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Viscous and Elastic Behavior Attributed to Polymer Entanglements

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VISCOUS AND ELASTIC BEHAVIOR ATTRIBUTED TO POLYMER ENTANGLEMENTS

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I. INTRODUCTION

Polymer chains are separated and behave as individual hydrodynamic units in sufficiently dilute solutions. A minimum polymer molecular weight, dependent on concentration, is necessary to produce the characteristic rheological effects generally attributed to entanglements. The minimum polymer molecular weights and concentrations for which entanglement effects are observed are called the characteristic entanglement compositions¹. Undiluted polymers exhibit such effects only above some minimum molecular weight. The common observation of entanglement effects indicates that they are not due solely to chemical or structural inhomogeneities. Polymer composition, e.g., polarity and perhaps tacticity, can lead, however, to changes in frequency and strength of entanglements. Entanglements appear to govern many important polymer characteristics, thus providing a strong motivation for their study.

Characteristic chain spacings between entanglements have been reported from various viscoelastic experiments, low shear viscometry, nonNewtonian flow, and from relaxation times measured by nuclear magnetic resonance. The different techniques generally give concordant values, although with a wide variation in precision.

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For a few polymers, *e.g.*, polydimethylsiloxane, the characteristic entanglement spacing has been calculated by each of the four techniques. For others, *e.g.*, poly-isobutylene and polystyrene, entanglement spacings have been reported by all except NMR.

Entanglement effects have been treated theoretically by analogy with theories of rubber elasticity. Other theories have been developed based on breakage and reformation of entanglements and on polymer chain slippage. Certain of these theories have been shown to have the same formalism and yield similar conclusions. In general, the entanglement hypothesis provides a consistent interpretation for a variety of rheological data on concentrated systems of amorphous polymers, this despite the fact that an entanglement has not as yet been directly "seen".

A discussion of entanglements and the first method of calculating entanglement spacings was given by Mark and Tobolsky². A review in the field of polymer viscosities for concentrated systems has been recently prepared³. Experimental details and theoretical derivations are given in texts^{4.5}. The notations used are defined in the Appendix.

II. ENTANGLEMENT THEORY

A. GENERAL MODELS

A number of theories have been developed to interpret the important polymer properties attributed to entanglements. Many theories incorporating entanglements employ mechanical and electrical analogies. The conclusions of the theories are in general agreement with established empirical correlations, although no single theory explains all the phenomena observed⁶⁻⁹. The most widely used basis for evaluating entanglements is the theory of rubber elasticity.

The basic ideas involving the theory of rubber elasticity were put forward in an explicit fashion in the 1930's by Guth and Mark¹⁰ and Kuhn¹¹. Their concept was that the highly elastic behavior of rubbers originated in an entropic effect. Thus, if a strip of rubber is subjected to a tensile strain, the restoring force exerted by it, is due to the fact that the entropy of the sample has decreased upon stretching. Without resorting to any molecular model, an expression for this restoring force can be developed from thermodynamics. For a rubber, the first law of thermodynamics becomes

$$dU = TdS - PdV + FdL^{-1} \tag{1}$$

(A list of symbols is given in the appendix.) The experiment to be imagined is a deformation of the rubber sample at constant temperature and volume. Under these conditions, the restoring force becomes, from Equation (1)

$$F = (\partial U/\partial L)_{T,V} - T(\partial S/\partial L)_{T,V}$$
(2)

This contains no assumptions and is a rigorously exact expression for the force. If now the assumption is made that the restoring force arises solely from an entropy change upon deformation and that the internal energy is not a function of the deformation, Equation (2) becomes

$$F = -T(\partial S/\partial L)_{T,V} \tag{3}$$

To proceed further, it is necessary to obtain an expression for the entropy of the network as a function of extension. This is accomplished using the Boltzmann expression

$$S = k \ln \Omega \tag{4}$$

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where Ω is the number of conformations which the chains of the rubber network can assume. The problem reduces to a calculation of Ω for the network. It is at this point that a molecular model for the real network must be introduced. In order to avoid intractable mathematical difficulties, it is necessary to introduce simplifying assumptions with the result that the molecular model becomes only a rough approximation to the actual situation. The most widely employed model is based on gaussian statistics. The appropriate model is that of the random chain which is long, volumeless, and can rotate freely about chain bonds. To obtain Ω for the network based on the gaussian model, the following assumptions are introduced:

- (i) Each individual network chain obeys Gaussian statistics.
- (ii) The total number of conformations of a network of such chains is the product of the number of conformations of the individual chains.
- (iii) The network junctions (crosslinking points) are fixed in space.
- (iv) The deformation is assumed to be affine, that is, the network junctions deform in the same way as the macroscopic dimensions of the sample.
 - v) The mean square end to end distance of the chains in the network is the same as the mean square end to end distance for the chains in free space.

Using the gaussian model the equation of state of rubber elasticity results:

$$F = nRT[(L_s/L_u)^2 - (L_u/L_s)].$$
 (5)

It is now necessary to examine the effect of the various assumptions involved in the derivation of Equation (5) and to compare it with experimental results. Perhaps the most important discrepancy with experiment introduced by assumptions (i) and (ii) is that agreement becomes progressively worse at higher extensions because gaussian statistics can only be reasonably applied at small strains. It can be shown that assumption (iii) can be removed without affecting the form of Equation (5) while assumption (iv) has consequences which are difficult to assess. Assumption (v) can be removed by introducing the so called "front factor" into Equation (5). This factor, $\langle r_e^2 \rangle / \langle r_0^2 \rangle$ is the ratio of the mean square end to end distance of the chains in the network to the mean square end to end distance of the same chains in free space. Thus Equation (5) becomes

$$F = nRT(\langle r_e^2 \rangle / \langle r_0^2 \rangle) \left[(L_s/L_u)^2 - (L_u/L_s) \right]$$
(6)

The difficulty with this approach is that there seems to be no way of independently measuring the "front factor".

