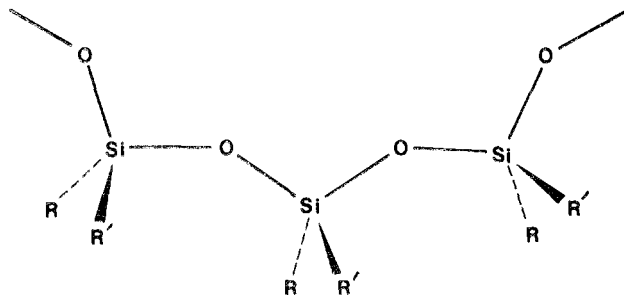
Figure 1. A schematic representation of a siloxane chain in the all-trans conformation, which is the form of lowest energy. The inequality of the skeletal bond angles, illustrated in the diagram, is of foremost importance with regard to the configurational characteristics of such chains. After eleven repeat units, this preferred conformation approximates a closed figure having very small values of both the end-to-end distance and dipole moment.

Figure 2. A sketch of the poly(1,3-dioxolane) chain in which the repeat unit is set off by the square brackets.

configuration-dependent properties under consideration. Skeletal bond angles and the locations of rotational states are required in general. In addition, for example, values of the skeletal bond lengths are required for calculations of the mean-square end-to-end distance $\langle r^2 \rangle_0$,[4] and bond dipole vectors are required for the mean-square dipole moment $\langle \mu^2 \rangle_0$.[6] The former quality is generally determined by means of light scattering or viscometric measurements, and the latter from measurements of dielectric constants. The chains are generally studied in dilute solution and at a number of temperatures in order to establish the temperature dependence of the property being investigated. The zero subscripts specify that these qualities pertain to the chain molecules in the *unperturbed* state, i.e., under conditions in which long-range interactions are nullified, generally by choice of a temperature, Θ, at which chain-segment attractions just balance the repulsions arising from the effect of excluded volume.[1,4]

As described in detail elsewhere,[4-11] values of $\langle r^2 \rangle_0$, $\langle \mu^2 \rangle_0$, and other configuration-dependent properties may be calculated from the conformational energies and structural information by means of matrix multiplication schemes paralleling those used to generate the configurational partition function. The temperature coefficient of any configuration-dependent property is, of course, readily obtained from values of that property calculated as a function of the temperature-dependent Boltzmann factors in the conformational energy. Of the various quantities which may be used to characterize chain configurations, the most widely used is the *characteristic ratio* $\langle r^2 \rangle_0 / n l^2$, where n is the number of skeletal bonds and l^2 is the average square of their lengths. This ratio measures the extent to which the actual unperturbed dimensions $\langle r^2 \rangle_0$ of a chain molecule differ from the dimensions $n l^2$ the chain would have if it were freely jointed.[4] It is thus a very convenient quantity for characterizing how the spatial configurations of a polymer chain depend on its structure, more specifically on its skeletal bond angles, locations of rotational states, and conformational preferences.

Interpretation and Prediction of Configuration-Dependent Properties

One class of chain molecules which has been very extensively studied with regard to configuration-dependent properties are the siloxanes [SiRR'-O-], shown schematically in Figure 1. Poly(dimethylsiloxane) (R = R' = CH₃) provides a good example of the approach

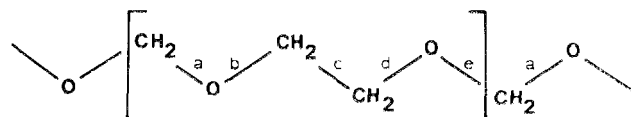taken in a typical configurational analysis of a chain molecule. Experimental values of the unperturbed dimensions and their temperature coefficient were compared with theoretical values calculated from rotational isomeric state theory, thereby obtaining energies for the various conformational states of the chain.[15] Trans states were thus found to be of lower energy than gauche states, this conformational preference possibly being due to favorable van der Waals interactions between pairs of CH_3 groups separated by four bonds.[15,16] Also of importance are $g^{\pm}g^{\mp}$ conformations which frequently give rise to severe steric interferences since they bring into proximity (on the same side of the chain) groups which are separated by four skeletal bonds. (These interactions are sometimes called "pentane-type interferences" since *n*-pentane is the simplest alkane in which they occur.)

