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# Stress–Strain Isotherms in Compression for Thermoreversible Polyethylene Gels

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ABSTRACT: Cooling dilute solutions of homopolymers and copolymers of ethylene caused crystallization of the polyethylene in such a way as to form continuous elastomeric gels. These gels are "thermoreversible" in that they reliquefy upon increase in temperature sufficient to remelt the polymer. Although the gels are very fragile, it was possible to do compression measurements on them in the vicinity of room temperature. The resulting approximate values of the elastic modulus $[f^*]$ for both whole polymers and fractions in the compression limit $\alpha \rightarrow 1$ increase markedly with increase in concentration $c$, with the largest increases occurring at the highest values of the molecular weight $M$, presumably because of diminished importance of dangling chains. Values of $[f^*]$ seem to increase approximately linearly with $c^2$, suggesting the importance of pairwise encounters between chain segments in the gelation process. The effect of $M$ on the modulus at $\alpha \rightarrow 1$ and at the critical concentration $c^*$ required for gelation is the same for whole polymers and fractions in the case of number-average molecular weight but not weight or viscosity average. This again indicates the importance of dangling chains on the gel structure and its mechanical properties. Random polyethylene copolymers with ethyl branches have decreased values of $[f^*]$ at the same concentration, as would be expected from the difficulty of incorporating branch points in a crystalline lattice. However, when the comparison is made at $c^*$, the values of $[f^*]$ are similar to those of the same molecular weight linear polyethylenes. Approximate molecular interpretation of the magnitudes of the modulus indicate that a chain in a gel formed near $c^*$ is to a large extent in the form of dangling ends, which are elastically ineffective.

## Introduction

There is presently a great deal of interest in the preparation, characterization, and utilization of polymeric gels, particularly those that are formed by means of physical cross-links, such as crystallites or intersegmental aggregations.[1–14] These latter types of gels are thermoreversible in that they reliquefy upon increase in temperature sufficient to melt the crystallites or break up the aggregates. Preparative techniques for such gels generally involve cooling solutions of the polymer, frequently at concentrations not much above those where typical lamellar crystallites precipitate from dilute solution. Characterization techniques include preparative and analytical GPC, fractional precipitation, and $^{13}$C NMR and Raman spectroscopy of the starting polymers; viscometry, scanning calorimetry, and visual observations of the initiation and cessation of flow for the gelation process; and SALS, SAXS, polarized light microscopy, scanning and transmission electron microscopy, and dynamic mechanical measurements for the gels themselves. Applications of the gels formed by crystallization include drawing them into highly oriented fibers of extraordinarily high tensile strength.[6,15–17]

Thermoreversible gels of polyethylene are among those that can be prepared by quiescent crystallization from dilute or moderately dilute solution.[3,5–8] When gelation occurs as a consequence of crystallization from solution, a very fluid system is converted to an elastic medium of infinite viscosity, the polymer system pervades the entire volume, and the gels formed by this mechanism are *thermally reversible*. Although a network structure is formed, these gels are quite different from those formed by covalently cross-linking a collection of chains wherein the resultant network is thermally stable. For the gels of interest in the present work the primary molecules are thus bound together, or connected, by lamellar crystallites.[3,5] In order to develop a network structure, a chain, on the average, must pass through at least two different crystallites.[18] The critical condition for network formation by this crystallization mechanism is reflected in the critical concentration $c^*$ for gelation. Below this concentration, crystallization from dilute solution in the form of a discontinuous precipitate takes place in the conventional manner; above this concentration, gelation, accompanying the crystallization process, is observed. The critical concentration depends on the molecular weight and molecular constitution of the polymeric species, the nature of the solvent, and the temperature.[3,5] Gelation is thus superposed on a crystallization process that is continuous with concentration. The basic lamellar crystallite structure and thermodynamic properties are maintained irrespective of whether in a precipitate or in a gel.