The assumptions, in addition to the points already discussed, imply that network chains can interpenetrate freely. This is obviously not true in the case of the actual network since the chains must occupy a finite volume. This means that the calculation of Ω based on the gaussian treatment will be somewhat too large since it includes interpenetrating conformations which are not available to the real network chains.

An entirely different limitation of the theory as presented here involves the energy contribution to the force. It was stated at the outset that all of the restoring force is assumed to be entropic in origin. This is generally incorrect for real rubber networks and, in general, there are energetic contributions arising from both intramolecular and intermolecular effects. The intramolecular contribution is expressed by the partial derivative $(\partial U/\partial L)_{T,V}$ in Equation (2). This term originates because not all chain conformations are of equal energy. [Thus, when a chain is deformed, rotation about backbone bonds occurs and a change in internal energy results. The intermolecular contribution would be zero if the conditions expressed in

Equation (2) were experimentally realizable, *i.e.*, if it were possible to keep the volume constant. However, under the usual experimental conditions, a volume dilation occurs on stretching. This is small because Poisson's ratio for a rubber is close to 0.5, but nevertheless it is finite for a real rubber network. Despite the many approximations in the theory, Equation (5) holds very well for many hydrocarbon rubber networks, at least at low strains.

The discussion to this point has been entirely concerned with rubber networks possessing permanent, chemical crosslinks. Application of the theory to entangled polymer systems rest on the idea that, in the pseudoequilibrium plateau zone, entanglements may be thought of as crosslinking points which are stable for time scales corresponding to this region of viscoelastic response. If this concept is correct it should be possible to calculate the molecular weight between entanglements from the pseudoequilibrium plateau modulus using Equation (5) as follows. The molecular weight between entanglements, M_e , is given by

$$M_e = n\rho \tag{7}$$

where ρ is the sample density. In addition, Young's modulus is given by

$$E = L(\partial F/\partial L)_T \tag{8}$$

In the limit of small strains, M_e follows from Equations (5), (7) and (8) as

$$M_e = 3\rho RT/E \tag{9}$$

Here E is the Young's modulus in the plateau zone. It must be remembered that the M_e calculated in this way is subject to all the inherent limitations of the Gaussian approximation discussed above. In addition, the contribution of the front factor has been neglected in arriving at Equation (9). This same type treatment also yields equations for M_e in terms of the plateau shear modulus. In addition to the above, more sophisticated treatments have been given.

Haward¹² has developed a mathematical model to describe isothermal stress strain curves in glassy thermoplastics which describes the large recoverable extension which can be observed with high polymers below their glass transition points. Using this method, entanglement spacings have been calculated for cellulose nitrate and polyvinyl chloride¹².

A new model for entanglements has also been suggested by Chompff^{13,14}. It accounts for the frictional force due to the velocity difference between two entangled molecules at the entanglement point. This leads to a modification of the diffusion equation in the Rouse theory for a single molecule as extended for crosslinked networks. The effect of an entanglement is considered equivalent to a purely viscous coupling at a point of contact between two chains. Slippage of this coupling must be much slower than the movement of a free molecule if it is to explain the presence of a group of long relaxation times beyond the glass transition region. From this theory relaxation spectra have been developed which are qualitatively consistent with flow properties of amorphous polymer systems¹⁴. A computer is required for calculation of molecular weights between entanglements. The effect of molecular weight distribution can be taken into account¹⁸.

The solutions of the Rouse diffusion equation have been reworked by Blatz. He found that an exact solution is achievable not only for the case of simple shear but also for the case of combined shear and tension¹⁵. It has also been shown that the statistical mechanics of entanglement produced by looping of polymer chains around an infinitely long straight bar can be treated exactly, essentially because successive turns of the chain around the bar can be considered as constituting a Markov process¹⁶.

Eyring and coworkers have derived an expression for the effect of entanglements from rate process theory using the concept of random walk of connected segments¹⁷. This derivation results in functions for high and low molecular weights which, at the characteristic entanglement molecular weight, M_c , combine with the result that the viscosity, η , dependence changes abruptly from $\eta \propto M^{4/3}$ below M_c to $\eta \propto M^{10/3}$ above M_c . A theory predicting $\eta \propto M^{3.4}$ has been advanced by Fujita from evaluation of free volumes⁵ of concentrated polymer solutions^{18,19}. Several such theories treat successfully low shear newtonian flow but offer no explanation for other features attributable to entanglements such as nonnewtonian flow and the viscoelastic plateau.

Chikahisha²⁰⁻²² has derived a two term equation based on the Born and Green theory which predicts $\eta \propto M$ and $\eta \propto M^3$ at low and high molecular weights, respectively, with a rather abrupt change between the two dependences at M_c . The approach is equivalent in some aspects to the earlier theory of viscosity of concentrated polymer solutions developed by Bueche²³⁻²⁶ using the Debye model of a freely draining polymer molecule. The following form of this expression has been derived by Bueche for low shear newtonian viscosity, η_0 .

$$_{0} = A_{0}S_{0}^{2}N\rho f/6M \tag{10}$$

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Of these terms, only the friction coefficient is not independently measured; and it can be estimated from viscoelastic relaxation spectra⁵. The friction coefficient is the force needed to pull a molecule through the matrix per unit velocity. It has be en considered to be a complicated term dependent on molecular weight²⁶. The term \bar{S}_0^2/M can be obtained from intrinsic viscosity or light scattering measurements on polymer solutions in solvents near a theta temperature.

Equation (10) has been supported by viscosity measurements by Fox and by others on systems containing polymer at concentrations and molecular weights lower than the characteristic entanglement composition²⁷. The theory predicts correctly, that in the limit of constant free volume⁵ viscosity should depend on the first power of molecular weight^{27,28}. The limit is approached on polymer dilution and at higher temperatures of measurement^{26,27,28}.