In the case of polydimethylsiloxane, $g^{\pm}g^{\mp}$ conformations bringing about pentane-type interferences between the bulky $Si(CH_3)_2$ groups are completely excluded, and those in which the smaller O atoms are thus involved are suppressed to low incidence.[15] The fact that trans states are preferred and correspond to very compact configurations (Figure 1)[15,17] explains, for example, why the unperturbed dimensions of this polymer are found to increase significantly with increase in temperature.[18,19] The increase in available thermal energy increases the number of gauche states, which are of higher energy and represent departures from the compact closed polygons illustrated in part in Figure 1. The conformational energies thus obtained can then be used to predict other configuration-dependent properties of this same molecule. For example, satisfactory results have been obtained in this way for dipole moments,[17,20,21] stress-optical coefficients (strain-induced optical anisotropy),[22] and cyclization equilibrium constants.[23]

It is also possible to use conformational energies determined for two or more relatively simple chain molecules to predict the configuration-dependent properties of a different, more complicated molecule. An example of this involves the polyformal poly(1,3-dioxolane) [CH_2-O-$(CH_2)_2$-O-], illustrated in Figure 2. Several of its properties have been successfully predicted[24] using conformational energies previously determined for the structurally related polyoxides, in particular poly(oxymethylene) [CH_2-O-][25,26] and

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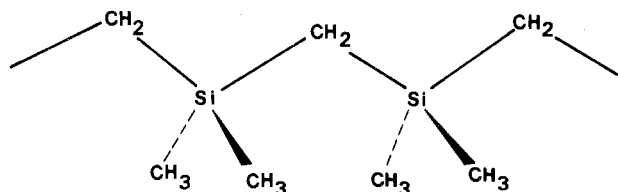(26) A. Abe and J. E. Mark, *J. Am. Chem. Soc.*, **98**, 6468 (1976).

Figure 3. The poly(dimethylsilmethylene) chain.

poly(oxyethylene) $[(CH_2)_2-O-]$.[26,27]

Finally, it is occasionally possible to predict some properties of a chain molecule from simple qualitative arguments. For example, in the case of poly(dimethylsilmethylene) $[Si(CH_3)_2-CH_2-]$,[28] shown in Figure 3, all accessible conformational states should be of approximately the same energy, since CH_3 and CH_2 groups are very nearly the same in their intramolecular interactions.[4] One would therefore predict, for example, that all of the configuration-dependent properties of this chain should be independent of temperature. This has in fact been confirmed in the case of both the unperturbed dimensions and the dipole moments.[28]

Chain Flexibility and Conformational Randomness

One type of chain flexibility concerns the ease with which the molecule can *change* configurations. This type of dynamic flexibility is of great practical importance because it affects the glass transition temperature T_g of the polymer, i.e., the temperature below which the polymer becomes glassy (relatively brittle), because of the freezing-in of the chain motions (changes in configuration). Although there are obviously intermolecular as well as intramolecular contributions to this transition temperature, a high value of T_g is generally taken to suggest relatively high barriers to bond rotations.[10] Such barriers are calculable, although only approximately, from the semiempirical potential-energy functions mentioned above. As should be expected, rigid cyclic structures, numerous or bulky side chains, skeletal bonds with partial double bond character, and bonding of pairs of chains into ladder-type structures all tend to decrease dynamic flexibility, and thus to increase T_g.