The thermodynamic properties and morphological features of the gels, as well as their kinetics of formation, have been studied in detail for gels of polyethylene and its copolymers.[3,5] However, mechanical properties, particularly equilibrium elastic ones, have not been extensively investigated for these quiescent unoriented gels. Studies of the elastic properties of such networks can be expected to give information with respect to their structure, particularly that of the important interlamellar region. In addition, the results should be helpful in understanding the properties of oriented fibers that are subsequently drawn from such gels.[6,15–17] For these reasons we have undertaken a study of the elastic properties of gels of linear polyethylene and its copolymers utilizing stress–strain isotherms in compression.

## Experimental Details

**Materials.** The samples of whole (unfractionated) polyethylene studied were typical commercial materials. Values of their number-average molecular weight $M_n$ and weight-average $M_w$ or viscosity-average $M_\eta$ molecular weight are given in columns three and four in Table I. A very wide range in molecular weights is represented by the unfractionated polymers. Several of these

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**Table I**
**Sample Molecular Weights, Critical Concentrations for Gelation, Moduli, and Estimates of Degree of Cross-Linking**

| | | mol wt,[a] g $\text{mol}^{-1}$ | | | | $10^{-3}M_c$,[d] g $\text{mol}^{-1}$ | |
|---|---|---|---|---|---|---|---|
| polyethylene | sample | $10^{-3}M_n$ | $10^{-3}M_w$ or $M_\eta$ | $c^*$,[b] % | $[f^*]$,[c] N $\text{mm}^{-2}$ | from $[f^*]$ | from $(f/A)/\epsilon$ |
| whole polymers | I | 5.80 | 10.1 | 1.7 | 1.1 | 2.9 | 2.9 |
| | II | 22.5 | 53.5 | 1.1 | 0.8 | 11.2 | 11.3 |
| | III | 11.0 | 150.0 | 1.0 | 0.95 | 5.5 | 5.5 |
| | IV | 91.0 | 500.0 | 0.9 | 2.5 | 40.8 | 45.5 |
| | V | | 1000.0 | 0.8 | 2.0 | | |
| | VI | 250.0 | 2000.0 | 0.6 | 3.65 | 74.0 | 125.0 |
| | VII | 800.0[e] | 8000.0 | 0.6 | 5.35 | 94.5 | 397.0 |
| fractions | F1 | 1.15 | 1.26 | 1.35 | 1.05 | 0.57 | 0.57 |
| | F2 | 1.67 | 1.93 | 1.0 | 1.3 | 0.83 | 0.84 |
| | F3 | 9.30 | 10.5 | 1.7 | 1.55 | 4.6 | 4.7 |
| | F4 | 21.6 | 23.3 | 1.0 | 1.1 | 10.7 | 10.8 |
| | F5 | 49.5 | 52.6 | 1.1 | 1.75 | 23.9 | 24.8 |
| | F6 | 101.0 | 120.0 | 1.0 | 3.35 | 43.6 | 50.2 |
| | F7 | 360.0 | 428.0 | 0.9 | 3.9 | 105.0 | 179.0 |
| copolymers[f] | P 108 | 103.0 | 108.0 | 2.5 | 3.8 | 48.1 | 51.5 |
| | P 420 | 400.0 | 420.0 | 1.2 | 3.4 | 132.0 | 199.0 |

[a] Number average and weight average or viscosity average. [b] Minimum concentration ($W/V$) required for gelation. [c] Reduced stress or modulus in compression, in the compression limit $\alpha \rightarrow 1$ and the concentration limit $c \rightarrow c^*$. [d] Molecular weight between cross-links (crystallites). [e] Estimated. [f] Comonomer gives 2.2 mol % ethyl branches.

polymers had been used to prepare gels studied in an earlier investigation.[3]

The fractions studied are listed in the second column of the middle portion of Table I. Fractions F1 and F2 were obtained from the Petrolite Corp. Their molecular characteristics have been reported previously.[19] The other fractions were obtained from Society Nationale Elf Quitane and had been prepared and characterized by gel permeation chromatography. Their values of $M_n$ and $M_w$ are also given in Table I.

The copolymers studied were hydrogenated polybutadienes obtained from the Phillips Petroleum Co. They contained 2.2 mol % of randomly placed ethyl branches and had narrow composition and molecular weight distributions. Their molecular weights are listed in the lower portion of Table I.