Viscosity behavior encountered at molecular weights equal to or greater than M_c differs from Equation (10), with the change postulated by Bueche to result from polymer chain entanglement. By analogy with the slippage of smooth ropes, flow velocity is expected to be reduced by an interchain slippage factor variously given specific values $\leq 0.5^{23-25}$. This factor is considered a measure of first order coupling of polymer chains. The same general form of Equation (10) can be applied above M_c but with a viscosity dependence on molecular weight which depends chiefly in the Bueche theory on the choice of slippage factor. The entanglement concept has alternatively been incorporated⁹ by shifting the power dependence of f or \bar{S}_0^2 at M_c . From the Bueche approach a dependence of $\eta_0 \propto M^{2.5}$ was originally derived²³. An additional term was later introduced²⁴ to increase the power dependence to $\eta_0 \propto M^{3.5}$. The latter is in agreement within experimental error with the empirical Equation (11), where N, the number of polymer chain atoms, is used instead of molecular weight.

$$\eta_0 = K_T N^{3.4} \text{ for } N > N_c$$
 (11)

Fox has shown that comparison of Equations (10) and (11) yields

$$\eta_0 = (A_0 \bar{S}_0^2 N_c \rho / 6M) [N/N_c]^{\alpha} f \qquad (12)$$

$$\alpha = 3.4 \quad \text{for} \quad N_w \ge N_c$$

$$\alpha = 1.0 \quad \text{for} \quad N_w \le N_c$$

Bueche's calculation of a network formed by entanglement²⁹⁻³¹ can be expressed as equivalent mechanical and electrical networks and uses the empirical 3.4 power dependence of viscosity on molecular weight instead of the 3.5 power derived earlier by Bueche³¹. The resultant equations have been frequently stated^{5,30,31}. Because of their complexity, computer solutions have been employed. Tables given by Ferry to evaluate the Marvin model numerically predict both maxima and minima for shear loss modulus, G'', and shear loss compliance, J'', in the rubbery plateau zone⁵. Not only are the maxima, G_m'' and J_m'' , predicted, but also their positions on the frequency scale, ω . An approximate evaluation indicates

$$G_m'' \simeq 0.32 \rho R T / M_o \tag{13}$$

$$\omega(G_m'') \simeq (95kT/a^2 L_0 Z^2) (M_e/M)^{1/2}$$
(14)

J'' is likewise approximated

$$J_m'' \simeq 0.32 M_e / \rho R T \tag{15}$$

$$\omega(J_m'') \simeq 48M_0^2 k T/a^2 L_0 M_e^2 \tag{16}$$

Suggestions have been made for use of other, similar numerical constants³²⁻³⁴.

A valuable approach to a molecular entanglement theory for the flow of amorphous polymer has been advanced by Graessley³⁵. Nonnewtonian flow has been attributed to a change in entanglement density with rate of shear. Yamamoto had also previously explained nonnewtonian flow as a result of a decrease in degree of entanglements with increasing shear rate³⁶. Entanglements are considered by Graessley the only resistance to flow and the only source of energy dissipation. The mean square distance between entanglement junctions is used in the calculations which indicate that at high shear rates $\eta \propto$ (shear rate^{-3/4}). This expression provides an approximate fit for considerable data, although the important effect of molecular weight distribution has not as yet been considered³⁵. Unlike most other theories for nonnewtonian flow, the approach by Graessley has real merit in considering the properties of deformed entanglement networks. Kaye has also stated an equation for nonnewtonian fluids which takes into account temporary crosslinks. The equation used the theory of Lodge and makes the rate of formation and breaking of crosslinks shear dependent so that it applies to nonnewtonian flow³⁷.

Present theory and experiment suggest that polymer molecular weight should be defined as weight average. In this form, Equation (12) provides an excellent qualitative description for the high temperature viscosity of undiluted, linear, amorphous polymers. At relatively low temperatures, within 100° C of T_{σ} , the viscosity expression will contain an additional term of the form of the WLF equation⁵.

Bueche has extended his theory to incorporate a term for Equations (10) and (12) for the effect of polymer chain branching. For identical molecular weights, the viscosity of a branched polymer, η_b , is related to that of linear polymer, η_l , by Equation (17), providing the chains are entangled^{26,38}. If the chains are not entangled the ratio

$$\eta_b / \eta_l = g^{7/2} \tag{17}$$

in Equation (17) becomes equal to g, *i.e.*, the square of the ratio of the radius of gyration of the branched molecule to that of the linear molecular (Reference 26, 38). The effect of branching on the friction coefficient is not evaluated. The significance of Equation (17) is that N_c is predicted to be smaller by a factor of g for linear polymers than for those which are branched. Fox and Allen have incorporated an equivalent term for polymer branching in Equation (12)²⁷. The effect

of long chain branching has also been discussed by Moore³⁹. The effect of polymer diluent will be discussed later.

Kraus has published viscosity data showing that the ratio of coil dimensions of linear to branched polymer of the same molecular weight is not constant but is a function of molecular weight. This does not agree with the above concepts, especially as the calculated branched dimensions are larger than those of the equivalent linear molecule for the case of high molecular weight polybutadienes⁴⁰⁻⁴².

B. POLYMER COMPOSITION

A relation between polymer chain dimensions and characteristic entanglement chain length was given by Bueche in 1957⁴³. In the entanglement region viscosity may be related to composition through $(\bar{S}_{0}^{2})^{3.4}$ as demonstrated by Fox and Allen²⁷. The work of Tobolsky on four polymers showed that the maximum relaxation time, which is proportional to η , is a function of $(\bar{S}_{0}^{2})^{3.3}$ for the region of entanglement⁹.

Fox, starting with Bueche's equation, derived a relationship for the characteristic polymer entanglement composition

$$X_c = \bar{S}_0^2 V / V_a \tag{18}$$

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Fox found that selection of 4.7×10^{-15} for X_c gave consistent correlations for characteristic entanglement compositions^{27,44}. Many linear, amorphous polymers have been shown to fit this correlation. At this time, polymethyl methacrylate may be considered the principal exception⁴⁴ to this and other relationships between M_c and composition⁴⁵.