The other type of flexibility involves the compactness of the molecule, as characterized by its unperturbed dimensions or characteristic ratio. These are equilibrium properties and, as described in the preceding section, are also closely related to the structure of the chain. The polyoxides illustrate these relationships particularly clearly.[26,29,30] The upper portion of Figure 4 shows that dependence of the characteristic ratio on the number y of methylene groups in the polyoxide repeat unit. The most flexible of the polyoxides in the equilibrium sense of having the smallest value of the characteristic ratio is poly(trimethylene oxide) $[(CH_2)_3-O-]$. It has this high degree of flexibility because of its rotational state preferences, as are illustrated in Figure 5. Rotations about the first two bonds in the repeat unit bring oppositely charged O atoms and CH_2 groups into proximity, and gauche states are therefore preferred about these bonds. Rotations about the other
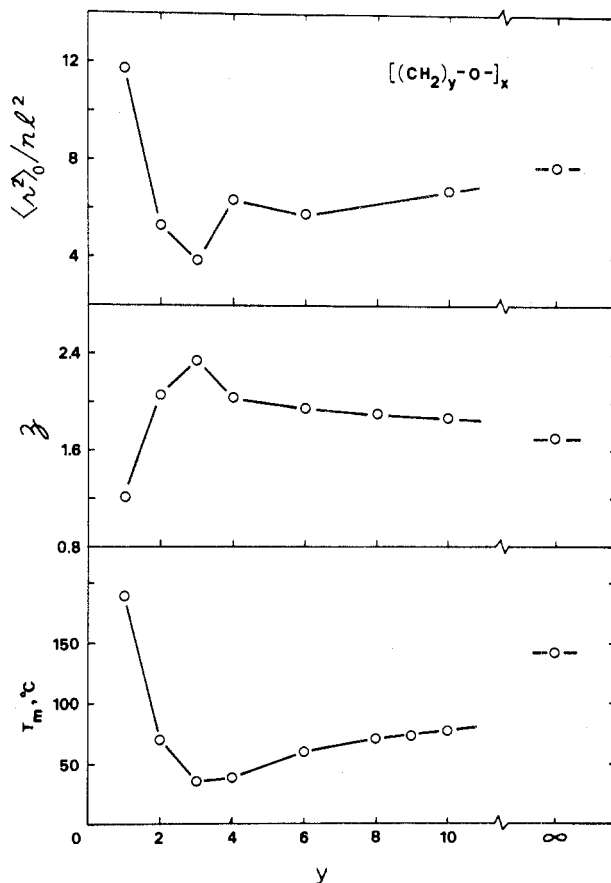
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Figure 4. Values of the characteristic ratio,[29] configurational partition function,[30] and melting point[29] for various polyoxides $[(CH_2)_y-O-]$ shown as a function of the number of methylene groups in the repeat unit.
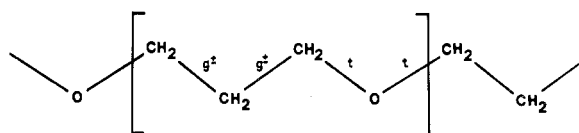

Figure 5. A sketch of the poly(trimethylene oxide) chain, in which $[g^{\pm}g^{\pm}tt]$ represents the minimum energy conformation of the molecule.[29]

two bonds bring two CH_2 groups into steric conflict, thus giving rise to the opposite preference, for trans states. As a result, the repeat unit as a whole is conformationally rather random or disordered, which corresponds to relatively compact configurations.[29] This is confirmed by values of the configurational partition function z calculated for the same series of molecules:[30] the larger the value of z, the larger the regions of configuration space accessible to the chain.[5] As is shown in the central portion of Figure 4, z does reach a maximum value for poly(trimethylene oxide), as expected from the above qualitative arguments.

It is also interesting to note that poly(trimethylene oxide) has the lowest melting point T_m of any polyoxide, as is demonstrated in the bottom portion of Figure 4.[29] Since $T_m = \Delta H_m / \Delta S_m$, the melting point of a substance depends on both the enthalpy of fusion, ΔH_m, and the entropy of fusion, ΔS_m. In the case of polymers, however, low melting points are generally due to relatively large entropies of fusion.[31] The low value of T_m

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for poly(trimethylene oxide) is thus consistent with a high degree of conformational disorder in the molten state, where the polymer chains are also in their random-coil, unperturbed states.[1,4,8,32] Such randomness would be associated with an unusually large configurational entropy for the amorphous chain molecule, and therefore with a correspondingly large value of ΔS_m and a relatively small value of T_m.