The decalin used as solvent was reagent-grade material obtained from Aldrich and was used as received. Its density and the densities of the polymers, if not already known, were determined by pycnometry.

**Preparation of Gels.** Previous experiments have indicated that the very high molecular weight polymers were difficult to dissolve at the concentrations desired. These were therefore first dissolved at much lower concentrations and then precipitated to give finely divided powders. In all cases, weighed amounts of polymer and decalin were mixed and then heated to the lowest temperature (130–150 °C) sufficient to bring about dissolution, with stirring. Concentrations were expressed as a weight to volume percent and were chosen to be somewhat larger than the known[3] minimum concentration $c^*$ required for gelation. These values of $c^*$ are given in the fifth column of the table. The solutions were then rapidly cooled, generally to 35 °C, to produce gelation. In the cases of two of the highest molecular weight polymers, VII and F7, the solutions had to be cooled to 0 °C, instead of 35 °C, to produce gels suitable for the compression measurements. Because of the fragility of the gels, the gelations were carried out in 10-mL beakers suitable for conducting the compression measurements described in the following section.

**Stress–Strain Measurements.** Forces $f$ were applied to the surface of each gel by placing known weights on top of a carefully positioned and extremely light polyethylene cylinder closed at the bottom with a circular disc of known surface area $A$. The height of the gel before and after the resulting deformation was measured with a cathetometer and used to calculate the compression $\alpha = H/H_i$. As expected, the gels were much too fragile to yield isotherms that were reversible, and therefore measurements were taken relatively rapidly.

In a highly approximate analogy with the representation of elongation results consistent with rubber elasticity theory, a reduced stress, or modulus, in compression was taken to be[20,21]

$$[f^*] \equiv f v_2^{1/3}/A(\alpha - \alpha^{-2}) \qquad (1)$$

where $v_2$ is the volume fraction of polymer in the gel. An alternative definition of the modulus also of importance is $(f/A)/\epsilon$, where $\epsilon \equiv (H_i - H)/H_i$. In both cases it is the value of the modulus in the limit $\alpha \rightarrow 1$ that is of primary interest in this study.

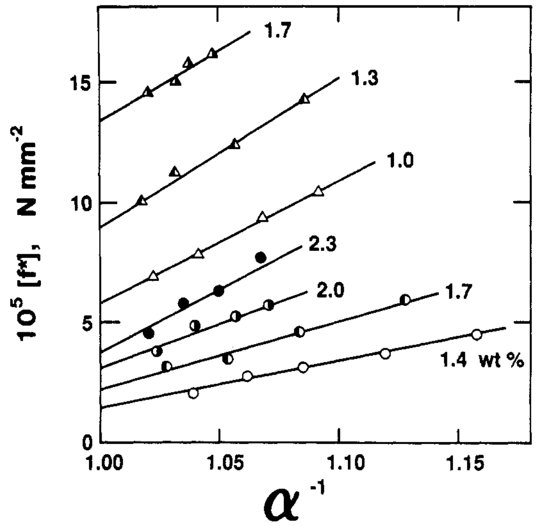

**Figure 1.** Typical stress–strain isotherms in compression at room temperature, specifically those obtained for the whole polymers III (circles) and VI (triangles). Each curve is further identified by the concentration of polymer in the gel. For convenience, the modulus is plotted against the reciprocal of the relative length or height, as is customary for isotherms obtained in elongation.[20,21]

## Results and Discussion

Figure 1 shows some typical stress–strain isotherms for different polymer concentrations. It is interesting to note that these values of $[f^*]$ are 3 or 4 orders of magnitude smaller than those of typical, covalently cross-linked elastomers. These differences are discussed in more detail below. In any case, as can be seen from this figure, the isotherms are approximately linear over the small range of compression that was investigated. Extrapolation of the data to $\alpha^{-1} \rightarrow 1$ was used to obtain estimates of the initial values of the modulus $[f^*]$ representing the nearly undeformed gel.