The chemical composition of the polymer and the volume and composition of the groups attached to the chain have been used for interpretation of M_e . For example, the molar volume of relatively short nonpolar pendant groups in vinylidene polymers can be related to the characteristic entanglement molecular weight⁴⁵. An increase in M_e is observed for both long and short pendant groups. The longer pendant groups function as diluent to polymer chain concentration rather than causing an increase in M_e by chain stiffening. This is illustrated by the behavior of poly-1-olefins and poly(*n*-alkyl methacrylates) where a decrease in T_g with increasing length of pendant group is observed.

For polyvinyl acetate M_c is predominantly determined by steric effects⁴⁵, showing that ester side groups are only weakly polar. The inclusion of the weakly polar ester groups gives rise to a behavior similar to chain methylene groups. A number of linear polyesters with different compositions have almost the same M_c , as reported by Fox and Loshaek⁴⁶. Conversion of this molecular weight to N_c gives a value of 290, the same as that of linear polyethylene⁴⁵. Bondi, for low molecular weight compounds, arrived at conclusions in excellent agreement with these results. Esters and equistructure hydrocarbons were found to have essentially the same viscosities and flow activation energies⁴⁷.

Conclusions given here relating N_c to polymer composition are not in agreement with earlier ideas, necessarily based on less information. The earlier, widely quoted, conclusions, were that for nonpolar polymers, N_c was 600–1400 (~1000) and for polar polymers N_c was 200–400^{46,48,49}.

C. POLYMER CONCENTRATION

Abrupt changes in the slope of plots of $\log \eta$ and $\log V$, as well as $\log \eta$ and $\log M$, have been used as a measure of the characteristic entanglement composition¹. The changes in viscosity as a function of concentration are usually not as abrupt

as viscosity changes as a function of molecular weight. In the former, a break in the plot may not be apparent even at temperatures near theta conditions where it should be most prominent⁵⁰. It is generally assumed, however, that $MV_c = M_eV$. The hypothesis of a characteristic or critical polymer volume concentration, V_e , as well as an M_e , seems to be justified by the magnitudes of the changes in power dependences of η at M_e and V at V_e . Experimental evidence shows that $(MV)_e$ is effectively constant for many polymers over a range of molecular weights and concentrations for solutions of a number of polar and nonpolar polymers⁵¹⁻⁵⁴. These findings are consistent with Bueche's theory⁴ and an absence of heats of entanglement.

Ferry has found, however, that $(MV)_c$ is not constant for certain polymer systems and fractional powers of this term were used⁵⁵⁻⁵⁷. Cornet⁵⁸ has postulated that the characteristic entanglement composition should be expressed at high and low molecular weight, respectively, by $(M^{1/2}V)_c$ and $(MV)_c$.

Onogi earlier had derived a general expression based on a packed spheres model⁵⁹. In his original work, the characteristic entanglement composition is predicted at $(M^{1/2}\rho W)_c$. This has been substantiated by viscosity data on 5–15 weight per cent solutions of polystyrene and polyvinyl chloride, as well as by other data of Asai on solutions of polyvinyl chloride and polymethyl methacrylate^{60,61}. Onogi has recently pointed out that the characteristic entanglement composition can be derived from the theory of Bueche to be $(M^{0.83}\rho W)_c^{4.50}$. Experimentally, Onogi has subsequently found the exponent for M at the characteristic entanglement composition to be 0.50 to 0.72, depending on the system⁵⁰. The solutions were linear and branched polyvinyl acetate and polystyrene in good and poor solvents. There are, however, other results indicating that $(MV)_c$ or $(M\rho W)_c$ is apparently constant for data on some of these systems for which fractional dependencies have been given¹. To summarize:

Author	Proposed Constant	Conditions
Bueche ⁴ and Fox ⁴⁶	$W ho M_{c}$	at $M = M_c$
Bueche and coworkers ⁶²	$W \rho M_c^{0.83}$	at $M = M_c$
Ferry and coworkers ⁵	$W ho M^{0.68}$	$M > M_c$ or $W > W_c$
Onogi and coworkers ⁵⁹	$W_c \rho M^{0.50}$	at $M = M_c$

Apparent variations in $(MV)_c$ with temperature have been attributed to heats of entanglements. In all cases, reported heats of entanglement are small, ≤ 5 kcal⁶³⁻⁶⁵. The term $(MV)_c$ is expected to increase 5-30 % per 100° C from coil expansion consistent with an apparent heat of entanglement of about 0.1-1.0 kcal/mole²⁷. From the available definitive data, *e.g.*, on polyethylene, polyisobutylene, polydimethylsiloxane, polystyrene, polyvinyl acetate, and, significantly, on polymethyl methacrylate, the temperature coefficient of $(MV)_c$ does not exceed coefficients of changes in coil dimensions. This implies that heats of entanglement are not involved in these systems.

III. MEASUREMENT TECHNIQUES

A. NEWTONIAN FLOW

Viscosity measurements at low shear rates provide probably the most definitive method for determining the characteristic entanglement composition. The measurements must be made on well defined polymer systems^{46,66}. The equipment required to measure viscosities in the region of low shear newtonian behavior is

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relatively simple. A variety of viscometer, including several types of capillary design, are well known. Newtonian viscosities for use in computing characteristic entanglement compositions can also be obtained from viscoelastic measurements.

The characteristic M_e for entanglement is usually determined as the molecular weight at which an abrupt increase is observed in the power dependence of the newtonian viscosity, η_0 , on polymer molecular weight. The power dependence of η_0 on M_w increases sharply to a constant value of 3.4 ± 0.1 as M_e is exceeded for many linear, amorphous polymers both in bulk and in concentrated solution. This has been illustrated in a single figure by Fox for each of seven different polymers⁴⁴. Figure 1 shows this behavior for blends and fractions of polyvinyl acetate²⁸. Viscosities in Figure 1 are reduced to a "fractional free volume" of 0.0325. There is no complete explanation for the deviation of the slope from the value of about 3.4 at very high viscosities, although chain branching is known to produce this effect⁶⁷. The value of 3.4 for the slope is essentially temperature independent because flow activation energy is insensitive to molecular weight in the region of entanglement.