In this regard, melting point depression measurements on poly-diluent systems have been used to obtain experimental values of ΔS_m.[1,33] Although it is very difficult to extract a reliable value of the configurational entropy from this quantity,[34] such results could help to elucidate, at least qualitatively, the configurational characteristics of the chains thus investigated.[35]

The flexibility of the side chains on a polymer is frequently also of considerable importance. For example, the entropy increase attending the mixing of side chains with solvent is thought to be of critical importance in the dissolution of polypeptides when in the helical rather than random-coil form.[36] Another example concerns chain backbone conformations in which the side chains are so close together that they can not experience as many configurations as they can in less congested conformations.[4,37,38] The side chains can thus cause an "entropic destabilization" of these former conformations, with a corresponding effect on the configurations and configuration-dependent properties of the chain.

Characterization of Polymer Structure

A number of important classes of polymer have stereochemical variability, for example, vinyl polymers [C*HR–CH$_2$–] with d or l pseudoasymmetric C* atoms[4,39] and diene polymers[4,40] [CR=CH–CH$_2$–CH$_2$–] with cis or trans double bonds. The configuration-dependent properties of such chains frequently depend greatly on the stereochemical structure of the chain. For example, the isotactic form (...$dddd$... or ...$llll$...) of poly(α-olefins) (R = alkyl in the vinyl case) generally have significantly larger unperturbed dimensions than does the syndiotactic (...$dldldl$...). This results from the fact that steric repulsions between R groups in the isotactic form force the chain into helical sequences of relatively high spatial extension (see following section). Thus, the study of the configuration-dependent properties of such chains can give valuable information on their stereochemical structure.

Rather different results have been obtained for the stereochemically variable siloxane, poly(methylphenylsiloxane) (R = CH$_3$, R' = C$_6$H$_5$ in Figure 1). Because of the relatively long Si–O bonds and the unusually large Si–O–Si bond angle, intramolecular attractions are much more important than steric re-
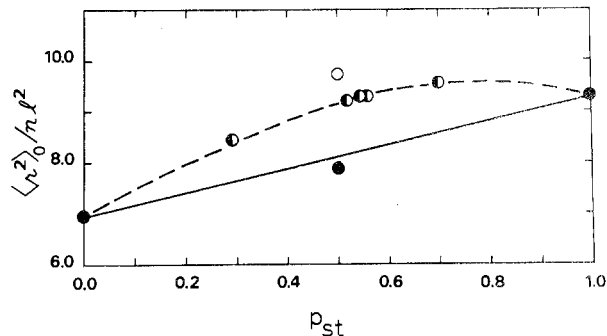

Figure 6. The characteristic ratio for styrene–methyl methacrylate copolymers shown as a function of the mole fraction of styrene units in the chain. The filled, half-filled, and open circles locate experimental results obtained for block, intermediate, and alternating copolymers, respectively. (Results obtained from ref 7 and 44.)

pulsions in this chain.[16] As a result, the dependence of the chain dimensions on stereochemical structure is very nearly the opposite of that shown by the poly(α-olefins). This different behavior does not of course preclude the possibility of using configuration-dependent properties to characterize the stereochemical composition of these chains as well.