These initial values of $[f^*]$ are plotted against the concentration $c$ in Figure 2 for all the samples studied. To place the complete set of data in perspective, straight lines were arbitrarily drawn through the set of data points for each sample, for both the whole polymers and fractions of the linear polyethylenes. The modulus is seen to increase significantly with increasing $c$, and the slopes of the

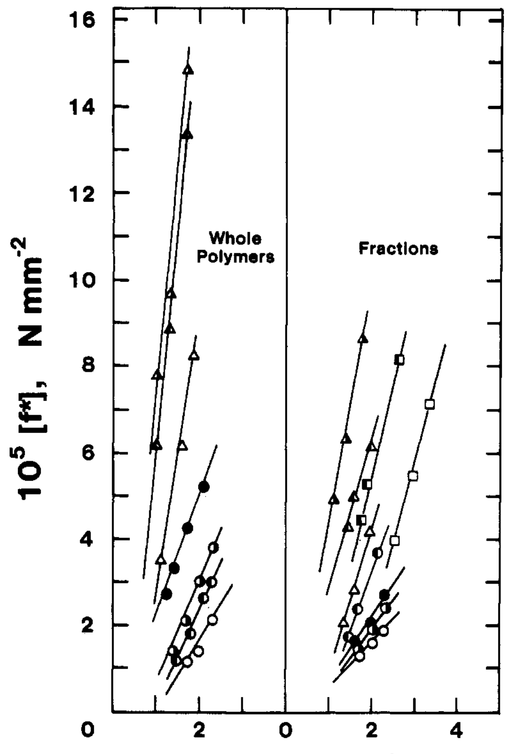

Figure 2. Concentration dependence of the modulus in the compression limit $\alpha \rightarrow 1$ for the whole polymers and fractions (including copolymers). The whole polymers are I (○), II (◐), III (◑), IV (●), V (△), VI (◮), and VII (▲). The fractions are F1 (○), F2 (◐), F3 (◑), F4 (●), F5 (△), F6 (◮), F7 (▲), P 108 (□) and P 420 (◧).

[$f^*$]–$c$ lines increase asymptotically with increase in molecular weight. This is presumably due to decrease in the number of chain ends, which have to be relegated to the interlamellar regions when crystallization (cross-linking) occurs. Such cross-linking is obviously more efficient when the number of such chain ends is minimized.

We should note that when compared at the same concentration and molecular weight, the copolymers have substantially reduced moduli relative to the homopolymers, reflecting in turn a difference in the structure of the disordered regions. A similar reduction in the initial moduli values in continuous extension has been noted between branched and linear polyethylene for bulk-crystallized samples.[22]

The dependence of the values of the initial modulus on concentration was analyzed more carefully, specifically by looking for curvature in the [$f^*$]–$c$ lines. Typical results, those for the whole polymers, are shown in Figure 3, where a more expanded concentration scale is used. Although the general pattern of the concentration dependence is still maintained, being less steep at the low molecular weights than at the higher ones, it is clear that there is curvature in these plots. In Figures 4 and 5 plots of the same values of [$f^*$] against the square of the concentration for the whole polymer and linear fractions, respectively, are given. It is clear from these plots that for both sets of polymers very good straight lines are obtained. A similar dependence of the modulus on the square of the concentration had been observed for gelatin gels by Ferry.[23,24]

The structures of the latter type gels have been interpreted as fringed micelles while the crystallites in the polyethylene gels have been shown to be lamellar in character.[3,5] Clearly the concentration dependence of the modulus does not reflect the overall morphology of the gel system, although in both cases crystalline polymers are involved. Neither does the $c^2$ concentration dependence appear to be universal for gelling systems. For example, for poly(vinyl chloride) gels the modulus varies with a higher power of concentration.[25,26] Isotactic polystyrene gels, in a variety of solvents, do not appear to give a simple power law at all.[27] However, these studies were carried out