In the region below the break in Figure 1, the measured slope changes with temperature, molecular weight, and concentration of diluent. The slope approaches a theoretical limit of 1.0 at lower concentrations and higher temperatures^{27,68,69}. This is because free volume, which influences viscosity, depends markedly on composition for conditions below the break. Reducing the measured viscosities to a reference state of constant free volume gives slopes with the theoretical value of 1.0 as shown in Figure 1. Similarly, other flow data which have been corrected to isofree volume conditions⁵ by Bueche and Kelley⁷⁰ and by Fox and Allen all yield a slope of 1.0 at low molecular weight^{27,71}. If weight average molecular weight is used, both fractions and blends have been reported to fall on one line with a slope of 1.0 below $M_c^{23,72}$; similarly, above M_c viscosity depends on $M_w^{46,73}$. These observations are confirmed by measurements on polyvinyl acetate with M_w/M_n ratios varying from almost 1 up to 34^{28} . Previous work suggested use of M_z for polymers where $M_w/M_n > 2^{62}$. Other theoretical work has suggested a more complicated dependence of viscosity on molecular weight averages^{74,75}.

Bagley, presenting some conceptual difficulties with M_e , has suggested that the discontinuity and slope of the log η_0 versus log M plots might best be discarded as an operational definition of entanglement⁷⁴. The rapid increase in viscosity above molecular weight M_e may be due to intramolecular rather than intermolecular effects,





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being perhaps associated with the very rapid increase in molecular motion⁷⁴ at molecular weights above M_e . Following such an explanation Bagley suggests that the definition of entanglements in terms of viscous behavior is unwarranted and that polymer melt entanglements can be more readily defined with reference to elastic rather than viscous effects, the influence of an entanglement on viscosity being much smaller.

A viscosity change for solutions as a function of polymer molecular weight is illustrated in Figure 2, which gives newtonian flow data of Fetters on solutions of narrow distribution polyisoprenes in decane⁵². The open circles represent polymers with a cis-1, 4 content of 70–85 per cent. The results in Figure 2 show a prominent break which occurs at the same characteristic entanglement composition at each of the two test temperatures. The break was also found at a series of polymer concentrations down to at least 2 volume per cent.

The characteristic entanglement composition has been calculated in two different ways from low shear Newtonian viscosity data as a function of concentration, C, at constant M. If the break is prominent, M_c may be taken as that value. Alternatively, the characteristic entanglement composition has been considered the minimum concentration required for a constant and high power dependence of viscosity on polymer concentration. The behavior generally observed⁵⁸ is illustrated in Figure 3 with solution viscosity data of Oyanagi and Matsumoto on polyvinyl alcohols in water⁴⁹. The dashed line corresponds to a slope of 5.0.

A constant high power dependence of η_0 on *C* is widely observed for amorphous polymers in the entanglement region. Usually, the power dependence is from 5–6. No complete theoretical explanation has been given for this phenomenon^{59,76,77}.

B. MAGNETIC RESONANCE RELAXATION

The characteristic entanglement molecular weight, M_c , is strikingly observed in nuclear magnetic resonance (NMR) data by the abrupt change in T_2 , transverse relaxation times, as a function of molecular weight. Such relaxation time data are shown in Figure 4, as developed by McCall, Douglass, and Anderson for a molecular weight series of polydimethyl siloxanes^{78,79}. The T_2 's were chosen so as to give the correct values in the exponential range⁷⁹. An abrupt change or break at M_c



FIG. 2.—Newtonian viscosity versus molecular weight; 4.9 wt. % polyisoprene in decanese (Reproduced by courtesy of the U.S. Government Dept. of Commerce from J. Research National Bureau of Standards).



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FIG. 3.—Viscosity versus concentration; polyvinyl alcohol in water, 30°C⁴⁹ (Reproduced by courtesy of J. Colloid Science).

has also been found in T_2 values obtained on linear polyethylene and on polyisobutylene⁸⁰⁻⁸². Characteristic entanglement compositions have been elucidated by NMR for only a few polymers and only by proton resonance. Polydimethyl siloxane and polyethylene are advantageously studied by NMR since they contain protons of only a single type.

Different mechanism supposedly control the two relaxation times, T_1 and T_2 , see Figure 4. The motions which govern newtonian flow of polymers appear to be related to the slow process which is responsible for T_2 . A plot of T_2 versus M_n , see Figure 4, suggests this relationship as it is similar in form to a plot of log η_0 versus log M_n . Therefore, both M and M_c may be found from T_2 measurements by NMR.

C. NONNEWTONIAN FLOW

Shear orientation and anisotropic flow, resulting from the long relaxation times attributed to entanglements, can be readily observed in measurements of viscosity as a function of shear. Shear orientation and anisotropic flow cause deviations from newtonian viscosity, that is viscosity independent of shear rate or stress.



FIG. 4.—Relaxation time versus molecular weight⁷⁹ (Reproduced by courtesy of *J. Polymer* Science).

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Figure 5 shows the plot developed by Hoffmann and Rother for the shear dependence of viscosity as a function of molecular weight for undiluted, narrow distribution polystyrenes⁸³. This is a rare quantitative determination of M_c by shear measurements. The onset of nonnewtonian flow is clearly identified with entanglement molecular weight revealed independently from low shear newtonian viscosity on the polystyrenes in Figure 5. For this system, limiting high shear newtonian viscosity, η_{α} , data form a linear extension from data below M_c , indicating a common slope of 2.0 at 190° C with the limit of error indicated by symbols with tails in Figure 588. Determinations of the onset and magnitude of nonnewtonian flow with increases in shear rate and stress may be used to measure M_c and $(MV)_c$. For a polar copolymer, two different characteristic entanglement compositions have been reported from measurements of nonnewtonian flow. The characteristic composition at highest molecular weight was attributed to conventional entanglements; the one at low molecular weight was ascribed to dipole interactions and/or hydrogen bonding⁸⁴. Experimentally, it has been shown for a number of linear amorphous polymer systems that an $M \ge M_e$ or $MV \ge (MV)_e$ is a necessary and sufficient requirement for observation of prominent nonnewtonian behavior at relatively low shear in steady flow^{8,83,85,86}.