Chain dimensions and dipole moments have also been used to characterize sequence distributions in binary chemical copolymers,[7,41,42] which can have their A and B repeat units in structures ranging from blocky (... AAAABBBB...) to alternating (...ABABABAB...). In the case of block copolymers, a property such as the characteristic ratio has a value which is simply a molar average of the same property for the two [A–] and [B–] "parent homopolymers". This occurs because a block copolymer has very few AB junctions and therefore virtually all of its intramolecular interactions are those also present in the two homopolymers.[7,41,42] In the case of a more nearly alternating copolymer, there are many such atypical AB inversions and, when A and B are chemically very different, there are numerous important interactions present which do not occur in either the [A–] or the [B–] homopolymer. The properties of this type of copolymer therefore can not be obtained by simply averaging the properties of the two homopolymers[43] and generally show a complicated dependence on composition and sequence distribution.[7] This is clearly demonstrated in Figure 6, which shows the experimentally determined compositional dependence of the characteristic ratio for three types of styrene–methyl methacrylate copolymers.[7,44]

Prediction of Crystalline State Configurations

Knowledge of the conformational energies of a chain molecule immediately permits identification of the configuration of minimum energy. Somewhat surprisingly, this is generally the configuration adopted by the chain when it crystallizes, with intermolecular or chain-packing effects apparently of relatively minor importance in this regard.[4] Figure 7 gives some illustrative examples. The minimum energy form of polymethylene (alias polyethylene) is the all-trans

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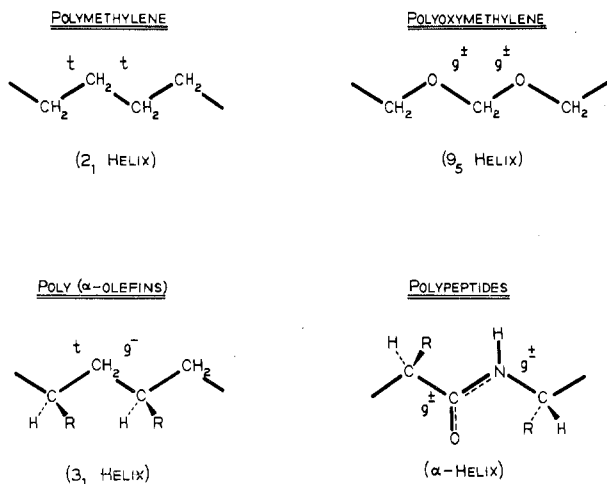
Figure 7. Low-energy conformations and the corresponding regular helical configurations adopted by four representative types of chain molecules.

configuration, since gauche states bring CH_2 groups into conflict. This corresponds to a (degenerate) 2_1 helix (two CH_2 repeat units per one turn of the helix). It is the well-known planar "zigzag" form in which polymethylene crystallizes.[4] The low-energy form of poly(oxymethylene) is the exact opposite—the all-gauche configuration—since bringing positive CH_2 groups and negative O atoms into proximity decreases the energy. This gives rise to the 9_5 helix in which poly(oxymethylene) crystallizes.[25]

In the case of the isotactic poly(α-olefins), the conformational energy is minimized by replacing the R···R steric conflicts with either R···H or H···R interactions. The ...tg^-tg^-... and the ...g^+tg^+t... configurations accomplish this and are thus of minimum energy; they correspond to the 3_1 helix in which such chains frequently crystallize.[39] The repeat unit of the polypeptide chain consists of three skeletal bonds, but the central bond has partial double bond character and is generally locked into the trans state as shown in the figure. The minimum energy configuration of a number of such polypeptides arises when both of the other bonds are in gauche states of the same sign.[4] The resulting regular configuration is the α-helix, renowned in the area of biopolymer chemistry.

The chain molecules shown in the preceding figures provide additional examples. Poly(dimethylsiloxane) (Figure 1) crystallizes in a slowly winding helix which is very close to an all-trans configuration,[4,15] poly-(1,3-dioxolane) (Figure 2) crystallizes in a helix in which bonds a, c, and e are gauche and b and d are trans,[24] and poly(trimethylene oxide) (Figure 5) crystallizes in a helix in which the first two bonds are gauche and the second two are trans.[29,45] The crystalline state configuration of poly(dimethylsilmethylene) (Figure 3) has not yet been reported, and it would be very difficult to predict since, as described earlier, there are no significant conformational preferences in this chain molecule.