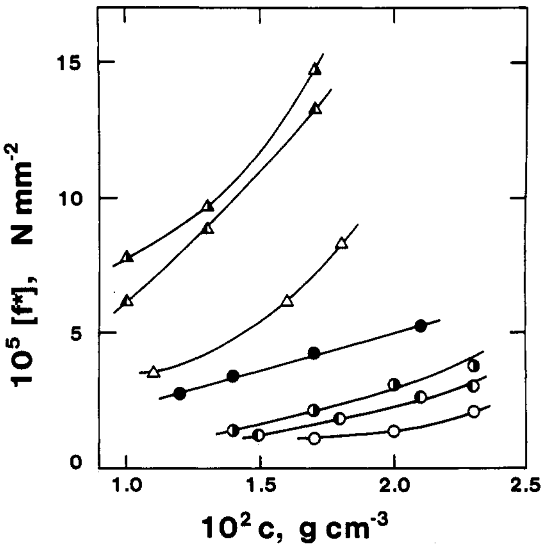

Figure 3. More careful examination of the concentration dependence of the modulus at $\alpha \rightarrow 1$ for the whole polymers. See legend to Figure 2 for identification of curves.

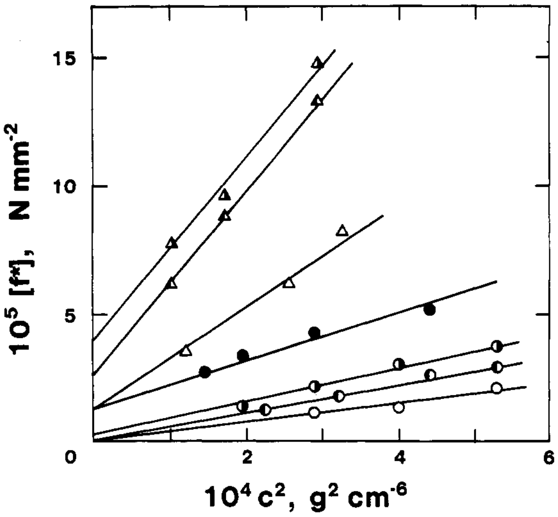

Figure 4. Moduli of the whole polymers at $\alpha \rightarrow 1$ shown as a function of the square of the concentration; see legend to Figure 2.

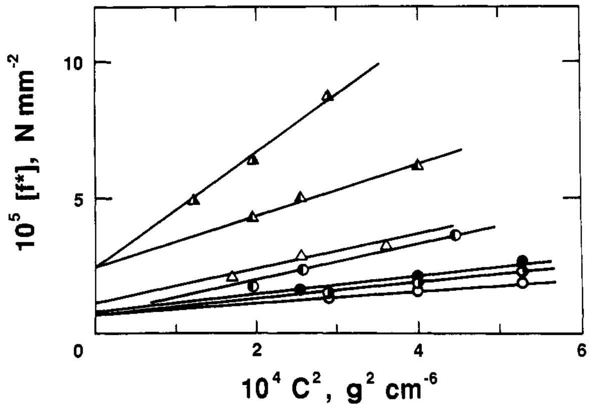

Figure 5. Moduli of the fractions at $\alpha \rightarrow 1$ shown as a function of the square of the concentration; see legend to Figure 2.

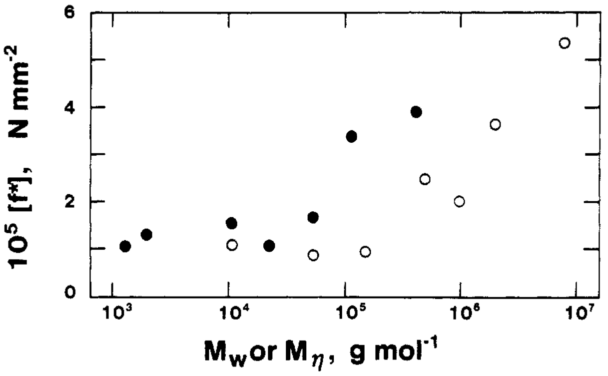

**Figure 6.** Modulus in the compression limit $\alpha \rightarrow 1$ and the concentration limit $c \rightarrow c^*$ shown as a function of the weight-average or viscosity-average molecular weight of the polymers. The whole polymers are represented by open circles and the (homopolymer) fractions by filled circles.