Figure 6 shows viscosity as a function of concentration for a polyisobutylene, $M_w 1.06 \times 10^6$, in decalin at 25° C⁸⁷. Correlations have been developed at a series of constant shear rates. Low shear data show a high, greater than fifth, power dependence of η_0 on V, polymer volume fraction, consistent with the entanglement region. Convergence of constant shear rate correlations at a common concentration indicates a characteristic entanglement composition, $(M_w V)_c$, of 19,000 in close accord with several values reported for undiluted polyisobutylene.

Correlations at constant frequency for the same system as in Figure 6 also definitively indicate the same entanglement composition. The success of correlations involving concentration is due in part to the fact that only a single polymer is used so that the molecular weight distribution, which influences nonnewtonian flow, is the same for all solutions.







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Characteristic entanglement composition may be defined from molecular weight as well as concentration correlations for nonnewtonian flow. Consistent with reduced variables for nonnewtonian flow, constant shear stress correlations intercept at the characteristic entanglement composition. Constant shear rate correlations with molecular weight generally show curvature but also intercept at the minimum concentration and molecular weight for nonnewtonian flow, which is the characteristic entanglement composition. Constant shear rate correlations are readily plotted from viscosity measurements but are unsatisfactory for defining M_c , particularly from data on high molecular weight polymers⁸⁸.

Figure 7 shows apparent limiting high and low shear newtonian viscosities, η_{α} and η_0 , respectively, as a function of molecular weight for polyacrylic acids in water. The intercept of these data, reported by Brodnyan and Kelley, definitively provides the characteristic entanglement composition⁸⁹. Anomalous viscosity changes for other polymer solutions have been interpreted as entanglements which are induced rather than reduced by shear⁹⁰. Schreiber has suggested that at least in certain cases a new critical quantity is needed to indicate the initial shear rate or stress above which nonnewtonian flow is noted even at molecular weights above M_e^{91} .





Energy or heat of flow activation, Q_r , calculated at constant shear rate, varies with shear only for nonnewtonian conditions. Therefore, determining the minimum M or MV for which Q_r varies with shear is an alternate and successful method of measuring M_c and $(MV)_c$ from nonnewtonian viscosity data⁹². The swelling of amorphous polymer on extrusion from a die under nonnewtonian conditions has been attributed to entanglements, *i.e.*, to those motions characterized by long relaxation times in the terminal zone of the viscoelastic spectrum⁹³.

D. VISCOELASTICITY

Low molecular weight polymers, $M < M_c$, have well understood viscoelastic properties^{5,94} and require no further discussion here. For higher molecular weight polymer systems involving entanglements, a more complex viscoelastic behavior is observed. Several experimental techniques have been used to observe the properties of the so called rubbery plateau zone⁹⁵, which has been generally attributed to entanglements. Measurements (a) to (d) described below have been widely used. These techniques are determination of shear and tensile creep as a function of timeand shear measurements as a function of frequency using torsional crystals and transducers^{5,96–98}. For polymer systems where $M > M_c$ or $MV > (MV)_c$, viscoelastic measurements of moduli show a leveling out or intermediate, rubberlike zone of low slope in plots of:

- a. Shear relaxation modulus vs time.
- b. Shear creep compliance vs time.

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- c. Shear storage modulus vs frequency.
- d. Shear storage compliance vs frequency.

The values of $(MV)_c$ and M_c correspond to the minimum concentration at a given molecular weight or the molecular weight for a bulk polymer at which the plateau in moduli or compliances is observed. The number of entanglements per molecule has been related to the width and height of the rubbery plateau⁹⁹. The molecular weight distribution of the polymer influences the definition of the rubbery plateau zone and the shape of the relaxation spectrum^{100,101}.

Application of rubber elasticity theory to determination of M_e has been discussed in section 2A. The calculation is made from E, see Equation (9), from the rubbery plateau value for G', the shear storage modulus, as a function of frequency, or from the pseudoequilibrium shear modulus, G(t), at the inflection in the stress relaxation curve by using Equation (19):

$$M_e = \rho R T/G \tag{19}$$

The inflection in the plateau zone for shear creep and storage compliance may also be used according to the equation:

$$M_e = \rho R T J \tag{20}$$

More sophisticated methods for computing M_e or N_e from maxima in shear loss modulus, G'', and compliance, J'', have been devised by Marvin, as stated earlier²⁹⁻³¹. In this theory, the quantity M_e appears as $M_e/2$, which is identified with the average molecular weight between the junction points of an equivalent network³¹. Equation (21) gives an approximation, based on the theory of Marvin³⁰, for N_e using the minimum¹⁰² in the loss tangent, $J''/J' = \tan \delta_{\min}$

$$\tan \delta_{\min} = 1.02 (M/N_e M_0)^{-0.80} \tag{21}$$

Equation (21) is a modification of an equation given earlier¹⁰³; and, subsequently, these values for N_{\bullet} were arbitrarily doubled⁶⁹. As the equation is applicable exactly only for monodisperse polymers, a distribution of molecular weights is expected to give higher values^{30,102}.

Using the maximum in loss compliance, J_m'' , and the theory of Marvin, the following equation has been given by Richards, Mancke, and Ferry¹⁰⁴

$$M_e = \rho R T J_m'' / 0.42 \tag{22}$$

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With the choice of another constant in Equation (22), M_e has also been calculated³² from G_m'' . This theoretical approach for calculating M_e must as yet be considered tentative, and the effect of molecular weight distribution and the distribution of entanglement chain lengths have not been adequately developed^{5,105}.

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IV. SUMMARY OF MEASUREMENTS

A. DISCUSSION

The characteristic entanglement composition, M_c or $(MV)_c$, for systems of linear amorphous polymers has been observed in several distinct ways. These include:

- a. Determination from viscoelastic measurements of the onset of the rubbery plateau.
- b. NMR determinations utilizing the abrupt change in transverse relaxation times.
- c. Use of Newtonian viscosities to find the change in power dependency of η_0 on M or C and

d. Location of the composition for the onset of nonnewtonian flow at low shear. These four methods generally give concordant values for M_e and $(MV)_e$.