Network Thermoelasticity

As already mentioned, the retractive force exhibited by an elongated elastomeric network is primarily en-

tropic in origin. If energetic effects were totally absent, then the force f at constant deformation would be directly proportional to the absolute temperature T (as is the pressure of an ideal gas at constant volume). The extent to which conformational energy changes make a contribution f_e to f can thus be gauged in force-temperature ("thermoelastic") studies by determining the extent to which the f–T relationship differs from perfect proportionality.[4,46–48]

Amorphous polymethylene networks have a large negative value of f_e,[4] and this is directly explicable in terms of the configurational characteristics of the chains. Macroscopic deformation requires an increase in the number of conformational sequences of high spatial extension. As is obvious from the sketch of polymethylene in Figure 7, this requires gauche to trans transitions, and this corresponds to a decrease in the energy[4,47,48]—hence, the negative value of f_e. Poly(dimethylsiloxane) networks, on the other hand, have a relatively large positive value of f_e.[18,19] The preferred configuration of this chain is also all-trans but, as can be seen from Figure 1, this corresponds to very small end-to-end distance. The required conformational changes are now therefore trans to gauche transitions. This increases the energy, thereby explaining the positive value of f_e.[15] In these and in numerous other cases,[47,48] there is very good agreement between the observed values of f_e and theoretical values based on the qualitative concepts outlined here.

Highly Extended Configurations in Deformed Polymer Networks

Configurational concepts also explain a number of unusual properties observed for elastomeric networks at very high deformations. For example, many polymer networks at high elongation show a rather abrupt and marked increase in modulus (ratio of stress to strain).[1,2] This increase is now known to be due to strain-induced crystallization.[49–51] Elongation of the elastomer decreases the entropy of the network chains, and the additional decrease in entropy required for crystallization to occur is therefore relatively small. Since the melting point goes inversely with the entropy of fusion, it is frequently increased to the extent that considerable amounts of crystallization are induced in the network at the temperature of deformation. The crystallites thus formed act as physical cross-links between the chains, as is shown in part a of Figure 8, and the increase in the effective degree of cross-linking increases the modulus of the network.[1,49–51] Strain-induced crystallization is obviously of great practical importance since it improves the ultimate strength and maximum extensibility of the material. Unfilled polymer networks incapable of the self-reinforcement provided by strain-induced crystallization remain weak, with relatively low ultimate properties.[1,49,52]

These concepts also explain the fact that, under some conditions, strain-induced crystallization *decreases* the

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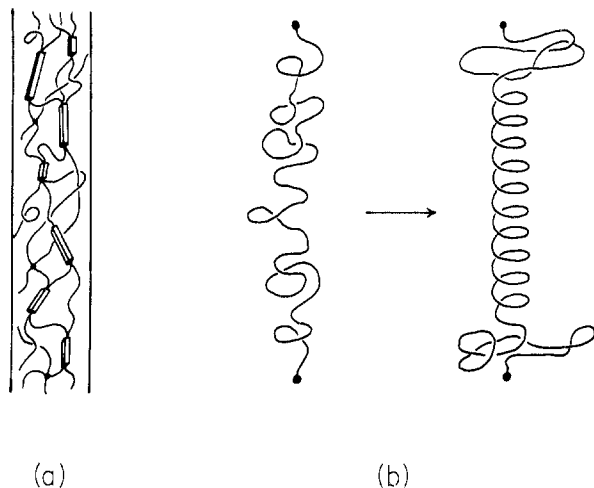
(a)   (b)

Figure 8. Strain-induced crystallization in a polymer network which has been elongated by a force along the vertical direction.[51] Part a shows the crystallites acting as multifunctional cross-links (greatly simplified) and the crystallite orientation in the direction of stretching. Part b shows how crystallization of a sequence of network chain units into a helical configuration of high spatial extension can decrease the deformation in the adjoining amorphous sequences in the chain.