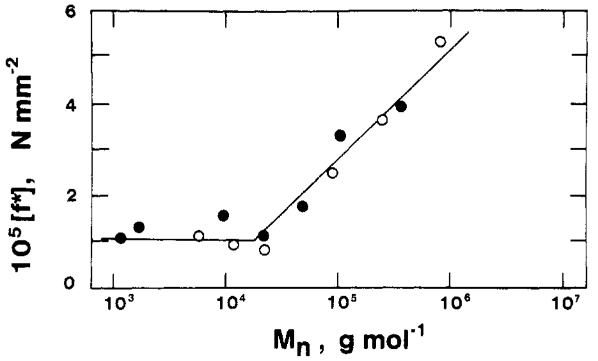

**Figure 7.** Modulus at $\alpha \rightarrow 1$ and $c \rightarrow c^*$ shown as a function of the number-average molecular weight. See legend to Figure 6.

over a very large concentration range where a simple power law would not be expected to hold. The $c^2$ dependence of the modulus that has been observed is consistent with the importance of pairwise encounters between chain segments in the gelation process. It does not mean, however, that a fringed micellar structure is involved.[27]

The linear extrapolations shown in Figures 4 and 5 were used to obtain values of the initial modulus at the critical concentration $c^*$ necessary for gelation. This quantity allows for a rational comparison to be made of the elastic properties of the undeformed gels. The resulting values are presented in the sixth column of Table I. The interesting relationship that exists between molecular weights and between whole polymers and fractions will be discussed in detail below. At this point, however, we should note that at $c^*$, the values of $[f^*]$ for $\alpha \rightarrow 1$ for the copolymers are about the same as those for the corresponding linear fraction under the same conditions.

The molecular weight dependence of $[f^*]$ for the homopolymer in the limits $\alpha \rightarrow 1$ and $c \rightarrow c^*$ are examined in Figures 6 and 7. The values of $[f^*]$ under these conditions are plotted as a function of weight-average or viscosity-average molecular weight in Figure 6. There is seen to be no correlation between the results for the whole polymers with those for the fractions, although the trends appear to be the same for both types of samples. However, a common curve does result when the same values of $[f^*]$ are plotted against the *number*-average molecular weight, as is shown in Figure 7. We see quite clearly in the figure that the same value of the modulus is obtained, irrespective of the sample being a whole polymer or fraction, when the data are analyzed on this basis. There are two segments in the plot of Figure 7. Below approximately $M_n = 10^4$ the modulus is independent of molecular weight. Above this molecular weight the modulus increases linearly as the logarithm of the chain length. This demarcation corresponds to the change that has been observed in the critical concentration with molecular weight.[5] At low molecular weights $c^*$ is independent of chain length while it decreases with chain length at higher molecular weights. Concomitantly a change occurs in the crystallite structure from an extended chain form to a "folded" lamellar structure. There is also a change in overall morphology, or superstructure, corresponding to these two regions.[5]

The commonality observed demonstrates the importance of the large number of end groups associated with short chains, which contribute overwhelmingly to $M_n$ but hardly at all to $M_w$ or $M_\eta$. Since the end groups are predominantly located in the interlamellar, disordered structural region, the major contribution of these structures to the initial modulus is underscored by these results.

The conclusion as to the importance of chain ends in the quiescent gels in governing the modulus could have important implications with regard to the mechanical properties of other types of gel structures. We have not as yet determined the modulus of the dried gels. However, since it is known that the major structural features do not change upon drying,[3] we would expect the influence of the end groups on the modulus to still persist. However, the modulus of highly axially oriented polyethylene is relatively insensitive to molecular weight.

It is well-known that highly oriented, high-strength, high-modulus fibers can be formed by drawing gels of high molecular weight polymers at elevated temperatures.[13] All the polymers that have been used heretofore in this process were very polydisperse with respect to molecular weight. If the modulus and strength are still governed by the end-group concentration, then these results suggest that lower molecular weights could be used for this purpose provided the polymers have narrower molecular weight distributions. This is consistent with the study by Smith et al.,[28] where it was shown that decreasing the polydispersity of the polyethylene in a filament increased its tensile strength by a factor of nearly 2. However, the oriented samples that they analyzed were prepared by a variety of methods and were not restricted to fibers formed from gels.