In the free radical polymerization of styrene, it has been observed that the onset of an acceleration of the polymerization due to increased solution viscosity can be quantitatively explained as occurring at a critical point. This critical point has the same form as commonly used for the characteristic entanglement composition, that is, a product of molecular weight and volume concentration. However, values of this constant are somewhat lower than for the values given for chain entanglements¹⁰⁶.

From theory and rough empiricism, $M_e = M_c/2$. This factor of two has been used by Bueche, Marvin, and others^{30,96}.

In previous summaries^{27,66}, M_c has been considered equal M_e . This has been justified by citation of gelation theory^{107,108}. The molecular weight between entanglements, M_e , should be a number average molecular weight by derivation from the theory of rubber elasticity. However, M_e determined from viscoelastic measurements and rubber elasticity theory is proportional to compliance. Empirically, compliance has been shown to depend on the higher molecular weight moments, M_w and M_z . Newtonian viscosity measurements depend on M_w .

Discrepancies have been reported between M_e and M_e greater than can be accounted for by the factor of two, for example, values given for polyethylene and polymethyl methacrylate. Lack of precision in values of M_e may be part of an explanation. Values of M_e can be better defined, and at best are reliable to 10 $\%^{1.27}$.

For the over half dozen polymers for which values of both M_e and M_e have been reported, the M_e values are generally in the range of 200–400. They do not show any

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convincing dependence on the corresponding values of M_c . Moreover, M_e show a wider variation among values reported for a single polymer than any consistent difference between polymers. From the scatter of data, it appears clear that $M_c \neq M_e$. For selected data, a correlation indicating $M_e = M_e$ could be plausible. A case can be better made for M_e being independent of M_c , so that at this time there appears to be no credible correlation between M_e and M_e .

The precision of measurement of M_c from newtonian viscosity determinations on bulk polymers has been given as $\pm 10\%$ by Fox and Allen, who regard their more recent lower values for polyisobutylene, polydimethylsiloxane, polystyrene, and polyvinyl acetate as having greater significance because of correction to constant free volume^{27,51}. However, values of M_c determined primarily from data on high molecular weight polymers should not be influenced by such corrections. The large number of literature values taken directly from measurements are considerably higher than the values recalculated by Fox and Allen.

The values for M_e derived from the frequency of the maximum in loss compliance, J_m'' , are apparently quite erratic and subject to considerable uncertainty, at least for the eight polymers evaluated in this way^{6,56}. Using the frequency of the maximum usually gives values for M_e 50 % greater than those computed from J_m'' . Intuitively this is reasonable since those from J_m'' should be close to a number average from analogy with crosslinked networks whereas M_e by the alternate calculation should correspond to a higher molecular weight average^{5,66}.

Gent and Vickroy have measured effective degree of crosslinking for polyethylenes as a function of radiation dose¹⁰⁹. They find that at high degrees of crosslinking an approximately linear relationship is obtained between the reciprocal of molecular weight and radiation dose. The linear plot has an intercept corresponding to molecular weight between physical crosslinks or entanglements of about 5,500 and the slope corresponding to about 2.9 crosslinks per 100 eV. This value for entanglement spacings is somewhat larger than obtained from viscosity measurements on uncrosslinked polyethylenes. A similar discrepancy is observed for natural rubber¹⁰⁹.

B. SPECIFIC POLYMERS

Characteristic entanglement compositions are mentioned here for some of the best data on the most common polymers. Schreiber, Bagley, and West have published the single, most definitive study on linear polyethylenes, which indicates an M_c of 4000 or an N_c of 286 from data on fractions¹¹⁰. Fox and Allen²⁷ computed an N_c of 460 for polyisobutylene. Former interpretations of the same data^{66,46} gave values of 608 and 610. The N_c of 608–610 is considered the best value and equivalent to an M_c of 17,000 derived by the two methods cited earlier⁸⁶.

The characteristic entanglement molecular weight for Hevea or natural rubber is not well established in spite of numerous measurements because all such tests have been done by the relatively imprecise viscoelasticity technique on single samples whose distributions have been generally defined poorly. A plausible N_e of 296 or $M_e \sim 5000$ for Hevea has been given. No values have been given for solutions of Hevea. A synthetic polyisoprene⁵² gave an $(MV)_e$ of 824. Fox and Flory gave an $N_e \sim 962$ for polystyrene¹¹¹. The preferred consistent set of values, $N_e = 720-731$, is based essentially on these same data^{6,66,86,87,112}. For polystyrene, $N_e = 693$ or $M_e = 35,000$ is obtained from newtonian viscosity data at *iso*free volume in agreement with measurements from uncorrected data¹¹³.

For polydimethylsiloxane, Bagley and West¹¹⁴ have published an M_c of 29,000, or an N_c of 784. Characteristic entanglement molecular weights for undiluted poly-

dimethylsiloxanes have been developed primarily from newtonian flow with fragmentary data by other techniques. No work on solutions of polydimethylsiloxane has been reported. Fox and Allen²⁷ have given $M_c = 22,500$ or $N_c = 570$ for polyvinyl acetate: these values are considered preferable to an N_c of 680 previously computed from these same data¹¹⁵.