modulus of the network before increasing it in the manner described above.[50,53,54] As shown in part a of Figure 8, the crystallites formed are oriented in the direction of stretching; furthermore, the chain sequences within a crystallite are in helical, highly extended configurations, as is illustrated in part b of the figure. The straightening and aligning of portions of the network chains thus decrease the deformation in the remaining, amorphous regions, with a corresponding decrease in the stress and network modulus.[51,55,56]

Interpenetration of Network Chains

In any molecular theory of rubberlike elasticity, it is necessary to establish a connection between the deformation imposed on the macroscopic sample and the resulting deformation of the network chains. It is generally assumed that such materials deform "affinely", i.e., that the components of the end-to-end vectors of the network chains change in direct proportionality to the dimensional changes of the elastomeric sample.[1,2] This is equivalent to assuming that the network junctions or cross-links are firmly embedded in the network medium. Recent theories and related experimental results[57-64] suggest, however, that elastomeric deformations may not be affine in the case of (i) some types of deformation (e.g., elongation to very high stress levels), (ii) some experimental conditions (e.g., highly swollen networks), and (iii) certain unusual
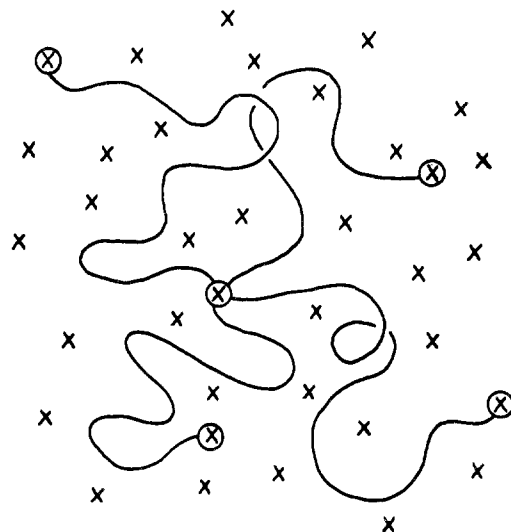
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Figure 9. Typical configurations of four chains emanating from a tetrafunctional cross-link in a polymer network. The circled cross-links are topological nearest neighbors, and the diagram illustrates the fact that within the domain of four such chains there are numerous additional cross-links, i.e., there is generally a great deal of interpenetration of configurational domains. (After ref 60.)

types of networks (e.g., those cross-linked in solution).

The extent to which a network deforms affinely is of crucial importance with regard to elastomeric properties since it has a marked effect on the elastic equation of state, which interrelates the stress, strain, temperature, and structure of the network.[1,2] The fact that a polymer network may deform affinely under some conditions but not others could thus explain a number of discrepancies between theory and experiment, in particular the observation[62] that actual stress–strain isotherms generally do not have the form which is predicted by all of the earlier molecular theories.[1,2]

In molecular terms, the extent to which a network deforms affinely depends directly on how firmly embedded the cross-links are, and this in turn depends on their degree of entangling with the network chains. The severity of this extangling can be estimated from the configurational characteristics of the chains,[65] more specifically their degree of interpenetration.[58-60] One may simply compare the end-to-end separation $\langle r^2 \rangle_0^{1/2}$ of a network chain with the average distance of separation of the cross-links, which can be calculated from the known degree of cross-linking. As is illustrated in Figure 9, the former generally greatly exceeds the latter, to the extent that there may be the order of a hundred cross-links spatially closer to a given cross-link than are the four which are its topological nearest neighbors. The junction–chain entangling resulting from this large amount of overlapping among the configurational domains would probably be sufficient to give an affine deformation at low stresses, but not at the higher stresses easily achieved in a typical stress–strain experiment. The resulting change from an affine to a non-affine deformation could explain[57-60] the otherwise puzzling dependence of the network modulus on strain.[62] Similarly, the unusual elastomeric properties[62]

(65) Configurational calculations have also been carried out in an attempt to characterize other structural features of a network, such as the number of intramolecular cross-links (chain "loops"). See A. E. Tonelli and E. Helfand, *Macromolecules*, **7**, 59, 832 (1974), **8**, 248 (1975), and pertinent references cited therein.

of networks which are highly swollen could be due to the effect of the diluent on the firmness with which the junctions are embedded, while those of a network prepared in solution[61] could be due to the solvent partially disentangling the chains prior to their incorporation into the network structure.