It is also possible to obtain some additional molecular information from the magnitudes obtained for the moduli of the gels. This can be done by making the basic assumption that the lamellar crystallites act as cross-links in the conventional sense, but with very large values of the functionality $\phi$. They are presumably considerably larger than the usual covalent cross-links, but this may not be important at the very high dilutions involved. For example, the relationship[19,29]

$$[f^*] = RT(d_0 v_2 / 2M_c)(1 - 2M_c/M_n) \qquad (2)$$

where $R$ is the gas constant, $T$ the absolute temperature, and $d_0$ the density of the solvent, can be used to estimate the effective molecular weight $M_c$ between cross-links (crystallites). This quantity is an (inverse) measure of the degree of cross-linking. The results thus obtained are presented in column seven of Table I. Alternatively, one can use the relationship[30]

$$(f/A)/\epsilon = (3d_0 RT / v_2^{1/3} M_c)(1 - 2M_c/M_n) \qquad (3)$$

These values of $M_c$ are given in the final column of the table.

There is seen to be only approximate agreement between the two estimates of $M_c$ in the case of the higher molecular weight whole polymers, but quite good agreement otherwise. Thus, polydispersity may be a significant problem

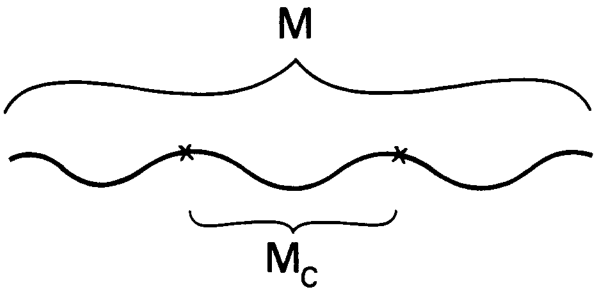

**Figure 8.** Sketch suggesting the structure of a polyethylene chain in a gel at $c \simeq c^*$, with the cross-links (crystallites) shown by the ×'s. A large fraction of such a chain would be in the two dangling ends, which are elastically ineffective.

in calculations of this type. In any case, $M_c$ makes up a considerable fraction of the total $M$, as is shown schematically in Figure 8. Thus, there may be only two or three cross-links per chain, which is of course consistent with their preparation at $c \simeq c^*$. Also, a considerable portion of each chain is in the form of dangling ends, which are elastically ineffective. This indicates that the gels are extremely fragile not only because of their very low polymer content but also because a great deal of the polymer present is in the form of elastically ineffective material.

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# Thermodynamic Properties of Star Polymers: Good Solvents

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ABSTRACT: We present the results of a high-precision Monte Carlo analysis of star polymers on the face-centered cubic lattice with up to $f = 6$ arms and up to an overall polymerization of $Nf \simeq 400$. With the help of an improved dimerization method we were able to increase the accuracy of previous investigations significantly. This is the first numerical investigation on stars, which analyzes a rather complete set of physical quantities ranging from the radius of gyration to the initial decay of the scattering function, including hydrodynamic properties.

## 1. Introduction

Star polymers have found a considerable interest in the literature both from experiment[1–11] and from theory.[12–33] From a theoretical point of view they are an interesting testing ground of modern scaling ideas as well as renormalization group calculations. These concepts can be tested and analyzed by computer simulations of star polymers. Typical quantities like the radius of gyration have also been measured by light[5,6,8,9] and neutron scattering.[8,10] Simulations up to now either are concerned with stars of relatively many arms[32] or only consider a rather selected set of physical quantities.[16,18,23–25,28,29,31] Lipson et al.[28,29] investigate star polymers on a lattice by the Rosenbluth–Rosenbluth Monte Carlo method.[34] This method also called biased sampling is known to be dangerous for good solvent chains[35] and consequently it is