TABLE I

POLYMERS WITH ESTIMATED ENTANGLEMENT LENGTHS

Polymer

3, 27, 67, 76, 78-80, 86, 109, 110, 112, 117, 121 Linear Polyethylene Branched polyethylene 8, 67, 86, 110, 112, 121, 122 Polvisobutylene 2, 6, 8, 27, 44, 45, 66, 70, 82, 86, 110, 111, 117, 123 - 133Polyisobutylene solutions Natural rubber Polystyrene Polystyrene, solutions and branched polymer Poly(dimethylsiloxane) Poly(vinyl acetate) Poly(vinyl acetate) solutions Poly(methyl methacrylate) Poly(methyl methacrylate) solutions Acrylonitrile methyl methacrylate copolymer 84 solutions Methyl methacrylate n-butyl methacrylate 156 copolymers Higher alkyl methacrylate polymers and solutions Poly(alkyl acrylates) Polyesters Polyester solutions 53 Polyethers Polyamides Poly(vinyl chloride) solutions Polytetrafluoroethylene 117 Poly(vinyl alcohol) solutions Poly(acrylic acid)solutions cis-Polybutadiene Polybutadiene solutions 65Polyisoprene Atactic polypropylene Ethylene propylene copolymer Polytetramethyl-p-silphenylsiloxane 44 Cellulose solutions Vulcanized SBR Poly(ethylene tetrasulfide) 117 Polycarbonate of bisphenol A and its

solutions

45, 46, 56, 86, 87, 103, 112, 126, 131, 132 4, 5, 27, 52, 66, 68, 117, 134 6, 18, 27, 44, 46, 50, 51, 66, 69-71, 73, 74, 81, 83, 86, 87, 110-113, 117, 127, 133, 135 27, 44, 50, 51, 87, 100, 136-143 8, 17, 27, 44, 46, 66, 67, 79-81, 86, 110, 112, 114, 127, 144-148 6, 27, 28, 44, 46, 78, 115, 149-152 44, 50, 53, 57 4, 6, 27, 34, 44, 66, 72, 105, 116, 119, 142 3, 4, 18, 27, 46, 49, 61, 72, 119, 127, 154, 155

Reference

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6, 27, 33, 53, 66, 117, 157-160

6, 66, 117, 152 3, 27, 46, 127, 161-163 27, 66, 86, 112, 164, 165 27, 46, 127 3, 53, 59, 60 49, 63, 138, 139, 155 34.89 40, 41, 44, 52, 117, 166 3, 52 117.167 104, 117, 122 49, 63, 168, 169 1223, 142, 170, 171

Tobolsky and coworkers have given viscoelastic data on polymethyl methacrylate^{88,116,117} from which at least three values of N_e have been calculated^{6,34,117}, 74, 124, and 204. Measurements on bulk fractions^{4,6,27,66,72,118} at 110–140° C have produced values from 88–172. Data show that the onset of the creep plateau, see Figures 5 and 8, Reference 72, actually occurs at $2.04 \times 10^4 < M_c < 3.6 \times 10^5$, corresponding to $N_c = 4080-7300$. This range is in reasonable agreement with an $N_e \sim 10,000$ obtained from η_0 and M_w as given by Sobue and coworkers¹¹⁹. However, these values are larger, by a factor of ten or more, than M_e 's calculated from rubber elasticity theory. Two studies of polymethyl methacrylate solutions have been made^{60,72}; one⁷² gives an $(NV)_c$ of 200–210. The concept of $(NV)_c$ as a constant is supported if the high set of values for undiluted polymethyl methacrylate is considered, for the low set $(NV)_c$ would not be constant. Barry and Fox have recently reevaluated the characteristics of this polymer³.

C. TABULATION OF POLYMERS STUDIED

Polymers on which rheological measurements have been obtained and entanglement lengths reported are listed in Table I. References are given for the original data, the interpretation, and re-citations. Results are for bulk polymer unless otherwise specified. Specific values of M_{ϵ} (MV)_c, M_{e} , and (MV)_e for many of the systems listed below have been cited above and listed elsewhere^{1,3,46,66,120}.

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VI. APPENDIX

	a	Root mean square end to end distance per square root of number of monomer units
У., -	<i>c</i> .	Used as subscript to denote characteristic entanglement conditions
	f	Friction coefficient per chain atom
	g	Square of the ratio of the radius of gyration for equivalent molecular
		weight branched to linear polymers
	k	Boltzmann's constant
	n	Number of moles of network chains, per unit volume
1 Mar 1	$\langle r_{e}^{2} \rangle / \langle r_{0}^{2} \rangle$	Ratio of the mean square end to end distance of the chains in the
		network to the mean square end to end distance of the same chains
		in free space; front factor
	$\omega(G_m'')$	Frequency for G_m''
	$\omega(J_m'')$	Frequency for J_m''
	A_0	Avogadro's number
	C	Polymer concentration
	E	Young's modulus
	F_{\perp}	Tensile force
	G	Shear modulus
	G(t)	Shear relaxation modulus
	G'	Shear storage modulus
	$G^{\prime\prime}$	Shear loss modulus
بر در در در د	$G_m^{\prime\prime}$	Maximum shear loss modulus
	J	Shear compliance
	J(t)	Shear creep compliance
31	J'	Shear storage compliance
	J''	Shear loss compliance

RUBBER CHEMISTRY AND TECHNOLOGY 22 J_m'' Maximum shear loss compliance K_{T} Temperature dependent coefficient \boldsymbol{L} Sample length L_s Stretched length Lu Unstretched length Translational friction coefficient per monomer unit L_0 M Molecular weight M_n Number average molecular weight Viscosity average molecular weight M_{v} M_{w} Weight average molecular weight M_{z} Z average molecular weight Molecular weight per monomer unit M_0 Characteristic entanglement molecular weight M_{c} Me Molecular weight between entanglements NNumber of chain atoms per molecule N_{c} Characteristic entanglement chain length in atoms N_{e} Chain length in atoms between entanglements $N_{\boldsymbol{w}}$ Weight average chain length in atoms Q_r PFlow activation heat at constant shear rate Pressure $R S_{\bar{S}_0^2} T_T T_{\rho} T_1$ Gas constant Interchain slippage factor or entropy Unperturbed mean-square radius of gyration Absolute temperature Glass transition temperature NMR longitudinal relaxation time T_2 UVNMR transverse relaxation time Internal energy Polymer volume fraction or volume V_a Volume per chain atom Vc Characteristic polymer volume concentration Ŵ Polymer weight fraction X_{c} Entanglement constant \boldsymbol{Z} Degree of polymerization δ Phase angle between stress and strain Viscosity η Low shear newtonian viscosity η_0 Limiting high shear newtonian viscosity η_{α} Viscosity of a branched polymer ηь Viscosity of a linear polymer of the same molecular weight for η_b η_l of a branched polymer Polymer or solution density, ρ Ω Number of conformations