Many of the above statements are still somewhat conjectural, and much experimental and theoretical work is currently being carried out in an attempt to evaluate and extend these concepts. In any case, the configurations of the chains are obviously of central importance with regard to rubberlike elasticity, as it is with regard to the other unique properties of polymeric materials.

The Ligand Polarization Model and the Spectra of Metal Complexes. A Complementation of the Crystal Field

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It is now generally accepted that any formally correct treatment of the electronic states of transition-metal and lanthanide complexes requires an explicit consideration of the electron exchange between the ligands and the metal ion and that independent-systems models which neglect the overlap of the charge distributions of the metal ion and the ligands are necessarily incomplete. In its applications, however, the main independent-systems model, crystal-field theory, has provided a range of qualitatively novel and testable expectations, despite all the limitations of that theory, whereas MO treatments of metal complexes incorporating metal–ligand overlap are more notable for the ex post facto rationalization of known quantities, often with the aid of a more or less extensive set of adjustable parameters.

Not all of the limitations of crystal-field theory are rooted in the neglect of metal–ligand electron exchange. A first-order independent-systems treatment of one-electron quantities, energies or charge distributions, rests upon one of two mutually exclusive limiting assumptions. Either the ligands perturb the metal ion, or the metal ion perturbs the ligands. Either a particular charge distribution of the ligands, generally taken to be that of the ground electronic state, perturbs all of the electronic states of the metal ion, as in crystal-field theory, or alternatively a particular charge distribution of the metal ion, usually a given d-electron or f-electron transitional distribution, perturbs all of the electronic states of the ligands. The latter course is adopted in the ligand-polarization model which is complementary, within the first-order independent systems scheme, to crystal-field theory.

Stephen Mason was born in England in 1923 and educated at Oxford University, where subsequently he taught chemistry and the history of science. After research in medical chemistry at the Australian National University, he became lecturer and then reader in chemical spectroscopy at Exeter University, and professor of chemistry first at the University of East Anglia and then at King's College, London. His principal research interests are directed to chiral structures and to molecular spectroscopy, particularly to the two subjects taken in conjunction with one another and with the history of scientific ideas.

The Transition-Probability Anomalies of Crystal-Field Theory

Crystal-field theory has been rather more successful in the treatment of the transition energies than the transition probabilities of d-electron and f-electron excitations in metal complexes. The theory originated during the late 1920s and the following decade from physicists more concerned with frequency relationships in the line spectra of the atoms and gaseous ions than with the line strengths, although spectral intensities were not neglected. In the study of the corresponding condensed-phase cases, attention was naturally directed to linelike spectra, notably those of the lanthanide(III) complexes in the solid state. The well-known Stark effect of the splitting of an atomic line in an electrostatic field provided a straightforward mechanism to account for the appearance of each gaseous Ln(III) line as a multiplet in the corresponding crystal spectrum. The number of components observed was related group-theoretically by Bethe (1929) to the symmetry of the electrostatic field due to the charged ligands and to the particular spectroscopic terms of the gaseous Ln(III) ion connected by the electronic transition.[1]

In extensions of the theory to the electronic transition probabilities of coordination compounds the basic model of the perturbation of the metal ion states by the static crystal field of the ground-state charge distribution in the ligands was retained. Laporte (1924) had shown that electric dipole transitions between two gerade or between two ungerade states are forbidden,[2] and in a pioneer study Van Vleck (1937) distinguished three mechanisms to account for the nonzero f–f transition probabilities of lanthanide complexes.[3] These invoked either the leading allowed moments of the electronic transition, an electric quadrupole or a magnetic dipole, or an enforced electric-dipole transition

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